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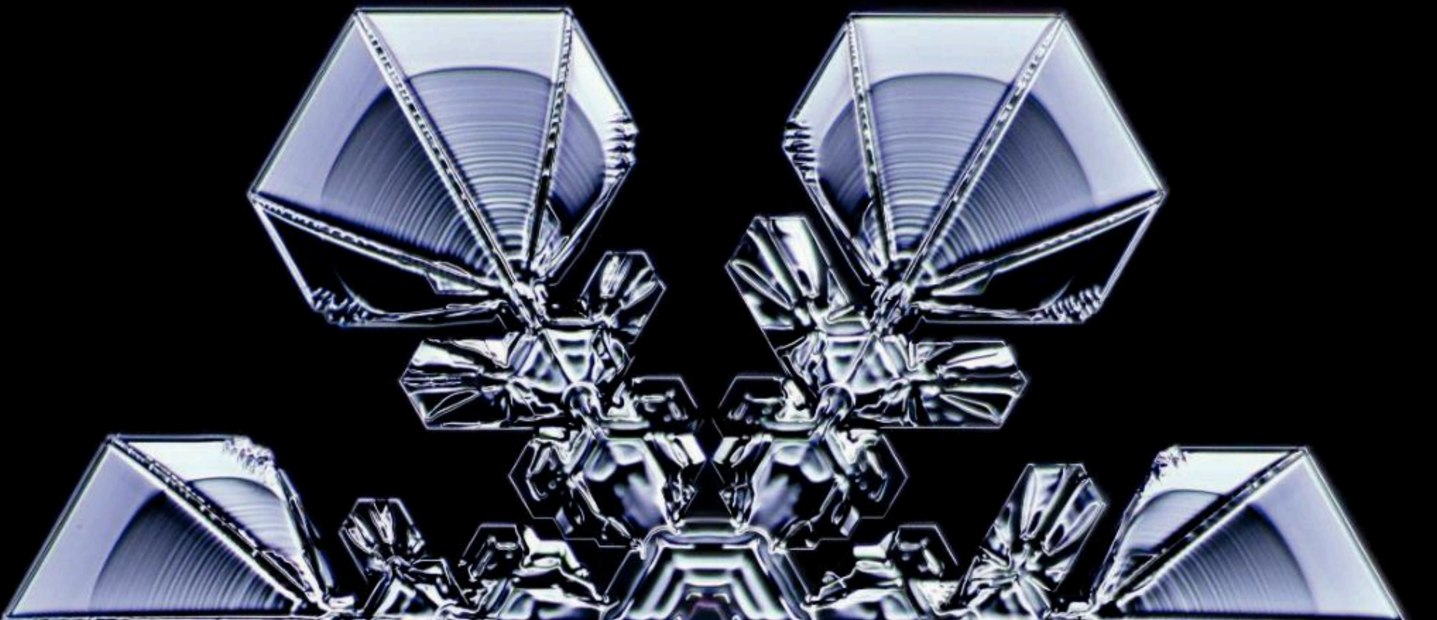
for Cambridge International AS & A Level

Philippa Gardom Hulme



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Contents

Introduction

The *Exam Success* series will help you to reach your highest potential and achieve the best possible grade. Unlike traditional revision guides, these new books give advice on improving answers, helping to show you what examiners expect of candidates. All the titles are written by authors who have a great deal of experience in preparing candidates for exam success.

Exam Success in Cambridge International AS and A Level Chemistry covers the requirements of the AS Level and A Level Cambridge 9701 Chemistry syllabus. The first 23 units cover the syllabus content, while Unit 24 provides advice on practical work for papers 3 and 5; and Unit 25 consists of questions in the styles of the five exam papers, with exam tips to support your work.

At the start of each unit, cross-references are given to *Chemistry in Context for Cambridge International AS & A Level*, should you wish to study the topic in more depth. Throughout the book, a grey vertical bar shows AS content, and a blue bar shows A Level content.

Each *Exam Success* book has common features to help you do your best in the exam:

Key points

☐ These summarise what you need to show that you can do in the exam. Check them off one by one when you are confident.

Worked examples

These give examples of questions, and show you how best to answer them.

Common errors

These are errors that students have made in past exams, helping you to avoid similar mistakes.

Remember

These include key information that you must remember if you are to achieve a high grade.

Practical skills

These describe practical skills that you might be tested on, and are intended as reminders of work you may have already done in the lab. They are not complete instructions with safety guidance.

Raise your grade

Here, you can read answers by candidates who did not achieve maximum marks, as well as find out how to improve their answers.

Exam-style questions

Each unit has examples of the sort of questions to expect in the exam. Answers are available on the OUP support website.

Key terms

These give easy-to-understand definitions of important terms.

Link

These show where in the book you can find more information about the topic.

Exam tips

These provide guidance and advice to help you understand exactly what examiners are looking for.

Maths skills

These remind you of the vital mathematical skills that you need in order to answer exam questions in chemistry.

Chemical tests

These describe how to use simple chemistry to identify substances.

Access your support website for additional content here:
www.oxfordsecondary.com/9780198409922

1 Atoms, molecules and stoichiometry

AS 1.1–1.10 pages 1–17

Key points

- ☐ Use ideas about moles and relative masses.
- ☐ Analyse mass spectra
- ☐ Calculate formulae.
- ☐ Write and use balanced equations.
- ☐ Do calculations involving reacting masses, gas volumes and solution concentrations.

Relative masses of atoms and molecules

Atoms, molecules and ions, as well as sub-atomic particles, have tiny masses. Chemists compare these using relative masses.

Key terms

The **relative atomic mass, A_r**, of an element is the weighted average mass of one atom of the element relative to one-twelfth the mass of one atom of carbon-12.

The **relative isotopic mass** of an isotope is the mass of one atom of the isotope relative to one-twelfth the mass of one atom of carbon-12.

The **relative molecular mass, M_r**, of an element or compound is the sum of the relative atomic masses of all the atoms in its molecular formula.

The **relative formula mass, M_r** of a compound is the sum of the relative atomic masses of all the atoms in its formula.

Remember

Relative atomic mass and *relative isotopic mass* are not the same thing – make sure you know the difference. Relative isotopic mass refers to one isotope only, but relative atomic mass takes into account the different isotopes of an element.

Exam tip

You need to learn all definitions very carefully – make sure that you are word perfect.

Remember

Isotopes are atoms of the same element with different numbers of neutrons.

Remember

You can find A_r values in the periodic table of the data booklet.

Remember

The values for relative masses have no units since their values are relative to the mass of something else, i.e. one-twelfth of the mass of a carbon-12 atom.

Worked example

What is the relative formula mass of aluminium sulfate, $Al_2(SO_4)_3$?

Answer

Relative formula mass, M_r, is the sum of all the relative atomic masses, A_r, of the atoms in the formula.

$A_r(Al) = 27.0$, $A_r(S) = 32.1$ and $A_r(O) = 16.0$

$$\text{So } M_r = (2 \times 27.0) + 3 \times [32.1 + (4 \times 16.0)]$$
$$= 54.0 + (3 \times 96.1)$$
$$= \mathbf{342.3}$$

Maths skills

Bidmas

In calculations, you must perform operations in the correct order. The mnemonic BIDMAS is useful for remembering this order:

- **B**rackets – if an expression shows two types of brackets (round and square), perform the operation in the inside brackets first.
- **I**ndices, which means powers, such as 3^2
- **D**ivision and **M**ultiplication
- **A**ddition and **S**ubtraction

For example, in the worked example above, $(2 \times 27.0) + 3 \times [32.1 + (4 \times 16.0)]$:

- Start by multiplying the numbers in the inside brackets: $(2 \times 27.0) = 54.0$ and $(4 \times 16.0) = 64.0$
- Then complete the operation in the outside brackets by doing the addition: $32.1 + 64.0 = 96.1$
- Next, perform the multiplication outside the square bracket: $3 \times 96.1 = 288.3$
- Finally, do the addition: $54.0 + 288.3 = 342.3$

The mole and the Avogadro constant

The **mole** is the amount of substance containing 6.02×10^{23} particles of that substance. It is the amount of substance containing as many particles as there are atoms in 12 g of carbon-12.

One mole of an element has a mass equal to its relative atomic mass in grams. One mole of a compound has a mass equal to its relative molecular mass in grams, or its relative formula mass in grams.

Key term

Mole: the mole, or mol, is the basic unit for measuring amounts of substances.

Remember

The kilogram, kg, is the unit for mass.

Worked example

What is the mass of:

a) one mole of sulfur trioxide molecules, SO_3

b) one mole of oxygen molecules, O_2?

Answer

a) Relative formula mass, $M_r = 32.1 + (3 \times 16.0)$
$= 80.1$

So the mass of 1 mol, $M = 80.1\,\text{g}$

b) Relative formula mass, $M_r = 2 \times 16.0$
$= 32.0$

So the mass of 1 mol, $M = 32.0\,\text{g}$

Exam tip

Read the question carefully. The question asks for the mass of one mole of oxygen molecules, O_2, not one mole of oxygen atoms, O.

To calculate the amount of substance in moles, use the equation below:

$$\text{Amount of substance (mol)} = \frac{\text{mass of substance (g)}}{\text{mass of 1 mol (g mol}^{-1}\text{)}}$$

Worked example

Gold (Au) is traded in kilobars. The mass of one kilobar is 1000 g. What amount of gold is this?

Answer

Relative atomic mass, $A_r = 197.0$

Mass of 1 mol, $M = 197.0\,\text{g mol}^{-1}$

$$\text{Amount of gold in one kilobar (mol)} = \frac{\text{mass of gold kilobar (g)}}{\text{mass of 1 mol (g mol}^{-1}\text{)}}$$

$$= \frac{1000\ \text{g}}{197.0\ \text{g mol}^{-1}}$$

$$= 5.076\ \text{mol}$$

Exam tip

Include units at all stages of your calculations. The units on both sides of the equation should be the same. If they are not, check for mistakes.

Maths skills

Significant figures

The number of digits, or figures, in a quantity show how accurately the quantity has been measured. These are the significant figures (see Table 1.1).

▼ **Table 1.1** The number of significant figures in some numbers

Number	Number of significant figures	Note
2308	4	A zero between other digits is significant.
2.308	4	
0.002 308	4	A zero before other digits is not significant.
230 800	4	A zero after other digits is not significant…
230.800	6	…except when it is after the decimal point.

The answer to the worked example above is given to 4 significant figures, since the data given in the question has 4 significant figures. When performing calculations, your answers should reflect the number of significant figures given or asked for in the question. When rounding up or down, make sure that you do not lose significant figures unnecessarily, nor use more significant figures than are justified.

The number 6.02×10^{23} is the **Avogadro constant, *L***.

Number of atoms, molecules or formula units
= amount of substance (mol) × Avogadro constant (mol^{-1})

Key term

Avogadro constant: the number of atoms, molecules or formula units in one mole of any substance. You can use the equation to calculate the number of atoms, molecules or formula units in a given amount of substance.

Remember

6.02×10^{23} is the same as 602 000 000 000 000 000 000 000.

Maths skills

Standard form

Scientists use standard form for quantities that are very large or very small. In standard form, a number has two parts:

- The first part is a decimal number with one digit before the decimal point, for example 2.3.
- The second part gives the power of 10, for example 10^{-3} or 10^{3}.

The number 2.3×10^{3} means 2300. You can work it out by multiplying 2.3 by 10^{3} (10^{3} is 1000).

The number 2.3×10^{-3} means 0.0023. You can work it out by multiplying 2.3 by 10^{-3} (10^{-3} is 0.001).

You need to use a special button on your calculator when using numbers in standard form. Make sure you know which button to use.

Worked example

A glass holds 250 g of water, H_2O.

a) Estimate the number of water molecules in the water in the glass.

b) Estimate the number of hydrogen atoms in the water in the glass.

Answer

a) Start by calculating the mass of 1 mol, *M*.

$$M = (2 \times 1.0\,\text{g}) + 16.0\,\text{g}$$
$$= 18.0\,\text{g}$$

Now calculate the amount of water, in mol.

$$\text{Amount of water (mol)} = \frac{\text{mass of water (g)}}{\text{mass of 1 mol (g mol}^{-1})}$$
$$= \frac{250\,\text{g}}{18\,\text{g mol}^{-1}}$$
$$= 13.9\ \text{mol}$$

Now calculate the number of molecules.

$$\text{Number of molecules} = 13.9\,\text{mol} \times 6.02 \times 10^{23}\,\text{mol}^{-1}$$
$$= 8.37 \times 10^{24}$$

Remember

There is no unit, since the answer is a number only.

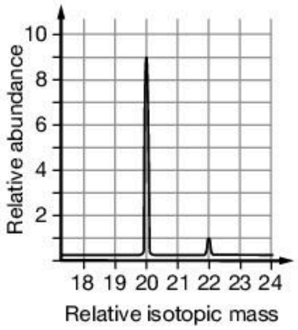
b) The formula H_2O shows that there are two atoms of hydrogen in each water molecule.

So the number of hydrogen atoms = 2 × number of water molecules

$$= 2 \times 8.37 \times 10^{24}$$
$$= 1.67 \times 10^{25}$$

The determination of relative atomic masses, A_r, from mass spectra

The mass spectrum of a naturally occurring sample of an element shows the relative isotopic mass of each isotope and the relative abundance of each isotope. The mass spectrum for neon (see Figure 1.1) shows that neon has two isotopes, with relative isotopic masses 20 and 22. There are 9 atoms of ^{20}Ne for every 1 atom of ^{22}Ne.



▲ **Figure 1.1** The mass spectrum of neon

You can find the relative atomic mass of an element if you know the relative abundance of each of its isotopes:

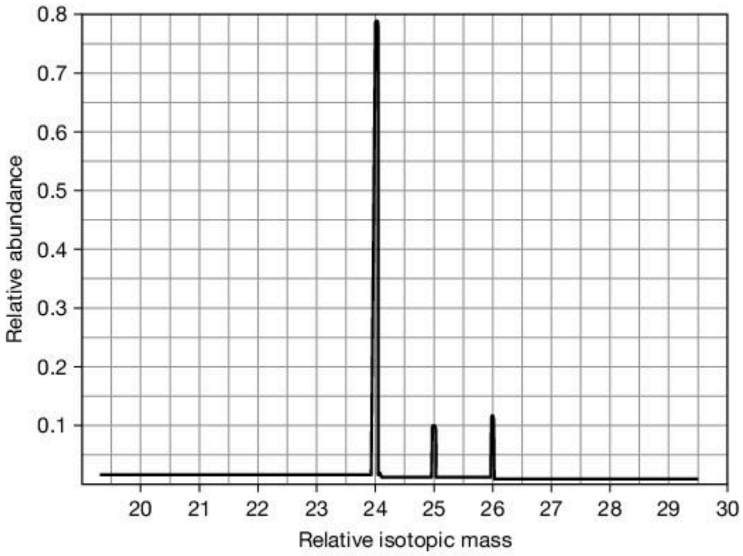
A_r = (fraction of sample that is isotope 1 × relative isotopic mass of isotope 1)
+ (fraction of sample that is isotope 2 × relative isotopic mass of isotope 2)

Link

There is more about mass spectrometry in Unit 22, Analytical techniques.

Worked example

The mass spectrum in Figure 1.2 is for naturally occurring magnesium. Use data from the mass spectrum to calculate the relative atomic mass of magnesium.



▲ **Figure 1.2** The mass spectrum of magnesium

Answer

A_r = (fraction that is ^{24}Mg × relative isotopic mass of ^{24}Mg)
+ (fraction that is ^{25}Mg × relative isotopic mass of ^{25}Mg)
+ (fraction that is ^{26}Mg × relative isotopic mass of ^{26}Mg)

$A_r = (0.79 \times 24.0) + (0.10 \times 25.0) + (0.11 \times 26.0)$

$A_r = 24.3$

Remember

In calculations, include all the isotopes that are shown on a mass spectrum. Figure 1.2 shows three isotopes of magnesium, which must all be included in the calculation.

The calculation of empirical and molecular formulae

Read the definitions for **empirical formula** and **molecular formula** carefully, and note the difference between them.

For example, a vitamin C molecule is made up of 6 carbon atoms, 8 hydrogen atoms and 6 oxygen atoms. Its molecular formula is $C_6H_8O_6$. Its empirical formula shows the simplest ratio of the number of atoms of each element, and is $C_3H_4O_3$.

You can calculate empirical and molecular formulae if you know the composition by mass of a compound:

1 Write down the masses of each element in a sample of the compound (you will be given this data).

2 Calculate the number of moles of each element.

3 Calculate the simplest ratio for the number of atoms of each element. This gives you the empirical formula.

4 Use the value of M_r to work out the molecular formula.

You can also calculate empirical and molecular formulae from combustion data. Question 2 in the worked example below shows how to do this.

Key terms

Empirical formula: this shows the **simplest whole-number ratio** for the atoms of each element in a compound.

Molecular formula: this shows the **actual number of atoms** of each element in one molecule of a compound.

Worked examples

1 A sample of a compound contained 1.320 g of carbon and 0.330 g of hydrogen only. Its M_r is 30.0. What is its molecular formula?

Answer

		carbon	hydrogen
1	Masses of elements in compound	1.320 g	0.330 g
	Mass of 1 mol of elements	12.0 g mol^{-1}	1.0 g mol^{-1}
2	Number of moles of each element in compound	$\frac{1.32\text{ g}}{12.0\text{ g mol}^{-1}}$ = 0.110 mol	$\frac{0.330\text{ g}}{1.00\text{ g mol}^{-1}}$ = 0.330 mol
3	Ratio of masses of atoms	$\frac{0.110}{0.110} = 1$	$\frac{0.330}{0.110} = 3$

So the empirical formula is CH_3.

The relative mass shown by the empirical formula = 12.0 + (3 × 1.0) = 15.0

Since M_r = 30.0, there are twice as many atoms in the molecular formula as in the empirical formula, so the molecular formula of the compound is C_2H_6.

2 On combustion, a sample of a compound containing only carbon and hydrogen produced 1.10 g of carbon dioxide and 0.90 g of water. Calculate the masses of carbon and hydrogen in the compound.

Answer

$$\text{Amount of } CO_2 \text{ (mol)} = \frac{\text{mass of substance (g)}}{\text{mass of 1 mol (g mol}^{-1})}$$

$$= \frac{1.10\text{ g}}{44.0\text{ g mol}^{-1}}$$

$$= 0.025\text{ mol}$$

One mole of CO_2 contains 1 mol of carbon, so 0.025 mol of CO_2 contains 0.025 mol of carbon.

So the mass of carbon in the sample of the compound
= amount of substance (mol) × mass of 1 mol (g mol^{-1})
= 0.025 mol × 12.0 g mol^{-1} **= 0.30 g**

$$\text{Amount of } H_2O \text{ (mol)} = \frac{\text{mass of substance (g)}}{\text{mass of 1 mol (g mol}^{-1}}$$

$$= \frac{0.90\text{ g}}{18.0\text{ g mol}^{-1}}$$

$$= 0.050\text{ mol}$$

One mole of H_2O contains 2 mol of hydrogen, so 0.05 mol of H_2O contains (2 × 0.05) = 0.10 mol of hydrogen.

So the mass of hydrogen in the sample of the compound
= amount of substance (mol) × mass of 1 mol (g mol^{-1})
= 0.10 mol × 1.0 g mol^{-1} **= 0.10 g**

Reacting masses and volumes of solutions and gases

Balancing equations

To calculate the masses of substances that react together, and the masses of products formed, you need to write balanced equations. Follow these steps to write a balanced equation:

1. Write a word equation.
2. Write chemical symbols of elements and chemical formulae for compounds below their names in the word equation.
3. Balance the equation by writing numbers to the left of the symbols and/or formulae until there are the same number of atoms of each element on both sides of the equation.
4. Add state symbols if possible, and certainly if you are asked to.

Worked example

When propane gas (C_3H_8) burns in a camping stove, the products are carbon dioxide and water. Write a balanced equation for the reaction.

Answer

Step 1 propane + oxygen → carbon dioxide + water

Step 2 $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$

Step 3 $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Step 4 $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

Common error

Candidates often confuse the small numbers in chemical formulae with the numbers of molecules. You must only change the large numbers to the left of symbols and formulae when balancing equations.

Remember

The numbers on the left of a formula apply to each type of atom in that formula.

It is useful to know the masses of reactants that react together, or the masses of products made. You can calculate reacting masses by following these steps:

1. Write a balanced equation.
2. Write the number of moles of the reactants and products of interest.
3. Use values of A_r and M_r to calculate reacting masses of reactants and products of interest.
4. Scale up – or scale down – these reacting masses.

Worked example

Calculate the mass of carbon dioxide produced on the complete combustion of 100 g of methane, and the mass of oxygen used in the reaction.

Answer

Step 1 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Step 2 1 mol of CH_4 reacts with 2 mol of O_2 to make 1 mol of CO_2

Step 3 $M\ (CH_4) = 16.0\,g$
$M\ (O_2) = 32.0\,g$
$M\ (CO_2) = 44.0\,g$

Since 1 mol of CH_4 reacts with 2 mol of O_2 to make 1 mol of CO_2, 16.0 g of CH_4 reacts with (2 × 32.0 g) = 64.0 g of oxygen to make 44.0 g of CO_2.

Step 4 Use ratios to find the masses of O_2 and CO_2.

$$\text{Mass of oxygen} = \frac{64}{16} \times 100\,g$$
$$= 400\,g$$

$$\text{Mass of carbon dioxide} = \frac{44}{16} \times 100\,g$$
$$= 275\,g$$

Reacting volumes of gases

As well as calculating reacting masses, you can also work out volumes of gases that react. Since 1 mol of any gas occupies the same volume (24.0 dm^3 at room temperature and pressure, or 22.4 dm^3 at standard temperature and pressure) you can use the volume of a gas to calculate its amount:

Remember

$1\,dm^3 = 1000\,cm^3 = 1$ litre

$$\text{Amount of gas (mol)} = \frac{\text{volume of gas } (dm^3)}{\text{molar volume } (dm^3\,mol^{-1})}$$

Worked example

Calculate the volume of carbon dioxide produced on complete combustion of 10.0g of heptane, C_7H_{16}, at room temperature and pressure.

Answer

$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

1 mol of heptane produces 7 mol of carbon dioxide.

$M_r(C_7H_{16}) = 100.0$ so 10.0 g is 0.1 mol

0.1 mol of heptane produces 0.7 mol of carbon dioxide

$$\text{Volume of 0.7 mol of } CO_2\ (dm^3) = \text{amount of gas (mol)} \times \text{molar volume } (dm^3\,mol^{-1})$$
$$= 0.7\,mol \times 24\,dm^3\,mol^{-1}$$
$$= 16.8\,dm^3$$

Volumes and concentrations of solutions

Chemists need to know how to make solutions of given concentrations. The concentration of a solution is given by the expression below:

$$\text{Concentration } (mol\,dm^{-3}) = \frac{\text{amount of solute (mol)}}{\text{volume of solution } (dm^3)}$$

Worked example

Normal saline solution used in hospitals is sodium chloride solution of concentration 0.154 mol dm^{-3}.

Calculate the mass of solute needed to make 10.0 dm^3 of the solution.

Answer

Amount of solute (mol)

$= \text{concentration (mol dm}^{-3}) \times \text{volume of solution (dm}^3)$

$= 0.154\,\text{mol dm}^{-3} \times 10.0\,\text{dm}^3$

$= 1.54\,\text{mol}$

$M_r(\text{NaCl}) = 23.0 + 35.5 = 58.5$

So mass of 1.00 mol = 58.5 g

Mass of 1.54 mol(g) $= 1.54\,\text{mol} \times 58.5\,\text{g mol}^{-1}$

$= 90.1\,\text{g}$

Remember

Rearrange the equation you are using so that the quantity you want to calculate is the subject.

Maths skills

Changing the subject of an equation

To change the subject of an equation, carry out the same operation, for example multiplying, to both sides of the equation to get the variable that you want on its own.

For example, in the worked example above,

$$\text{concentration (mol dm}^{-3}) = \frac{\text{amount of solute (mol)}}{\text{volume of solution (dm}^3)}$$

To get *amount of solute* on its own multiply both sides by *volume of solution* and then cancel out:

$$\text{concentration (mol dm}^{-3}) \times \text{volume of solution (dm}^3) = \frac{\text{amount of solute (mol)}}{\cancel{\text{volume of solution (dm}^3)}} \times \cancel{\text{volume of solution (dm}^3)}$$

$$\text{concentration (mol dm}^{-3}) \times \text{volume of solution (dm}^3) = \text{amount of solute (mol)}$$

Stoichiometric relationships

You can use reacting masses, volumes and solutions to work out the amounts of reactants and products in chemical reactions. This makes it possible to deduce **stoichiometric relationships**.

Follow these steps to work out the equation for a reaction:

1. Find by experiment the masses or volumes of reactants and products.
2. Convert the masses and volumes to amounts in moles.
3. Work out the simplest whole-number ratios for the amounts in moles.

Key terms

Stoichiometric relationship: the stoichiometric relationship for a reaction is the simplest whole-number ratio for the molar amounts of reactants and products.

Worked example

0.460g of sodium reacts with 0.240 dm³ of chlorine, measured at room temperature and pressure. The product of the reaction is sodium chloride, NaCl. Show that the equation for the reaction is: $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$

Answer

$$\text{Amount of Na in moles} = \frac{0.460\,\text{g}}{23.0\,\text{g mol}^{-1}} = 0.020\,\text{mol}$$

$$\text{Amount of Cl}_2\text{ in moles} = \frac{0.240\,\text{dm}^3}{24.0\,\text{dm}^3\,\text{mol}^{-1}} = 0.010\,\text{mol}$$

The ratio of the amounts of $\text{Na}:\text{Cl}_2$ is

0.020 mol : 0.010 mol

2 : 1

Raise your grade

(a) Define the term *mole*. [1]

The relative atomic mass of an element in grams. ✗

This definition is incomplete – the candidate needs to be word perfect when learning definitions.

(b) 1.00 g of a sample of a compound of empirical formula $C_xH_yO_z$ was burnt in excess oxygen.

The carbon dioxide produced was absorbed by soda lime granules in a test tube, and the water produced was absorbed by anhydrous calcium chloride in another test tube. The table shows the increase in mass of the two test tubes and their contents.

Substance in test tube at start	Mass of test tube and contents at start /g	Mass of test tube and contents at end /g
Soda lime	32.22	33.69
Anhydrous calcium carbonate	31.98	32.58

(i) Calculate the masses of carbon dioxide and water produced in the reaction.

Mass of carbon dioxide = 33.69 g − 32.22 = 1.47 g

Mass of carbon dioxide = 1.47 g

Mass of water = 0.60 g ✓ [1]

Both answers are correct. The candidate has shown their working clearly for carbon dioxide, and included the units. It would be useful to show the working for water as well.

(ii) Calculate the amounts of carbon and hydrogen in the sample.

mass of 1 mole of CO_2 = 44 g, so in the sample there are 1.47 ÷ 44 g = 0.0334 mol of CO_2.

mass of 1 mole of water = 18 g, so in the sample there are 0.03333333333333 mol of H_2O

Amount of carbon = 0.0334 mol ✓

Amount of hydrogen = 0.033333333333 mol ✗ [3]

The first answer is correct, but the second answer is the amount of water, not the amount of hydrogen. Also, the number of significant figures should be no more than the number of significant figures given in the data in the question.

Again, the candidate should have shown their working for the water calculation.

(iii) Calculate the masses of carbon, hydrogen and oxygen in the sample. [3]

There are 0.0334 mol of carbon in the sample. This has a mass of 12 g mol^{-1} × 0.0334 mol = 0.4008. ✓

Mass of hydrogen = 0.0333 since its A_r is 1. ✗

This answer is incorrect. 1 mol of H_2O has 2 mol of H atoms, so the mass of H in the sample = 0.0334 × 2 = 0.0668 g

Mass of oxygen = mass of sample − (mass of carbon + mass of hydrogen)

= 1.00 g − (0.4008 g + 0.0333 g) = 0.566 g ✓ (ecf)

This answer gains a mark, since the working is correct. The value substituted in the equation for the mass of H should be 0.0668 not 0.0333. The correct answer is 0.5324 g. ‘ecf’ stands for ‘error carried forward’.

Mass of carbon = 0.4008 g
Mass of hydrogen = 0.0668 g
Mass of oxygen = 0.5324 g

(iv) Deduce the values of x, y and z in $C_xH_yO_z$.

Amount C in sample = 0.0334 mol (from part (ii))

Amount of H in sample = 0.0333 mol (from part (ii))

Mass of O in sample is 0.566 g ÷ 16 g mol^{-1} = 0.035 mol

The amounts are all approximately the same, so the ratio is 1:1:1.

x = 1 ✔
y = 1 ✔ (ecf)
z = 1 ✔ (ecf)

[3]

The candidate has shown their working, which is correct. For this reason they gain full marks for this part of the question.

The correct amount of oxygen is 0.5324 g ÷ 16 g mol^{-1} = 0.0333

This gives the correct ratio as C : H : O
0.0334 : 0.0666 : 0.0333

Then divide the three numbers by the smallest number, 0.0333, to get the simplest ratio.

This gives $x = 1$, $y = 2$ and $z = 1$

(v) The relative molecular mass of $C_xH_yO_z$ is 60. Deduce the molecular formula of the compound.

molecular formula = CHO ✗ [1]

The correct empirical formula (from (iv)) is CH_2O. The value of M_r for this is given by $12.0 + (2 \times 1.0) + 16.0 = 30.0$
This is half the value of the M_r given, so the correct molecular formula is $C_2H_4O_2$.

(c) Soda lime granules are used to absorb the carbon dioxide that is breathed out by a patient in an operation. Soda lime is a mixture of calcium hydroxide with smaller amounts of water, sodium hydroxide and potassium hydroxide.

(i) Carbon dioxide reacts with calcium hydroxide to make calcium carbonate and water.
Write an equation for the reaction. [1]

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$ ✔

(ii) A patient exhales 7 dm^3 of gases every minute, measured at room temperature and pressure.
Her exhaled breath contains 3% carbon dioxide.
Calculate the mass of water produced as a result of the reaction in **(i)** in one minute. [3]

Volume of CO_2 per minute = $\frac{3}{100} \times 7\,\text{dm}^3 = 0.21\,\text{dm}^3$

1 mol of gas occupies 24 dm^3 at room temperature and pressure,

so amount of CO_2 = $\frac{0.21\,\text{dm}^3}{24\,\text{dm}^3\,\text{mol}^{-1}} = 8.75 \times 10^{-3}$ mol ✔

The equation shows that 1 mol of CO_2 makes 1 mol of H_2O

so amount of water = 8.75×10^{-3} mol ✔

1 mol of water has a mass of $(2 \times 1.0) + 16 = 18$ g

So mass of 8.75×10^{-3} mol of water = 0.158 g

Mass of water = 0.158 g ✔

This answer is correct, and the working is clearly shown throughout. It gains full marks.

Exam-style questions

1 What is the relative formula mass of aluminium sulfate, $Al_2(SO_4)_3$?

A 123 **B** 150 **C** 315 **D** 342 [1]

2 **(a)** Define the term *relative atomic mass*. [1]

(b) The table shows the isotopes in a naturally occurring sample of zinc.

Use data from the table to calculate the relative atomic mass of zinc.

Show all your working, and give your answer to three significant figures. [2]

Relative isotopic mass	Relative abundance (%)
64	49
66	28
67	4
68	19

3 Nonane is a component of kerosene, which is used as jet fuel.

100 g of nonane, C_9H_{20}, was completely burnt in a jet engine, forming carbon dioxide and water.

(a) Construct a balanced equation for the reaction. [1]

(b) Calculate the amount of nonane burnt, in moles. [2]

(c) Calculate:

(i) the amount of oxygen, O_2, required, in moles [2]

(ii) the mass of oxygen required, in grams [2]

(iii) the volume of oxygen required, in dm^3, at room temperature and pressure.

Assume that one mole of gas occupies $24.0\,dm^3$ under these conditions. [2]

(d) Estimate the volume of air required for the reaction.

Assume that air is 21% oxygen by volume. [1]

(e) Calculate the mass of carbon dioxide formed. [2]

4 A salt, X, has the formula $(NH_4)_aFe_b(SO_4)_c.dH_2O$.

(a) A sample containing 0.981 g of X was dissolved in water.

The solution was added to barium chloride solution, $BaCl_2$, and a precipitate formed.

The mixture was filtered and the precipitate was dried and weighed.

The mass of precipitate formed was 1.17 g.

(i) Deduce an ionic equation for the reaction of barium and sulfate ions in solution to make a precipitate of barium sulfate. [1]

(ii) Calculate the amount of precipitate formed, in moles. [2]

(iii) Deduce the amount of sulfate in 1.00 g of X, in moles. [1]

(iv) Calculate the mass of sulfate in 1.00 g of X, in grams. [2]

(b) A fresh 0.981 g sample of X was added to sodium hydroxide solution.

$0.120\,dm^3$ of ammonia gas was produced.

(i) Calculate the amount of ammonia, NH_3, produced, in moles.

Assume that one mole of gas occupies $24.0\,dm^3$. [2]

(ii) Calculate the mass of ammonium, NH_4^+, in 1.00 g of X. [2]

(c) A fresh 0.981 g sample of X was dissolved in water to make $25.00\,cm^3$ of solution.

The solution was titrated with $0.020\,mol\,dm^{-3}$ potassium manganate(VII) solution.

$25.00\,cm^3$ of the potassium manganate(VII) solution was required.

The equation for the reaction is

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(i) Calculate the amount of MnO_4^- used in the reaction. [2]

(ii) Calculate the amount of Fe^{2+} in the sample of X. [2]

(iii) Calculate the mass of Fe^{2+} in the sample of X. [2]

(d) **(i)** Use your answers to parts (a), (b) and (c) to calculate the mass of water in 0.981 g of X. [2]

(ii) Calculate the amount of water in 0.981 g of X, in mol. [2]

(e) Deduce the values of *a*, *b*, *c* and *d* in the formula of X. [2]

2 Atomic structure

Key points

☐ Describe the structure of the atom.
☐ Identify sub-atomic particles.
☐ Distinguish between isotopes.
☐ Deduce electronic configurations of atoms and ions.
☐ Interpret ionisation data.
☐ Explain and use ideas about electron affinity.

Particles in the atom

Atoms are made up of three types of **sub-atomic particles** – protons, neutrons and electrons. Table 2.1 shows their properties.

Key term

Sub-atomic particles: the particles that make up atoms.

▼ **Table 2.1** Masses and charges of sub-atomic particles

Sub-atomic particle	Relative mass (atomic mass units)	Relative charge
Proton	1	+1
Neutron	1	0
Electron	$\frac{1}{1840}$	–1

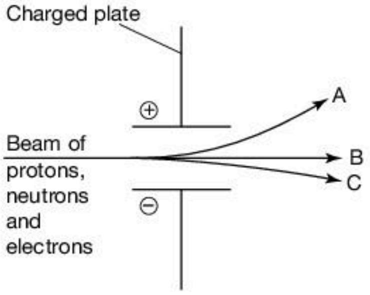
Atoms have a tiny positively charged nucleus, which is made up of protons and neutrons. Almost all of the mass of an atom is in its nucleus. Electrons move around in the space outside the nucleus.

Worked example

A narrow beam of protons, neutrons and electrons enters an electric field. The beam splits up as shown in Figure 2.1.

a) Deduce and explain which types of sub-atomic particle are shown by beams A, B and C.

b) Explain why beam A is deflected more than beam C.



▲ **Figure 2.1** A particle beam entering an electric field

Answer

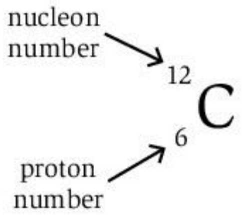
a) Beam A is made up of electrons, since negative electrons are attracted to the positively charged plate. Beam C is made up of protons, since positive protons are attracted to the negatively charged plate. Beam B is made up of neutrons, since neutral neutrons are not deflected by an electric field.

b) Beam A is deflected more than beam C because electrons have a smaller mass than protons.

★ Exam tip

The question asks you to deduce *and explain*, so you need to write down how you know which beam is which.

Every atom has a **proton number** and a **nucleon number**. They are shown like this:



You can use proton and nucleon numbers to calculate the numbers of protons, neutrons and electrons in atoms and ions.

Key terms

Proton number: an atom's proton number is the number of protons in the atom.

Nucleon number: an atom's nucleon number is the sum of the numbers of protons and neutrons.

Nucleons: protons and neutrons. They are called nucleons because they occupy the nucleus.

Worked example

Give the numbers of protons, neutrons and electrons in the ion $^{31}_{15}P^{3-}$.

Answer

Number of protons = 15
Number of neutrons = 31 – 15 = 16

Since the formula shows an ion, the number of electrons is not equal to the number of protons. The charge on the ion is −3, so there are three more electrons than protons in the ion.

Number of electrons = number of protons + 3
= 15 + 3
= 18

★ Exam tip

Learn all definitions carefully. You need to be word perfect.

★ Exam tip

Show all your working. This will help you to avoid mistakes and to check your work. If your working is correct you might get some of the marks, even if your answer is incorrect.

Isotopes

Most elements have atoms with different masses. These are called **isotopes**. The isotopes of an element have:

- the same number of protons, and the same proton number.
- different numbers of neutrons, and so different nucleon numbers.

Key term

Isotopes: atoms of the same element with different numbers of neutrons, and so different nucleon numbers.

✗ Common error

Candidates often confuse **ions** and isotopes.

- Ions are charged particles – different ions of an element have the same number of protons but different numbers of electrons.
- Isotopes are atoms of an element with different relative masses – atoms of different isotopes of an element have the same numbers of protons and electrons but different numbers of neutrons.

✗ Common error

Candidates sometimes forget to include the word 'atoms' when defining isotopes. Make sure you include it.

Worked example

Give the numbers of protons and neutrons in the isotopes of gold with the chemical symbols below.

a) $^{197}_{79}Au$ **b)** $^{195}_{79}Au$

Answer

a) Number of protons = proton number = 79
Number of neutrons = nucleon number – proton number
= 197 – 79
= 118

★ Exam tip

You can check your answers by adding the numbers of protons and neutrons. The total should be equal to the nucleon number given in the chemical symbol.

b) Number of protons = 79
Number of neutrons = 195 – 79 = 116

Electrons in atoms: electron configuration

Electrons exist in atoms in shells, or energy levels. For example, a sodium atom has 11 electrons. You can describe its electronic configuration simply as 2.8.1. This means that a sodium atom has:

- 2 electrons in an energy level with **principal quantum number** $n = 1$
- 8 electrons in an energy level with principal quantum number $n = 2$
- 1 electron in an energy level with principal quantum number $n = 3$

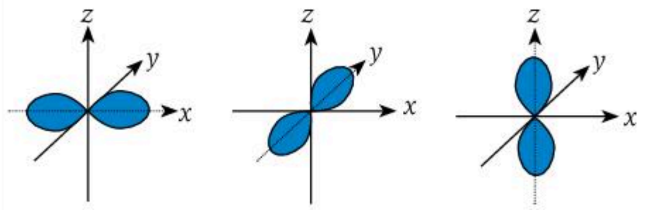
Within each energy level, electrons are in sub-shells, or **orbitals**. Each orbital can hold up to two electrons. An energy level may have:

- one s orbital
- three p orbitals
- five d orbitals.

Figures 2.2 and 2.3 show the shapes of s and p orbitals.

Exam tip

You need to be able to sketch the shapes of the s and p orbitals, so practise drawing them.



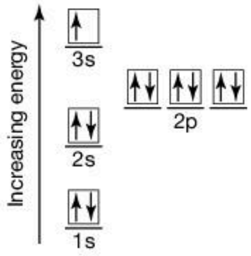
▲ **Figure 2.3** The three p orbitals in an energy level

The relative energy levels of the orbitals increase as follows, from 1s to 4p:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p

Since electrons fill orbitals in order of increasing energy, the electronic configuration of a sodium atom is: $1s^2\ 2s^22p^6\ 3s^1$

You can also show electronic configurations as electrons in boxes, as in Figure 2.4.



▲ **Figure 2.4** The electronic configuration of sodium

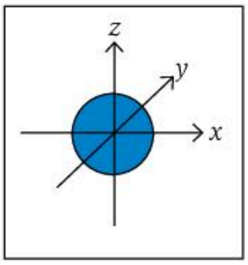
Worked example

State the electronic configurations of:

Key terms

Principle quantum number, n: the energy level number, or shell number.

Orbital: an area outside the nucleus that can hold up to two electrons.



▲ **Figure 2.2** An s orbital

Link

There is more about orbitals in Unit 12, Transition elements.

Common error

Candidates sometimes forget that the 3d orbital has a higher relative energy than the 4s orbital. So the electronic structure of potassium is: $1s^2\ 2s^22p^6\ 3s^23p^6 4s^1$ *not* $1s^2\ 2s^22p^6\ 3s^23p^6 3d^1$

a) ${}^{20}_{40}\mathrm{Ca}$ **b)** ${}^{37}_{17}\mathrm{Cl}^-$

Answer

a) The atom has 20 electrons. The orbitals are filled up in order of increasing energy, so the electronic configuration is: $1s^2\ 2s^22p^6\ 3s^23p^64s^2$

b) A chlorine atom has 17 electrons, and a chloride ion has 18 electrons. The electronic configuration is: $1s^2\ 2s^22p^6\ 3s^23p^6$

★ **Exam tip**

When you have written an electronic configuration, check that you have included the correct total number of electrons by adding up the small numbers.

Trends in ionisation energy

Energy is required to remove electrons from atoms to form ions:

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

Three factors influence the **first ionisation energy** of an atom:

- the distance of the outermost electron from the nucleus
- the size of the positive nuclear charge
- the shielding effect of inner electrons.

Key term

First ionisation energy: the energy required to remove one electron from each atom in one mole of gaseous atoms to make one mole of gaseous ions with one positive charge.

Worked examples

1 Table 2.2 shows the first ionisation energies of some Group 1 elements. Describe and explain this trend.

▼ **Table 2.2** First ionisation energies of some Group 1 elements

Element	First ionisation energy /kJ mol^{-1}
Sodium	494
Potassium	418
Rubidium	403
Caesium	376

Answer

Going down Group 1, the first ionisation energy decreases. There are two reasons for this:

- As the distance from the positive nucleus to the negative outermost electron increases, the attraction between the positive nucleus and the outermost electron decreases, resulting in decreasing ionisation energies down the group.
- Going down the group, there are more electrons in inner shells. These shield the outermost electron from the positive charge of the nucleus. This effect decreases ionisation energies down the group.

Both reasons above outweigh the effect of the increasing nuclear charge from top to bottom of the group.

2 Figure 2.5 shows the relative first ionisation energies of the Period 2 elements.

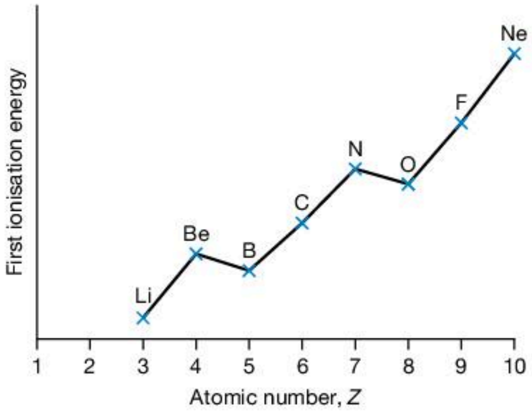
Describe and explain:

a) the general trend across Period 2

b) one exception to the general trend.

★ **Exam tip**

In the worked example, the answer is divided into two points. Each paragraph gives one reason for the trend. When you answer exam questions which require explanations, organise your work into paragraphs. Each paragraph should make one main point, or group of points.



▲ **Figure 2.5** First ionisation energies of the Period 2 elements

Answer

a) The general trend is that first ionisation energy increases across the period. There are two reasons for this.

The first is that the nuclear charge increases across the period, so attraction between the nucleus and outermost electron increases.

The second reason is that atomic radii decrease across the period, so the distance from the positive nucleus to the negative outermost electron decreases. This means that the attraction between the positive nucleus and the outermost electron increases.

Together, increasing nuclear charge and decreasing atomic radii result in an overall increase in first ionisation energies across Period 2.

b) The first ionisation energy of Be is greater than that of B, because of their electronic configurations: Be is $1s^22s^2$ and B is $1s^22s^22p^1$.

Since the 2p orbital has a higher energy than the 2s orbital, less energy is needed to remove an electron from a 2p orbital in B than is needed to remove an electron from a 2s orbital in Be. The first ionisation energy of Be is therefore greater.

Or

The first ionisation energy of O is less than that of N. One oxygen p orbital has two electrons, which repel each other, so less energy is required to remove one.

Link

There is more about patterns across periods in Unit 9, Chemical periodicity.

Ionisation energy and electronic configurations

Lithium has three electrons, so three ionisation energies:

- The first ionisation energy is for: $\text{Li(g)} \rightarrow \text{Li}^+\text{(g)} + e^-$
- The second ionisation energy is for: $\text{Li}^+\text{(g)} \rightarrow \text{Li}^{2+}\text{(g)} + e^-$
- The third ionisation is for: $\text{Li}^{2+}\text{(g)} \rightarrow \text{Li}^{3+}\text{(g)} + e^-$

▼ **Table 2.3** The three ionisation energies for lithium

Ionisation number	Ionisation energy /kJ mol^{-1}
1	519
2	7300
3	11 800

Table 2.3 shows that the values of ionisation energy increase down the column. This is because, after an electron is removed, the remaining electrons are attracted more strongly to the nucleus.

You can use successive ionisation energies for an element to predict electronic configurations.

Worked example

Table 2.4 shows the first four ionisation energies of an element, X. Predict its group in the periodic table.

▼ **Table 2.4** The first four ionisation energies of element X

Ionisation number	Ionisation energy /kJ mol^{-1}
1	577
2	1820
3	2740
4	11 600

Answer

The element is in Group 3.

Remember

You can work out the group by looking for big jumps in ionisation energy. Since the big jump is between the third and fourth ionisation energies in Table 2.4, the fourth electron is being removed from an inner shell.

Electron affinity

Energy is released when electrons are added to atoms to make ions:

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

Key term

Electron affinity: the energy released on adding one mole of electrons to one mole of gaseous atoms to make one mole of gaseous negative ions.

Worked example

Table 2.5 shows the **electron affinity** values of the Group 17 elements. Describe and explain this trend.

▼ **Table 2.5** Electron affinities of the Group 17 elements

Element	Electron affinity /kJ mol^{-1}
Fluorine	328
Chlorine	349
Bromine	325
Iodine	295

Answer

From chlorine to iodine electron affinity decreases. This is because incoming electrons are less strongly attracted to the nucleus as a result of increased shielding from inner electron shells, and of the increased distance between the nucleus and the outer shell.

However, the electron affinity of fluorine is less than that of chlorine. This is because of the repulsive force exerted by the electrons that are crowded into the small space around the fluorine nucleus.

Raise your grade

1 Boron exists naturally as two stable isotopes, ^{10}B and ^{11}B.

(a) Write down

(i) the proton number of the ^{10}B isotope. [1]

5 ✓

This answer is correct. The candidate used the periodic table in the data booklet to find the proton number.

(ii) the nucleon number of ^{10}B isotope. [1]

$5 + 10 = 15$ ✗

The correct answer is 10, which is shown in the chemical symbol of the isotope, ^{10}B. The nucleon number is the sum of the number of protons and neutrons in the atom. The candidate has mistakenly added the proton number to the nucleon number to calculate their answer.

(b) The table shows the relative isotopic mass and the relative abundance of each stable isotope of boron.

Isotope	Relative isotopic mass	Relative isotopic abundance
^{10}B	10.01	19.9
^{11}B	11.01	80.1

(i) Define the term *relative isotopic mass*. [1]

Relative isotopic mass is the mass of an isotope. ✗

This definition is incomplete. The complete definition is that *Relative isotopic mass is the mass of an isotope relative to $\frac{1}{12}$ of the mass of an atom of carbon-12.*

★ **Exam tip**

It is vital to learn definitions carefully, until you are word perfect.

(ii) Calculate the relative atomic mass of naturally occurring boron. Give your answer to three significant figures. [2]

$$\text{relative atomic mass} = \frac{(19.9 \times 10.01) + (80.1 \times 11.01)}{100}$$

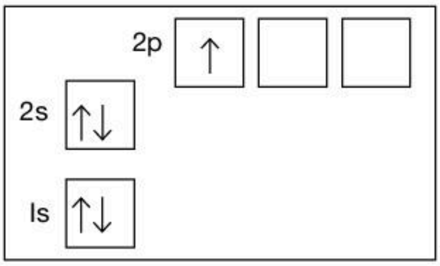
relative atomic mass = 1080 (3 sig.fig.) ✗

The candidate used the correct equation and showed her working clearly, so achieving the first mark for the question. However, she forgot to divide by 100, so losing the second mark. If the candidate had thought about her answer, she would have realised that it is much too big. The correct answer is 10.8.

★ **Exam tip**

Check your answers to see if they are of a sensible order of magnitude.

(c) (i) Complete the diagram below to show the electronic configuration of boron. [1]



✔

(ii) Write the electronic configuration of boron in the form $1s^2$… [1]

1s2 2s2 2p1 ✘

The candidate has shown that she knows the number of electrons in each orbital, but she has not used the correct format – the number of electrons in each orbital must be shown as a small superscript number. The correct answer is $1s^2\ 2s^2\ 2p^1$.

2 (a) Define the term *first ionisation energy.* [1]

The energy required to remove one electron from each atom in one mole of gaseous atoms to make one mole of gaseous ions with one positive charge. ✔

The candidate has learnt this definition carefully, and so achieved the mark.

(b) The second ionisation energy of aluminium is 1820 kJ mol^{-1}. Write an equation to represent the process that occurs. [1]

$Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$ ✘

This equation represents the third ionisation energy. The second ionisation energy is the energy required to remove the second electron to make an ion with a +2 charge, so the correct answer is: $Al^+(g) \rightarrow Al^{2+}(g) + e^-$

Exam-style questions

1 What are the numbers of protons, neutrons and electrons in $^{51}_{23}\mathrm{V}^{3+}$? [1]

A 28 protons, 23 neutrons, 25 electrons

B 28 protons, 23 neutrons, 31 electrons

C 23 protons, 23 neutrons, 26 electrons

D 23 protons, 28 neutrons, 20 electrons

2 The table shows the successive ionisation energies of four elements. Which element is in Group 2 of the periodic table? [1]

Element	Ionisation energy /kJ mol^{-1}			
	First	**Second**	**Third**	**Fourth**
A	736	1450	7740	10 500
B	577	1820	2740	11 600
C	786	1580	3230	4360
D	1060	1900	2920	4960

3 The elements nihonium and moscovium were named in 2016. Each element has several isotopes.

(a) Define the term *isotope*. [1]

(b) The chemical symbol for one moscovium isotope is $^{288}_{115}\mathrm{Mc}$. Give its proton and nucleon numbers. [1]

(c) The chemical symbol for one nihonium isotope is $^{286}_{113}\mathrm{Nh}$.

(i) Calculate the number of neutrons in an atom of the nihonium isotope shown above. [1]

(ii) Another nihonium isotope has 165 neutrons.

Write its full chemical symbol, showing its proton and nucleon numbers. [1]

4 Element X has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^5$.

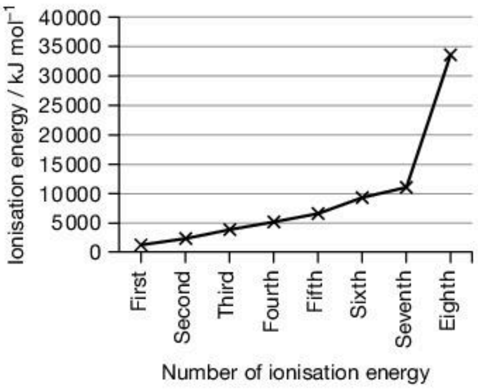
(a) Sketch the shape of a single p orbital. [1]

(b) Give the proton number of element X. [1]

(c) In which group of the periodic table is element X? [1]

(d) Give the electronic configuration of the X^- ion. [1]

(e) The graph below shows successive ionisation energies for element X.



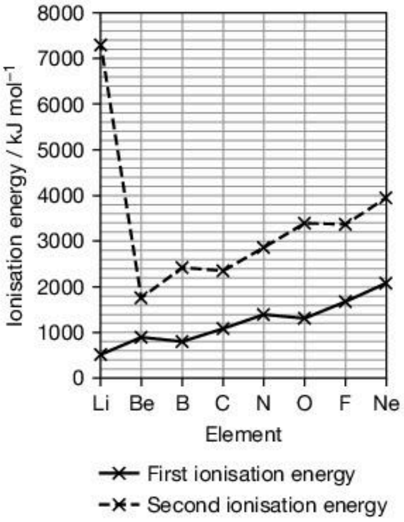
(i) Describe and explain the overall trend shown on the graph. [2]

(ii) Explain the difference between the seventh and eighth ionisation energies. [1]

(iii) Write an equation to represent the fifth ionisation energy. [1]

(iv) The difference between the fifth and sixth ionisation energies is greater than the difference between the fourth and fifth ionisation energies. Explain why. [1]

5 The graph below shows the first and second ionisation energies of the elements in Period 2.



(a) Describe and explain the general trend in first ionisation energies from left to right of Period 2. [2]

(b) Write down the electron configurations of N and O, and use these to explain why the first ionisation energy of O is less than that of N. [2]

(c) Explain why the second ionisation energy is greater than the first ionisation energy for all the elements in Period 2. [1]

(d) Describe and explain the difference in second ionisation energy for Li and Be. [2]

3 Chemical bonding

AS 3.1–3.14 pages 42–63

Key points

- ☐ Use dot-and-cross diagrams to describe ionic, covalent and co-ordinate bonding.
- ☐ Explain and predict the shapes of molecules.
- ☐ Describe hydrogen bonding and van der Waals forces.
- ☐ Use ideas about electronegativity to explain dipoles.
- ☐ Describe metallic bonding.
- ☐ Describe, interpret and predict the effect of different types of bonding on physical properties.

Ionic bonding

When a metal reacts with a non-metal, electrons are transferred from the metal atom to the non-metal atom, forming an **ionic bond**. This process forms positive and negative ions with full outer electron shells.

Key term

Ionic bond: a bond made when electrons are transferred from atoms of a metal (or occasionally a non-metal, as in the case of ammonium ions) to atoms of a non-metal to make oppositely charged ions. The ions are held together by strong electrostatic forces acting in all directions.

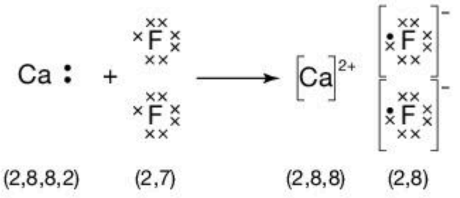
Worked example

a) Draw a dot-and-cross diagram to describe the transfer of electrons in the formation of CaF_2. Show the outer electrons only.

b) Explain the size of the charges on the ions formed.

Answer

The calcium atom transfers one electron to each of two fluorine atoms.



The calcium ion has 20 protons and 18 electrons, so it has a charge of +2.

The fluoride ions have 9 protons and 10 electrons, so they each have a charge of −1.

Covalent and co-ordinate bonding

In most non-metal elements, and in compounds of non-metals, atoms join together by sharing electrons. One shared pair of electrons is a single **covalent bond**. In most covalently bonded compounds, each atom gains a full outer electron shell. In a few compounds, a **co-ordinate bond** is formed by the sharing of a pair of electrons provided by one atom.

Key terms

Covalent bond: a bond made by sharing a pair of electrons between two atoms.

Co-ordinate bond: a type of covalent bond in which both electrons are donated by one atom.

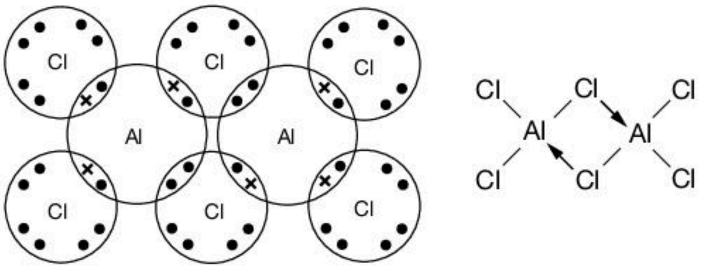
Worked example

Draw dot-and-cross diagrams to show the bonding in CO_2 and Al_2O_6. Draw and describe the bonds formed in each case.

Answer

In CO_2 each bond consists of two shared pairs of electrons. These are double bonds.

In Al_2O_6 two of the bonds are co-ordinate bonds. In these bonds, both electrons are donated by one chlorine atom.



Exam tip

When you draw dot-and-cross diagrams, check that each atom has a share of 8 electrons in its outer shell, or two for hydrogen.

Remember

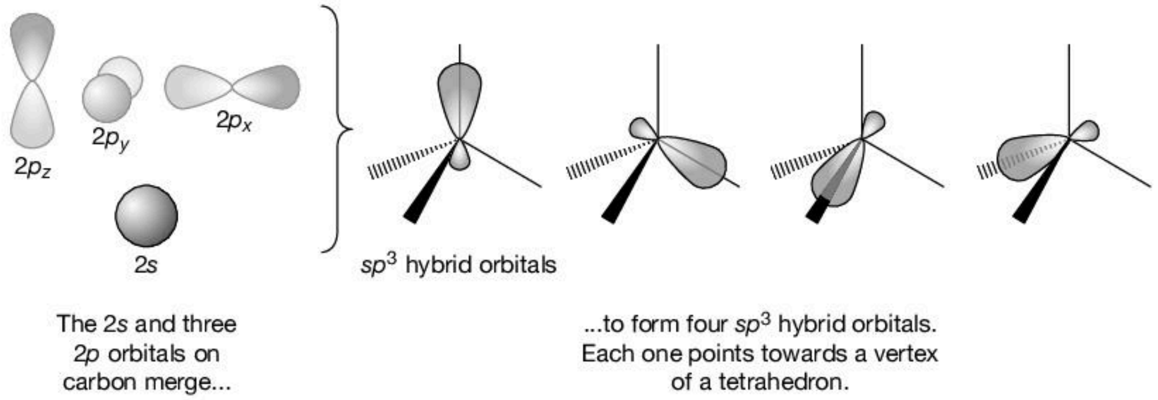
Co-ordinate bonds are shown by arrows. The foot of the arrow shows which atom donated the lone pair of electrons.

Covalent bonding and orbital overlap

You can also describe covalent bonding in terms of orbital overlap. When atomic orbitals overlap, bonds form between atoms. Some atoms form hybrid orbitals, in which s and p orbitals merge. An example of **hybridisation** is illustrated in Figure 3.1.

Key term

Hybridisation: the merging of s and p orbitals on the same atom to form new hybrid orbitals, such as sp^3 orbitals.

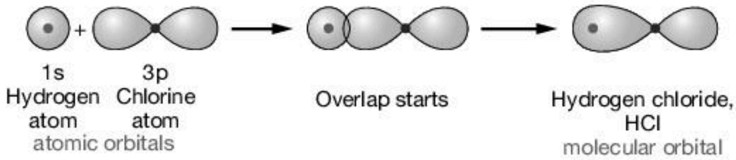


▲ **Figure 3.1** sp^3 hybridisation in carbon

Orbital overlap forms two types of bonds: σ and π bonds.

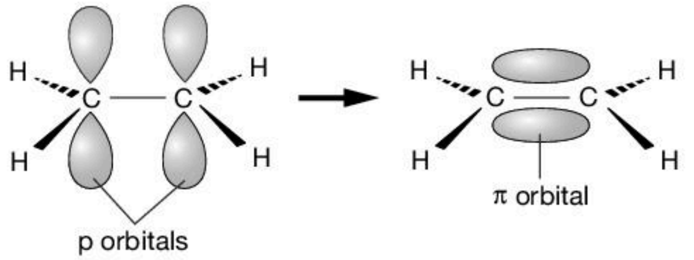
- A σ bond forms from the overlap of:
  - two s orbitals, for example in H_2

- an s orbital and a p orbital, for example in HCl



- two p orbitals, for example in Cl_2
- an s orbital and any hybrid orbital, for example an s orbital and an sp^3 orbital in CH_4
- two hybrid orbitals, for example two sp^3 orbitals between the carbon atoms in C_2H_6.

- A π bond forms from the sideways overlap of two p orbitals in double and triple bonds, for example in ethene, C_2H_4.



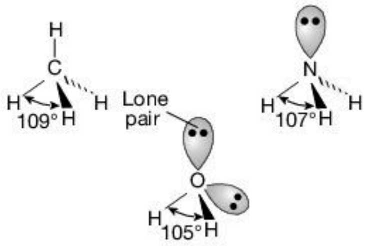
Remember

σ is pronounced 'sigma' and π is pronounced 'pi(e)'.

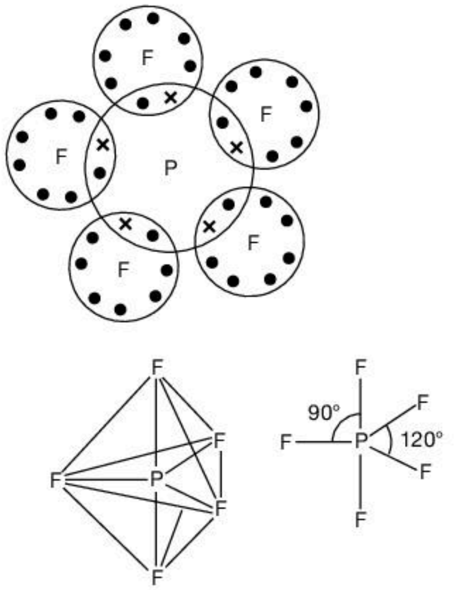
Shapes of molecules

The model of electron-pair repulsion explains the shapes of molecules, and the bond angles within them. The model describes how electron pairs in molecules, including lone pairs and those in bonds, repel each other and get as far apart as possible. For example,

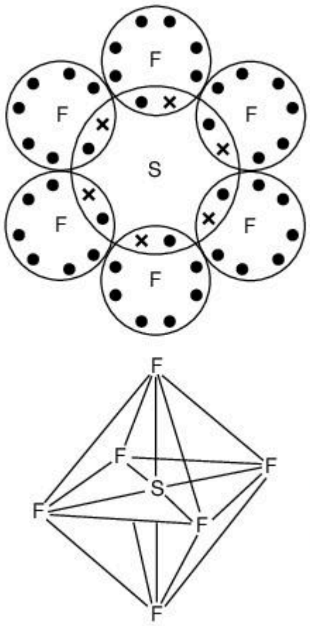
- Methane is tetrahedral, with four equal bond angles of 109°.
- Ammonia is pyramidal, with three equal bond angles of 107°.
- Water is non-linear, with a bond angle of 105°.



▲ **Figure 3.2** The shapes of molecules depend on the number and type of bonds and lone pairs.



▲ **Figure 3.3** PF_5 has a trigonal bipyramidal shape.



▲ **Figure 3.4** SF_6 has an octahedral shape.

Remember

A lone pair of electrons in a molecule has a stronger repelling effect than bonded electron pairs.

Worked example

a) Complete the table below.

Molecule	Shape of molecule in terms of the atoms joined to each carbon atom	Bond angle /°
Ethane, C_2H_6		
Ethene, C_2H_4		

b) Explain why ethane and ethene molecules have these shapes and bond angles.
Use ideas about hybrid orbitals in your answer.

Answer

a)

Molecule	Shape of molecule in terms of the atoms joined to each carbon atom	Bond angle /°
Ethane, C_2H_6	tetrahedral	109
Ethene, C_2H_4	trigonal planar	120

b) In each carbon atom of **ethane**, one 2s and three 2p orbitals merge to form four sp^3 hybrid orbitals. Three of these sp^3 orbitals overlap with the 1s orbital of a hydrogen atom, forming three σ bonds. Each carbon atom has one remaining sp^3 orbital. These overlap to form a σ bond between the two carbon atoms. This means that each carbon atom is surrounded by four pairs of electrons in σ bonds. These repel each other to get as far apart as possible, so the bond angle is 109° and the shape is tetrahedral.

In each carbon atom of **ethene**, one 2s and two 2p orbitals form three sp^2 hybrid orbitals. Two of these sp^2 orbitals overlap with the 1s orbital of a hydrogen atom, forming two σ bonds. Each carbon atom has one remaining sp^2 orbital, and one remaining 2p orbital. The sp^2 orbitals overlap to form a σ bond between the two carbon atoms. The 2p orbitals also overlap, forming a π bond between the two carbon atoms. There is a double bond between the carbon atoms. In ethene, each carbon atom is surrounded by three bonds (two single and one double). These repel each other to get as far apart as possible, so the bond angle is 120° and the shape is trigonal planar.

★ **Exam tip**

Plan explanations by making notes first.

★ **Exam tip**

When you have written an explanation, check it carefully to make sure you have included all the necessary details.

Link

There is more about the compounds ethane and ethene in Unit 15 Hydrocarbons.

Breaking and making covalent bonds in chemical reactions

In a chemical reaction:

- Bonds are **broken** in the reactants, requiring energy from the surroundings.
- Bonds are **made** in the products, releasing energy to the surroundings.

Covalent bonds between different atoms have different bond energies. The greater the bond energy, the greater the strength of the force holding the atoms together – and the greater the energy required to break the bond.

Remember

Bond energies are sometimes called bond enthalpies.

Worked example

Use the average bond energy values given in Table 3.1 to calculate the estimate the energy change for the reaction shown, in kJ mol^{-1}.

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

▼ **Table 3.1** Average bond energy values

Bond	Bond energy /kJ mol^{-1}
C—H	410
O=O	496
C=O	740
O—H	460

Answer

Bonds broken: 4 C—H and 2 O=O

Bonds made: 2 C=O and 4 O—H

Energy required to break bonds = $(4 \times 410\,\text{kJ mol}^{-1}) + (2 \times 496\,\text{kJ mol}^{-1})$
$= 2632\,\text{kJ mol}^{-1}$

Energy released on making bonds = $(2 \times 740\,\text{kJ mol}^{-1}) + (4 \times 460\,\text{kJ mol}^{-1})$
$= 3320\,\text{kJ mol}^{-1}$

The overall energy change for the reaction = $2632\,\text{kJ mol}^{-1} - 3320\,\text{kJ mol}^{-1}$
$= -688\,\text{kJ mol}^{-1}$

Remember

Use BIDMAS in calculations like this – first calculate what is shown in the brackets, then complete the calculation to get the answer.

Link

There is more about using bond energies to calculate energy changes of reactions in Unit 5, Chemical energetics.

Different bonds have different lengths. In general, the greater the number of electron pairs in the bond, the shorter the **bond length**. For example, C—C is longer than C≡C.

Key term

Bond length: the mean distance between the nuclei of two atoms that are bonded together in a molecule.

Intermolecular forces

When two atoms with different **electronegativity** values share an electron pair in a covalent bond, the electrons are unequally shared. This results in polar bonds.

Key terms

Electronegativity: the attraction of a bonded atom for the pair of electrons in a covalent bond.

Bond polarity: the separation of charge which occurs when atoms of different elements are joined by a covalent bond so that the attraction for the shared electron pair is unequal.

Polar molecule: a molecule in which there is an overall separation of charge.

Remember

Electronegativity increases from left to right of a period, and from bottom to top of a group.

Worked example

State and explain which bond has a greater bond polarity, H—Br or H—F.

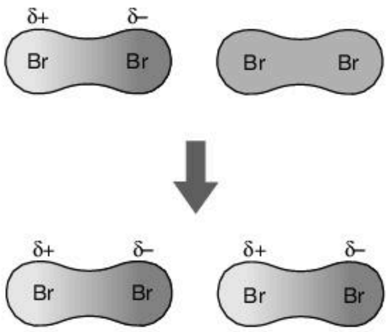
Answer

F is more electronegative than Br, so the charge separation is greater in H—F than in H—Br. This means that the bond polarity in H—F is greater.

Polar molecules such as H—Br have **permanent dipoles**. Non-polar molecules such as Br—Br do not have permanent dipoles, but the continuous motion of their electrons results in instantaneous electric dipoles. These induce dipoles in neighbouring molecules.

Key term

Permanent dipole: this occurs in a polar molecule in which one part has a positive partial electrical charge ($\delta+$) and another has a partial negative charge ($\delta-$).



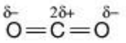
▲ **Figure 3.5** The instantaneous dipole in the molecule on the left induces a dipole in a nearby molecule.

Worked example

State and explain which of these molecules have permanent dipoles: CO_2 H_2O CH_3Cl

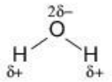
Answer

CO_2 has no permanent dipole because the polarities in the two polar bonds cancel out.

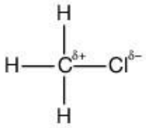


$$\overset{\delta-}{O}=\overset{2\delta+}{C}=\overset{\delta-}{O}$$

H_2O has a permanent dipole because the two hydrogen atoms are not arranged symmetrically on the central oxygen atom.



CH_3Cl has a permanent dipole because there is just one polar bond.



Remember

Polar molecules have induced dipole interactions *and* permanent dipole–permanent dipole interactions.

Permanent and temporary dipoles result in intermolecular forces between molecules, called **van der Waals forces**. These intermolecular forces affect the physical properties of substances.

Key term

Van der Waals forces: intermolecular forces between molecules.

Worked example

Explain the boiling point data in Table 3.2.

▼ **Table 3.2** Boiling points of some noble gases

Element	Boiling point /°C
Helium	−269
Neon	−246
Argon	−186
Krypton	−153

Answer

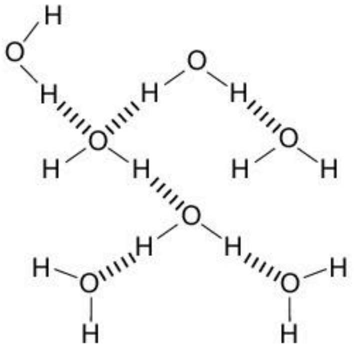
As the number of electrons in an atom increases, the instantaneous and induced dipoles become larger. The strength of the attractive forces between molecules increases, so more energy is needed to overcome these forces in order to boil the liquid.

Common error

Candidates sometimes forget to include all parts of an explanation, particularly towards the end of the explanation. Make sure you make all the points needed for a full explanation.

Hydrogen bonds

Hydrogen bonds are a special type of permanent dipole–permanent dipole interaction. They exist in molecules with a hydrogen atom attached to a very electronegative atom that has a lone pair of electrons, for example N, O and F.



▲ **Figure 3.6** Hydrogen bonds in water

Key term

Hydrogen bond: a strong intermolecular attraction between a hydrogen atom that is joined to a nitrogen, oxygen or fluorine atom.

Worked example

Which of these substances can form hydrogen bonds? Explain your answer.

HF H_2S CH_3CH_2OH H_2 $CHCl_3$

Answer

HF and CH_3CH_2OH can form hydrogen bonds. Their bonds include hydrogen atoms joined to a very electronegative atom.

Common error

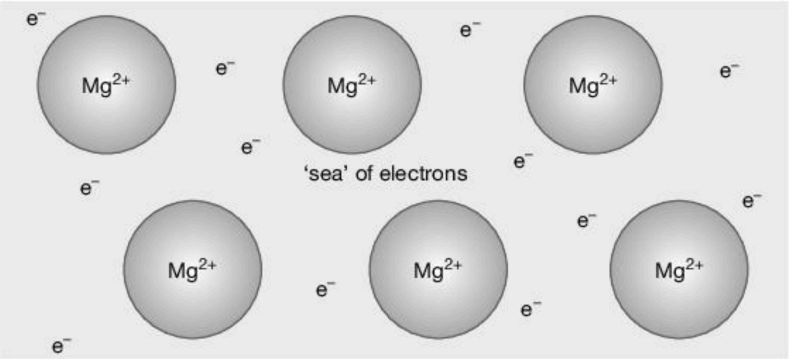
Some candidates think that $CHCl_3$ forms hydrogen bonds. It cannot, since the hydrogen atom is joined to the carbon atom, not to the much more electronegative chlorine atom.

Metallic bonding

Metallic bonding is a lattice of positive ions surrounded by delocalised electrons.

Key term

Metallic bonding: metallic bonding involves a strong electrostatic attraction between a lattice of positive metal ions and the surrounding delocalised electrons.



▲ **Figure 3.7** Metallic bonding in magnesium, showing two electrons for every magnesium ion

Bonding and physical properties

The type of bonding in a substance affects its properties. Table 4.2 in Unit 4, States of matter, shows how.

Raise your grade

1 The Group 15 elements form hydrides with the formula XH_3, where X is a Group 15 element.

(a) The compound with the formula PH_3 is called phosphine.

(i) Draw a dot-and-cross diagram to show the bonding in a phosphine molecule. [1]

The candidate correctly showed the bonded electron pairs, but did not include the lone pair of electrons. The correct dot-and-cross diagram is:

(ii) Predict the shape of a phosphine molecule. [2]

trigonal pyramid ✔

Explain your prediction.

The electron pairs repel each other, and get as far apart as possible. ✘

The explanation is incomplete. The candidate needs to state that the three bonded electron pairs, as well as the lone pair of electrons, repel each other and get as far apart as possible.

(b) The table shows some data for NH_3 and PH_3 molecules.

Molecule	Bond angle /°	Bond length /nm
NH_3	107	0.101
PH_3	93	0.142

Compare the bond angles in the two molecules, and suggest an explanation for the difference [2]

The bond angle is smaller in PH_3 than in NH_3. This is because the bonds are longer in PH_3. ✘

Again, this explanation is incomplete, so the candidate gains no marks for this answer. The candidate needs to add that the longer bond length in PH_3 means that P—H bond has a lower electron density than the N—H bond. The repulsion of the bonded electrons is therefore greater in NH_3 than in PH_3.

(c) The table shows electronegativity values for the Group 15 elements, and hydrogen.

Element	Relative electronegativity on Pauling scale
N	3.0
P	2.1
As	2.0
Sb	1.9
Bi	1.9
H	2.1

(i) Define the term *electronegativity*. [1]

Electronegativity is the attraction for electrons in a bond. ✘

This definition is correct but incomplete. The candidate needs to add more detail. A better definition is *Electronegativity is the attraction of a bonded atom for the pair of electrons in a covalent bond.*

(ii) Use data from the table above to predict which one of the Group 15 hydrides has polar bonds. [2]

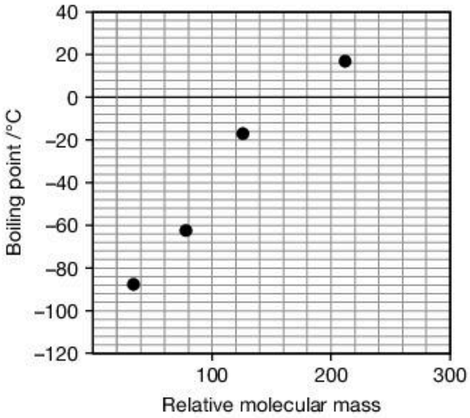
NH_3 ✓

Explain your prediction.

The difference in electronegativity between N and H is significant, but the differences in electronegativity between atoms of P, As, Sb and Bi and H are negligible. ✓

This answer gains full marks. The candidate has explained both why NH_3 has polar bonds and why molecules in the other hydrides are not polar.

(d) The grid shows the boiling points of four Group 15 hydrides (PH_3, AsH_3, SbH_3 and BiH_3) plotted against relative molecular mass.



(i) Describe and explain the boiling point trend for these Group 15 hydrides: PH_3, AsH_3, SbH_3, and BiH_3. [2]

The boiling point increases as the molecules get bigger. ✗

The answer is incomplete. The candidate needs to point out that, from PH_3 to BiH_3 the number of electrons in the molecules increases. This means that the instantaneous and induced dipoles become larger. This increases the strength of the attractive forces between molecules, which means that more energy is needed to overcome these forces when the liquid boils.

(ii) Use the trend on the graph to predict the boiling point of NH_3 if it follows the trend. [2]

$M_r = 14 + (3 \times 1) = 17$ ✓

Extrapolating on the graph, predicted boiling point = −100 °C. ✓

This is a good answer. The candidate has calculated M_r for NH_3 and shown their working. They have then extrapolated on the graph correctly.

(iii) The measured boiling point for NH_3 is −33 °C.

Explain the difference between this value and the one you predicted from the graph. [2]

Hydrogen bonds. ✓✗

The candidate has gained one of the two marks. To gain the second mark she needs to add more detail, stating that there are hydrogen bonds in NH_3 because N is electronegative and it has a lone pair of electrons. Hydrogen bonds are attractive forces between a H atom in one molecule and the lone electron pair on the N atom in another molecule.

Exam-style questions

1 Which of these chlorides has the smallest bond angle? [1]

A $BeCl_2$

B BCl_3

C PCl_3

D OCl_2

2 Choose your answer to this question by selecting on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

Which of the statements about NH_3, CH_4 and C_8H_{18} are correct?

(1) The boiling point of C_8H_{18} is higher than the boiling point of CH_4.

(2) Liquid NH_3 has hydrogen bonds only between its molecules.

(3) The boiling point of NH_3 is lower than the boiling point of CH_4.

3 Describe the intermolecular forces in the substances below when in the liquid state.

Explain your answers.

(a) Cl_2

(b) PF_3

(c) CH_3OH

(d) $CH_3CH_2NH_2$

(e) BF_3

(f) H_2S

4 The table gives the properties of five substances, A to E.

Substance	Melting point /°C	Boiling point /°C	Electrical conductivity of solid	Electrical conductivity of liquid
A	−38.9	357	good	good
B	−182	−162	poor	poor
C	801	1413	poor	good
D	1063	2970	good	good
E	714	1412	poor	good

(a) Which two substances are metals? [1]

(b) Which substance exists as simple molecules? [1]

(c) Which two substances are likely to be soluble in water? [1]

(d) Name and describe the bonding in substance E. [2]

5 This question is about the bonding in chlorine and its compounds.

(a) Draw dot-and-cross diagrams to show the bonding in Cl_2, $MgCl_2$, Al_2Cl_6 and $CHCl_3$. [4]

(b) **(i)** Define the term *co-ordinate bond.* [1]

(ii) Label any co-ordinate bonds in your dot-and-cross diagrams. [1]

(c) One of the substances whose dot-and-cross diagrams you have drawn has polar molecules.

(i) Give the formula of this substance. [1]

(ii) Explain why it has polar bonds. [1]

(d) Explain why $CHCl_3$ does not form hydrogen bonds. [1]

(e) List these three substances in order of increasing boiling point:

Cl_2, $MgCl_2$, $CHCl_3$ [1]

Explain how you decided on this order. [2]

4 States of matter

AS 4.1–4.18 pages 65–89

Key points

☐ Give the assumptions for the kinetic theory and the conditions for a gas to behave ideally.

☐ Use the equation $pV = nRT$.

☐ Describe the liquid state and changes of state involving liquids.

☐ Describe the lattice structures of solids with different types of bonding.

☐ Outline the importance of hydrogen bonding.

☐ Discuss the importance of recycling.

☐ Suggest the structure and bonding in a substance given data on its physical properties.

The gas state

The kinetic theory explains physical properties in terms of particle movement. The kinetic theory for an ideal gas is based on these assumptions:

- Its particles occupy negligible volume.
- Its particles exert no forces on each other.
- Its particles collide with each other, and the container walls, with no change of energy.

Remember

An ideal gas does not actually exist, but many gases behave as if they were ideal at ordinary temperatures and pressures.

Worked example

Explain why

a) a gas approaches ideal behaviour at low pressure and high temperature

b) at a given temperature and pressure, helium behaves more like an ideal gas than ammonia does.

Answer

a) At low pressure the particles are further apart and exert less force on each other than at high pressure. At high temperature gas particles move faster, so the forces between them become less significant.

b) A helium particle, He, has a smaller volume than an ammonia particle, NH_3. The forces of attraction between helium particles are very weak; those between ammonia particles are less weak.

The general gas equation is:

$$pV = nRT$$

where R is the ideal gas constant, $8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

You can use the equation to calculate the relative molecular mass, M_r, since $n = \frac{m}{M}$ where m is the mass of the gas and M is the mass of one mole, which is the relative molecular mass, M_r, in grams.

Remember

The units for temperature, T, are kelvin, K. The temperature in K is equal to the temperature in °C+273.

Worked example

A 0.159 g sample of a gas, X, was vaporised. The vapour had a volume of 0.162 dm^3 at 98 °C and 101 kPa. Calculate the relative molecular mass of X.

Answer

The general gas equation is $pV = nRT$

Substituting $n = \frac{m}{M}$ gives $pV = \frac{mRT}{M}$

Rearranging gives $M = \frac{mRT}{pV}$

Substituting the given values $M = \frac{0.159\,g \cdot 8.31\,JK^{\ 1}\,mol^{\ 1} \cdot 371\,K}{101 \cdot 10^{3}\,Pa \cdot 0.162 \cdot 10^{\ 3}\,m^{3}}$

$$M = 30.0\,g\,mol^{-1}$$

so $M_r = 30.0$

Common error

Some candidates use incorrect units in the general gas equation. The units of temperature are K, not °C. Values of pressure must be expressed in Pa (not kPa) and volumes must be expressed in m^3, not dm^3.

Remember

When you change the subject of an equation, do the same operation, for example multiplying, to both sides of the equation to get the variable you want on its own. In this example, both sides are divided by *pV* and multiplied by *M*.

Exam tip

When manipulating equations, do each step separately and state what you are doing each time. This means that, if you make a mistake, an examiner can see what you have done and may be able to award you some of the available marks.

The liquid state

In the liquid state, particles have less energy than in the gas state. They have vibrational, rotational and translational motion, so they can move around each other. The particles touch each other, but are slightly further apart than in the solid state.

Some substances, for example water, have hydrogen bonds between their particles in the liquid state. Hydrogen bonding explains

- the high boiling points of NH_3, H_2O and HCl compared with similar hydrides
- the high **surface tension** of water
- the high **viscosity** of concentrated sulfuric acid, H_2SO_4.

The liquid state is involved in two changes of state:

- Melting is the change from solid to liquid. Energy is required to overcome the attractive forces that hold the particles in a solid in a regular arrangement.
- Vaporisation is the change of state from liquid to gas. Energy is required to overcome the attractive forces between the particles in the liquid, and to separate these particles from each other.

Key terms

Surface tension: the property of a liquid that makes it behave as if its surface is enclosed in an elastic skin.

Viscosity: a measure of how easily a substance flows. A substance has a high viscosity if it does not flow easily.

Worked example

Table 4.1 shows the energy changes for changes of state of water, H_2O, and neon, Ne. The relative masses of H_2O and Ne particles are similar.

▼ **Table 4.1** Water and neon changing state

Process	Substance and change of state	Energy change /kJ mol^{-1}
A	$H_2O(s) \rightarrow H_2O(l)$	6.01
B	$H_2O(l) \rightarrow H_2O(g)$	40.7
C	$Ne(l) \rightarrow Ne(g)$	1.80

a) Explain the difference in energy change for processes A and B.

b) Explain the difference in energy change for processes B and C.

c) Predict which is greater, the energy change for process C or the energy change for $NH_3(l) \rightarrow NH_3(g)$.

Answer

a) Process B requires more energy than process A. In process A, solid water melts, and energy is required to overcome the attractive forces that hold the molecules in a regular arrangement. In process B, liquid water becomes a gas, and energy is required both to overcome the attractive forces between the molecules in the liquid, and to move them far apart from each other.

b) Process B requires more energy than process C. In both processes, energy is required to overcome the attractive forces between the particles in the liquid, and to move them far apart from each other. There are hydrogen bonds between water molecules in the liquid state, but only van der Waals forces in liquid neon. This means that the energy to overcome the attractive forces between water molecules is greater than for neon atoms.

c) The energy change for $NH_3(l) \rightarrow NH_3(g)$ is greater.

★ **Exam tip**

When asked to explain a difference, make sure you describe both situations before comparing them.

Imagine a liquid in a sealed container. Particles evaporate from the surface of the liquid, forming a vapour. Since the vapour cannot escape, some of its moving particles re-enter the liquid. Eventually, the rate of vaporisation is equal to the rate of condensation – the system has reached equilibrium.

Link

There is more about equilibria in Unit 7, Equilibria.

Key term

Vapour pressure: the pressure of the vapour which is in equilibrium with the liquid.

✗ **Common error**

Candidates sometimes confuse *evaporation* and *boiling*. Evaporation happens from the liquid surface only, and happens at any temperature. Boiling occurs only at the boiling point. It involves bubbles of vapour forming throughout the liquid, rising to the surface, and escaping.

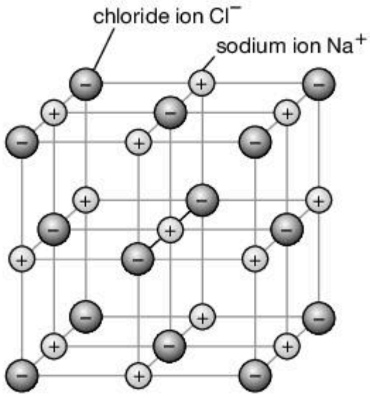
The solid state

In the solid state, particles are in fixed positions. There are several types of bonding in the solid state. The type of bonding gives a solid its structure.

Ionic structures

Sodium chloride is made up of Na^+ and Cl^- ions. The ions are arranged in a cubic lattice. Strong electrostatic forces of attraction, which act in all directions, hold the lattice together.

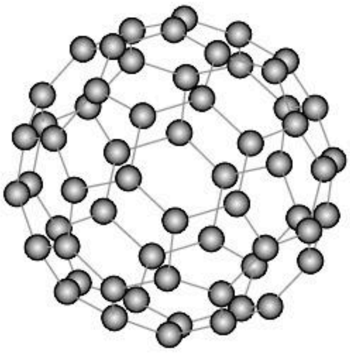
Magnesium oxide, MgO, has the same lattice structure as sodium chloride.



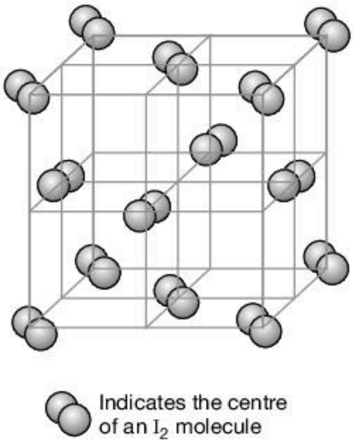
▲ **Figure 4.1** Part of a sodium chloride lattice

Simple molecular structures

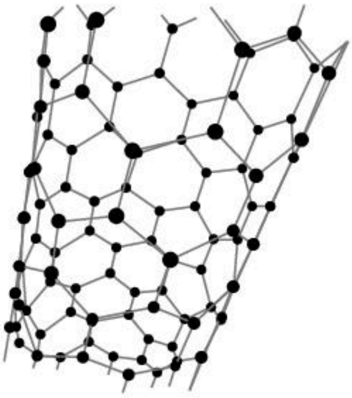
Iodine, buckminsterfullerene (C_{60}) and carbon nanotubes have simple molecular structures. The atoms within the molecules are joined together by covalent bonds. There are van der Waals forces between neighbouring molecules.



▲ **Figure 4.2** The structure of buckminsterfullerene, C_{60}



▲ **Figure 4.3** Part of the crystal structure of iodine, I_2



▲ **Figure 4.4** Part of the structure of a carbon nanotube

Worked example

Some substances have simple molecular structures in the solid state. Name the types of bonding

a) within a covalent molecule

b) between neighbouring molecules.

Answer

a) covalent

b) van der Waals intermolecular forces.

★ Exam tip

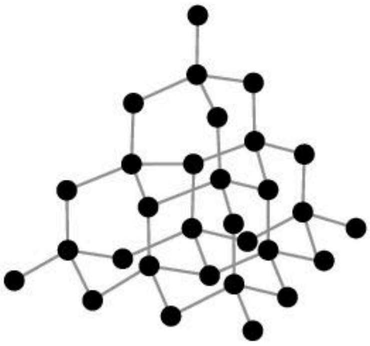
This question asks for the names of types of bonding only. There is no need to describe the bonding in detail.

Giant molecular structures

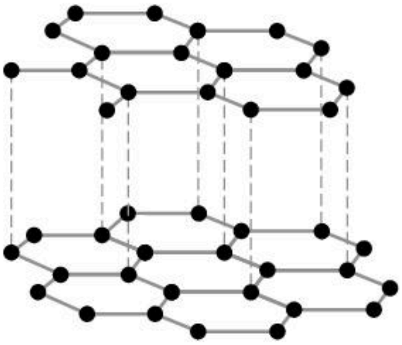
Three carbon **allotropes** – diamond, graphite and graphene – have giant molecular structures (see Figures 4.5–4.7). Silicon(IV) oxide has a similar structure to diamond. The atoms are joined together by covalent bonds.

Key term

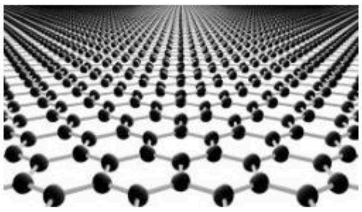
Allotropes: different forms of an element with different arrangements of the atoms.



▲ **Figure 4.5** Part of the giant molecular structure of diamond



▲ **Figure 4.6** Part of the giant molecular structure of graphite



▲ **Figure 4.7** Part of the giant molecular structure of graphene

✗ Common error

Common error Some candidates confuse *graphene* and *graphite*. Make sure you can describe the differences between them correctly.

Worked examples

1 Give the number of covalent bonds each carbon atom has in

- **a)** graphite
- **b)** buckminsterfullerene
- **c)** graphene
- **d)** diamond.

Answer

By counting the numbers of bonds in the diagrams, the numbers of covalent bonds are

- **a)** 3
- **b)** 3
- **c)** 3
- **d)** 4

2 Compare the structure and bonding of magnesium oxide with that of diamond.

Answer

Both magnesium oxide and diamond have giant lattice structures.

Magnesium oxide consists of oppositely charged Mg^{2+} and O^{2-} ions. They are held together in a regular structure by electrostatic forces of attraction between the oppositely charged ions. The forces act in all directions.

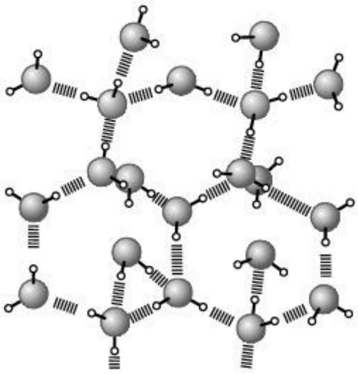
Diamond does not have ions. Its neutral atoms are held together in a regular structure by covalent bonds. The covalent bonds act only between the two carbon atoms they are joining together, not in all directions.

★ Exam tip

If you are asked to compare two things, describe each thing and write about their similarities and differences.

Hydrogen-bonded structures

Ice has a hydrogen-bonded structure. In an ice crystal, each H_2O molecule is held in position by four hydrogen bonds to other H_2O molecules (see Figure 4.8).



▲ **Figure 4.8** Part of the structure of ice: each set of parallel lines represents a hydrogen bond

Metallic structures

Metallic crystals consist of a lattice of positive ions surrounded by delocalised electrons. The positive ions are arranged in layers.

Link

The structure of a metal is shown in Figure 3.7 in Unit 3, Chemical bonding.

The solid state – structure and properties

The structure and bonding of a substance give the substance its properties. The properties of a substance determine its uses (Table 4.2).

▼ **Table 4.2** The properties of substances with different lattice structures

Type of bonding	Melting and boiling points	Electrical conductivity	Solubility
Ionic	high	low in solid state, good in liquid state and aqueous solution	soluble in polar solvents
Simple molecular	low	poor	insoluble in polar solvent, some are soluble in some non-polar solvents
Giant molecular	high	most are poor conductors, graphite, graphene and carbon nanotubes are good conductors	insoluble in most solvents
Hydrogen-bonded	low	poor conductors	soluble in polar solvents
Metallic	high	good conductors	insoluble

Finite materials and recycling

All the materials we use are obtained from materials extracted from the Earth, the oceans, or the atmosphere. The raw materials from which metals, ceramics and many plastics are obtained are finite resources – they will not last forever.

Obtaining raw materials, and making useful materials from them, have impacts on people, wildlife and the environment. This is why **recycling** is important. Recycling

- reduces waste
- reduces energy resource use
- reduces the amounts of raw materials extracted from the Earth
- reduces damage to the environment at extraction and manufacturing sites.

Key term

Recycling: the process of collecting and processing waste materials so that they can be made into new objects.

Raise your grade

1 **(a)** State three assumptions of the kinetic theory for an ideal gas. [3]

The particles have negligible volume. ✔

The particles exert small forces on each other. ✘

The particles collide with each other with no change in energy. ✘

The candidate gains one of the three available marks. The second statement is incorrect – the assumption is that particles exert no forces on each other. The third statement is incomplete – the candidate needs to add that there is also no change of energy when gas particles collide with the container wall.

(b) A sample of an ideal gas occupies 0.203 dm^3 at 25 °C and 105 kPa.

(i) Calculate the amount of gas, in moles. [3]

$pV = nRT$

So $n = \frac{pV}{RT}$ ✔

$n = (105 \times 0.203) \div (8.31 \times 25) = 0.103$ mol ✘

The candidate remembered and rearranged the general gas equation correctly. However, she did not convert the units when substituting values into the equation – the units for temperature are K, the units for volume are m^3, and the units for pressure should be converted from kPa to Pa.
The correct working and answer are given below:

$$n = \frac{105 \times 10^3\,\text{Pa} \times 0.203 \times 10^{-3}\,\text{m}^3}{8.31\,\text{JK}^{-1}\,\text{mol}^{-1} \times (273 + 25)\,\text{k}}$$

$$= 0.00861 \text{ mol}$$

(ii) The mass of gas present is 0.138 g. Calculate M_r for the gas. [2]

$n = \frac{m}{M}$

$M = \frac{m}{n}$

$M = \frac{0.138\text{ g}}{0.103\text{ mol}}$

$M = 1.34\text{ g mol}^{-1}$

so $M_r = 1.34$ ✔✔ ecf

(error carried forward)

The candidate showed all her working, and gained both marks for the question. However, the value obtained is incorrect because the candidate substituted the incorrect value of n, calculated in part ii.

The correct answer is

$$M = \frac{0.138\text{g}}{0.00861\text{ mol}}$$

$$M = 16.0 \text{ g mol}^{-1}$$

So $M_r = 16.0$

(iii) State the volume occupied by the gas if the temperature is doubled and the pressure is unchanged. [1]

$pV = nRT$

$V = \frac{nRT}{p}$

So if the temperature doubles the volume also doubles to 0.406 dm^3. ✔

The candidate correctly examined the equation and realised that *V* is directly proportional to *T*. This means that, when *T* doubles, *V* also doubles.

Exam tip

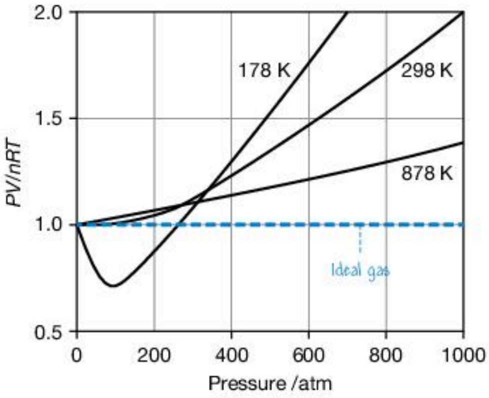
Sometimes, you do not need to do a calculation - think carefully before you start a question about the easiest and quickest way of approaching it.

(c) Nitrogen, N_2, does not behave as an ideal gas at low temperature and pressure. Explain why. [3]

The particles of an ideal gas have negligible volume, but N_2 molecules do not have a negligible volume. ✔ Also, nitrogen particles do exert very small forces on each other, but the particles of an ideal gas do not exert forces on each other. ✔

The candidate gained two of the three marks for this question, since she clearly stated two differences between nitrogen and an ideal gas. However, since three marks are available for the question she should have made three points. The point that she did not make is that that when particles of an ideal gas collide with each other, and the container walls, there is no change in energy. But when nitrogen molecules collide with each other and the container walls, there is a change in energy.

(d) The graph shows the effects of temperature and pressure on the behaviour of nitrogen.



(i) Give the value of $\frac{pV}{RT}$ when $n = 1$. [1]

$pV = nRT$

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

So when $n = 1$ the value $= 1$ ✔

(ii) On the graph, sketch a line to display your answer to part **i**. [1]

(iii) Describe how the behaviour of nitrogen is different from ideal gas behaviour as temperature changes.

It gets less ideal. ✘ [1]

It is not clear whether the candidate is referring to a temperature increase or decrease. The candidate needs to expand the statement to:

As temperature increases, the gas behaves more like an ideal gas.

? Exam-style questions

1 Which of these substances conducts electricity in the liquid state but not in the solid state? [1]

A C_{60}

B Ca

C $CaCl_2$

D SiO_2

Choose your answer to questions 2 and 3 by selecting on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

2 **E** is a crystalline solid. It conducts electricity in the solid state.

Which of these substances might **E** be? [1]

1 ruthenium

2 graphene

3 decane, $C_{10}H_{22}$

3 Which statements explain why it is important to recycle aluminium?

1 A greater amount of waste results when 1 kg of aluminium is obtained from its ore than from recycling.

2 Less energy is required to obtain 1 kg of aluminium by recycling than from its ore.

3 The low density, and its protective oxide coating, mean that aluminium is suitable for making aeroplanes and drinks cans.

4 The table shows data for two substances that are in the liquid state at room temperature.

Substance	Molecular formula	Melting point /°C	Boiling point /°C
Ethanol	CH_3CH_2OH	–118	78.5
Tetrachloromethane	CCl_4	–23.0	76.8

(a) Describe the structure and bonding in ethanol at the following temperatures:

(i) −120 °C [3]

(ii) 20 °C [3]

(b) Describe and explain the intermolecular forces in tetrachloromethane, CCl_4, at −25 °C. [3]

(c) A sample of ethanol at 0 °C is placed in a sealed container.

The sealed container is placed in a laboratory at 20 °C.

(i) Explain what is meant by the term *vapour pressure*. [1]

(ii) Describe and explain how the vapour pressure changes in the sealed container as it warms up. [2]

5 Describe simply the lattice structures and bonding in

(a) calcium sulfide, CaS [3]

(b) calcium, Ca [3]

(c) sulfur, S_8 [2]

(d) The table shows some properties of CaS, Ca and S_8. The substances are represented by the letters **X**, **Y** and **Z** – not by their chemical formulae.

Substance	Melting point /°C	Does the substance conduct electricity in the solid state?
X	842	yes
Y	115	no
Z	2525	no

(i) Which letter in the table represents CaS? [1]

(ii) Which letter in the table represents Ca? [1]

(iii) Which substance or substances in the table might conduct electricity in the liquid state? Explain your answer. [2]

5 Chemical energetics

AS 5.1–5.11 pages 92–107
A 5.12–5.13 pages 107–110;
5.15 pages 112–114;
23.1–23.5 pages 442–450

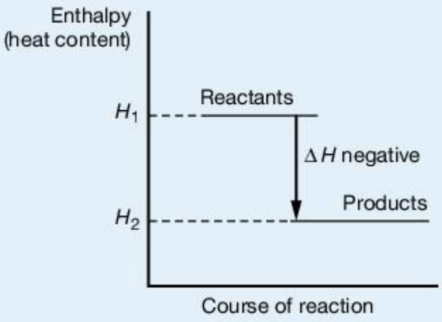
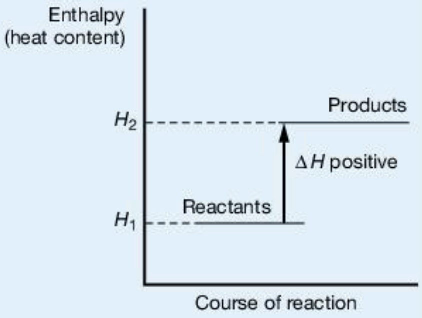
Key points

- ☐ Explain that chemical reactions involve energy changes.
- ☐ Use the terms *enthalpy change of reaction*, *standard conditions* and *bond energy*.
- ☐ Calculate enthalpy changes from experimental results.
- ☐ Use the term *lattice energy* and identify and explain factors that affect its value.
- ☐ Use Hess' Law to construct energy cycles and calculate enthalpy changes that cannot be found directly.
- ☐ Use average bond energy values in calculations.
- ☐ Construct and interpret reaction pathway diagrams.
- ☐ Draw Born–Haber cycles and use them in calculations.
- ☐ Explain what entropy is, and explain and predict entropy changes that occur in
    - changes of state
    - temperature changes
    - reactions involving gases.
- ☐ Calculate entropy changes for reactions from standard entropies of reactants and products.
- ☐ Explain what Gibbs free energy is, and use the Gibbs free energy equation to
    - calculate ΔG for a reaction
    - predict whether a reaction will be spontaneous
    - predict the effect of temperature change on the spontaneity of a reaction.

Enthalpy change, ΔH

Chemical reactions involve energy changes, usually as changes in the heat content, or **enthalpy**, of the reacting substances. These energy changes can be **exothermic** or **endothermic**.

▼ **Table 5.1** Exothermic and endothermic reactions

	Exothermic	Endothermic
Energy is transferred from…	system to surroundings	surroundings to system
The system…	loses energy	gains energy
The sign of ΔH is…	negative	positive
At first, the temperature…	increases	decreases
The reaction profile looks like this…		

✗ Common error

Some students think that if the temperature increases at first, the reaction is endothermic. This is incorrect. In an exothermic reaction, the temperature increases at first as the energy that is transferred by the reaction heats up the system. Then the reacting mixture cools as energy is transferred to the surroundings.

Enthalpy change values in data tables are for **standard conditions** of 298 K and 100 kPa. Standard concentration is 1 mol dm^{-3}. The standard state of a substance is its state at 298 K and 100 kPa.

Key terms

The **standard enthalpy change of combustion, =$\Delta H^{\ominus}_{c}$** of a substance is the enthalpy change when one mole of the substance is completely burnt in oxygen under standard conditions.

The **standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$** of a substance is the enthalpy change when one mole of the substance forms from its elements under standard conditions.

The **standard enthalpy change of hydration, $\Delta H^{\ominus}_{\text{hydration}}$** is the enthalpy change when one mole of gaseous ions are hydrated under standard conditions.

The **standard enthalpy change of solution, $\Delta H^{\ominus}_{\text{solution}}$** is the enthalpy change when one mole of a substance is dissolved under standard conditions so that no further heat change occurs on adding more solvent.

The **standard enthalpy change of neutralisation, $\Delta H^{\ominus}_{\text{neutralisation}}$** of a substance is the enthalpy change when the reaction of an acid and a base forms one mole of water under standard conditions.

The **standard enthalpy change of atomisation, $\Delta H^{\ominus}_{\text{at}}$** is the enthalpy change when one mole of gaseous atoms form from an element under standard conditions.

Bond energy of a bond A–B in a given compound is the energy required to break one mole of those bonds under standard conditions in the gas state. Bond energy values are endothermic.

Worked example

Which enthalpy changes are represented by the equations below?

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

b) $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

c) $Na^+(g) + aq \rightarrow Na^+(aq)$

d) $NaCl(s) + aq \rightarrow NaCl(aq)$

e) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$

f) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

Answer

a) combustion

b) atomisation

c) hydration

d) solution

e) formation

f) neutralisation

Lattice energy

Lattice energy is the energy change when one mole of an ionic solid forms from its gaseous ions under standard conditions. Lattice energy values are exothermic. The values depend on two factors – ionic charge and ionic radius:

- The greater the ionic charge, the greater the lattice energy. This is because the attraction between 2+ and 2– ions is stronger than the attraction between 1+ and 1– ions, for example.
- The smaller the ionic radius, the greater the lattice energy. This is because smaller ions can pack more closely, so increasing the attraction between them.

Key term

Lattice energy: the energy change when one mole of an ionic solid forms from its gaseous ions under standard conditions.

Worked example

Explain the differences in lattice energies between LiF and KI and between LiF and MgO.

Substance	Lattice energy /kJ mol^{-1}
LiF	–1036
KI	–649
MgO	–3889

Answer

The lattice energy for LiF is greater than that for KI because the ions in LiF are smaller than those in KI. This means that the ions in LiF are more closely packed, so the attraction between them is greater.

The lattice energy for MgO is greater than that for LiF because the attraction between the 2+ and 2– ions in MgO is stronger than the attraction between the 1+ and 1– ions in LiF.

Calculating enthalpy changes

You can calculate enthalpy changes from experimental results using the equation:

$$\Delta H = -mc\Delta T$$

Worked example

A student used burning propane, C_3H_8, to heat 500 g of water. The mass of propane used was 2.90 g. The temperature of the water increased by 60.0 °C. The **specific heat capacity** of water is given in the data booklet.

a) Estimate the enthalpy change of combustion of propane.

b) The actual value of the enthalpy change of combustion of propane is −2202 kJ mol^{-1}. Suggest a reason for the difference between this value and the value calculated in part **a**.

Key term

Specific heat capacity, c: the specific heat capacity of a substance is the energy required to raise the temperature of 1 g of the substance by 1 K.

Answer

a)

For the combustion of 2.90 g of propane:

$\Delta H = -mc\Delta T$

$\Delta H = -500\,\text{g} \times 4.2\,\text{J g}^{-1}\,\text{K}^{-1} \times 60.0\,\text{K}$

$\Delta H = -126\,000\,\text{J}$

$\Delta H = -126\,\text{kJ}$

Mass of 1 mol propane $= (3 \times 12.0) + (8 \times 1.0) = 44.0\,\text{g}$

Amount of propane burned, in moles $= \dfrac{2.90\,\text{g}}{44.0\,\text{g mol}^{-1}}$

$= 0.0659\,\text{mol}$

Enthalpy change on burning 1 mol of propane $= \dfrac{-126\,\text{kJ}}{0.0659\,\text{mol}}$

$= -1910\,\text{kJ mol}^{-1}$

b) The value from the experiment is less than the actual value because not all the energy is transferred to the water in the experiment; some energy is transferred to the container and to the air.

★ **Exam tip**

Always include units in calculations. This helps to avoid mistakes, and to work out the units of the answer.

Hess' Law

Calculating enthalpy changes that cannot be found by direct experiment

Hess' Law is used to calculate the enthalpy change of a reaction that cannot be measured directly. In the worked example below, the enthalpy change of formation of methane is calculated from enthalpy of combustion data.

Key term

Hess' Law: this law states that the enthalpy change in making given products from given reactants is the same whatever route is taken, provided that the conditions do not change.

Worked example

Calculate the enthalpy change of formation of methane from the $\Delta H^\ominus_c$ data below.

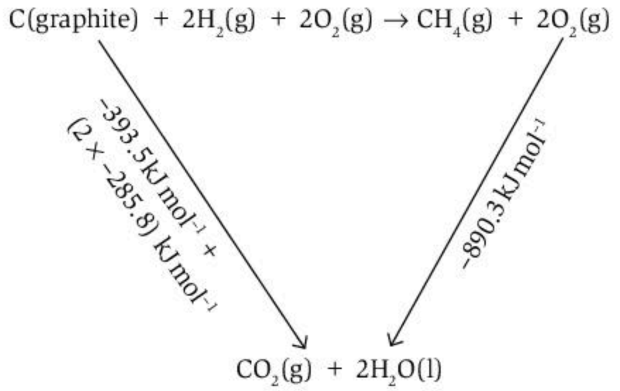
$\Delta H^\ominus_c(CH_4(g)) = -890.3\,\text{kJ mol}^{-1}$

$\Delta H^\ominus_c(C(\text{graphite})) = -393.5\,\text{kJ mol}^{-1}$

$\Delta H^\ominus_c(H_2(g)) = -285.8\,\text{kJ mol}^{-1}$

Answer

The energy cycle below gives all the $\Delta H^\ominus_c$ values, and shows how the value of $\Delta H^\ominus_f$ is calculated.



$\Delta H^\ominus_f\,(CH_{4(g)}) = [-393.5 + (2 \times -285.8)]\,\text{kJ mol}^{-1} - (-890.3\,\text{kJ mol}^{-1})$

$= -74.80\,\text{kJ mol}^{-1}$

★ **Exam tip**

In enthalpy cycles, the sign of an enthalpy change is:

- as shown if you are following the arrow in the direction it is drawn
- reversed if you are following the arrow in the opposite direction.

Calculating enthalpy changes from average bond energies

Enthalpy changes can be estimated from average bond energies. The average bond energy of a certain bond, X—Y, is the average value of the bond energy for that bond in several similar compounds.

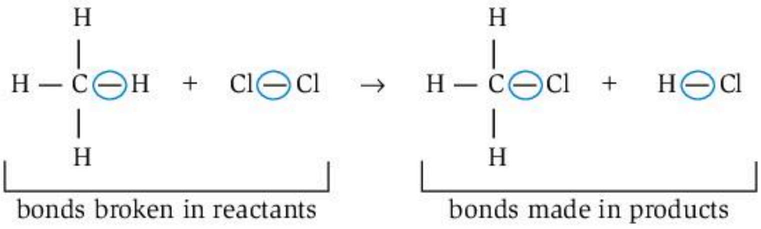
Worked example

Calculate the enthalpy change for the reaction shown below using bond energies and average bond energies from the data booklet.

$$CH_4(g) + Cl_2 \rightarrow CH_3Cl(g) + HCl(g)$$

Answer

The bonds broken and made are shown below.



Energy transferred to break bonds in reactants = 410 kJ mol^{-1} + 242 kJ mol^{-1}

Energy transferred on making new bonds in products = –340 kJ + –431 kJ mol^{-1}

$\Delta H_r^\ominus$ = energy transferred to break bonds + energy transferred on making new bonds
= (410 kJ mol^{-1} + 242 kJ mol^{-1}) + (–340 kJ mol^{-1} + –431 kJ mol^{-1})
= –119 kJ mol^{-1}

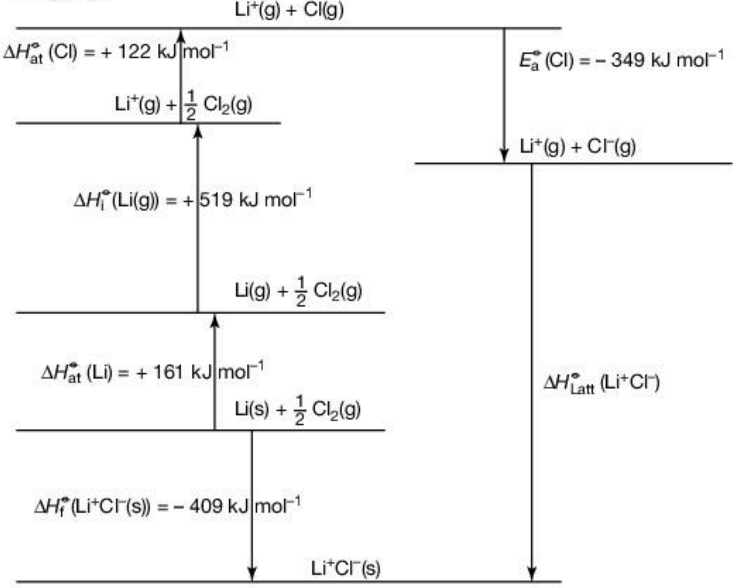
Born–Haber cycles

Born–Haber cycles are useful for calculating lattice energy values.

Worked example

Draw a Born–Haber cycle for lithium chloride, and use it to calculate the lattice energy of the compound.

Answer



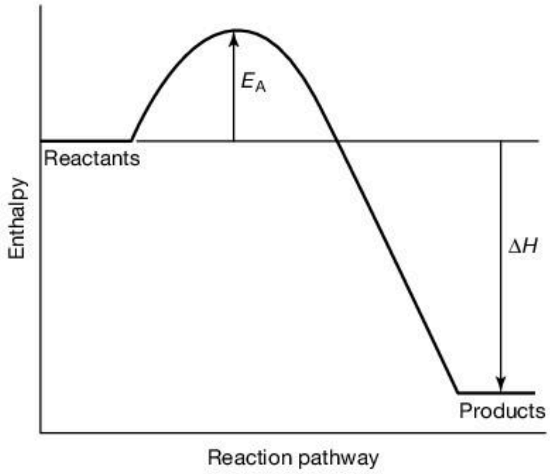
$\Delta H^\ominus_{Latt}$ = (+ 349 – 122 – 519 – 161 – 409) kJ mol^{-1}
= – 862 kJ mol^{-1}

Exam tip

When using Born–Haber cycles to calculate lattice energies, start from the gaseous ions, and move round the cycle to the ionic solid. Remember to reverse the sign of an enthalpy change if you are moving in the opposite direction to that shown by the arrow.

Reaction pathways

A reaction pathway shows the enthalpy change and the activation energy of a reaction.



▲ **Figure 5.1** A reaction pathway

Entropy changes, ΔS

Entropy, *S*, is a measure of the 'disorder' of a system. A system becomes more stable when its energy is spread out in a more disordered state.

For a spontaneous change, the overall entropy must increase, and the entropy change, ΔS, must be positive.

Key term

Entropy, *S*: a measure of the 'disorder' of a system.

Worked example

Predict whether ΔS is positive or negative for the changes shown below. Justify your predictions.

a) $CO_2(s) \rightarrow CO_2(g)$

b) cooling water from 70 °C to 20 °C

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

Answer

a) The entropy change is positive because there are more ways of arranging energy in a gas than in a solid.

b) The entropy change is negative because there are fewer ways of arranging energy when the heat content is less.

c) The entropy change is negative because the number of moles of gas molecules decreases. This means that there are fewer ways of arranging the energy in the products than in the reactants.

The standard entropy change of a reaction, $\Delta S^\ominus$, can be calculated from the standard entropies, $S^\ominus$, of the reactants and products. The value of $\Delta S^\ominus$ is equal to the sum of the standard entropies of the products minus the sum of the standard entropies of the reactants.

Maths skills

The symbol Σ

The symbol sigma, Σ, means sum. So

$$\Delta S^\ominus \text{ of a reaction} = \Sigma \text{ standard entropies of products} - \Sigma \text{ standard entropies of reactants}$$

Worked example

Calculate $\Delta S^\ominus$ for the reaction shown below.

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

Substance and state	$S^\ominus$ /J K^{-1} mol^{-1}
$CH_4(g)$	186
$O_2(g)$	205

Substance and state	$S^\ominus$ /J K^{-1} mol^{-1}
$CO_2(g)$	214
$H_2O(l)$	70.0

Answer

$\Delta S^\ominus = [S^\ominus(CO_2(g)) + 2S^\ominus(H_2O(l)] - [S^\ominus(CH_4(g)) + 2S^\ominus(O_2(g)]$

$\Delta S^\ominus = [214\,J\,K^{-1}\,mol^{-1} + (2 \times 70)\,J\,K^{-1}\,mol^{-1}] - [186\,J\,K^{-1}\,mol^{-1} + (2 \times 205)\,J\,K^{-1}\,mol^{-1}]$

$\Delta S^\ominus = -242\ J\,K^{-1}\,mol^{-1}$

Gibbs free energy change, ΔG

Gibbs free energy change for a reaction is calculated from the equation

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

Worked example

Calculate $\Delta G^\ominus$ for the complete combustion of methane to form carbon dioxide and water at 298 K Use these data:

$\Delta H_c^\ominus\ (CH_4(g)) = -890.4\,kJ\,mol^{-1}$

$\Delta S_c^\ominus\ (CH_4(g)) = -242\,J\,K^{-1}\,mol^{-1}$

Answer

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

$\Delta G^\ominus = -890.4\,kJ\,mol^{-1} - (298\,K \times -0.242\,kJ\,mol^{-1})$

$\Delta G^\ominus = -818.3\,kJ\,mol^{-1}$

Remember

Units of $\Delta S^\ominus$ are often given in J mol^{-1}. You need to convert them to kJ mol^{-1} in ΔG calculations.

For a spontaneous reaction or process, the sign of $\Delta G^\ominus$ must be negative. This means that, for a given reaction, the temperature influences whether the reaction is spontaneous or not.

Substituting into the expression $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ gives $\Delta H^\ominus - T\Delta S^\ominus < 0$ for a spontaneous reaction.

Worked example

Calculate the minimum temperature at which the reaction below is spontaneous. $\Delta H = 86.0\,kJ\,mol^{-1}$ and $\Delta S = 170\,J\,K^{-1}\,mol^{-1}$

$$CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$$

Answer

Rearranging $\Delta H - T\Delta S < 0$ gives $\Delta H < T\Delta S$

and $$\frac{\Delta H}{\Delta S} < T$$

Substituting gives $$\frac{86.0\,kJ\,mol^{-1}}{0.170\,kJ\,K^{-1}\,mol^{-1}} < T$$

$$505\,K < T$$

Maths skills

Symbols

The symbol < means *less than* and the symbol > means *more than*. You can treat these symbols in the same way as an = sign in expressions involving $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$.

Raise your grade

1 **(a)** Define the term *standard enthalpy change of formation*. [1]

Enthalpy of formation is the enthalpy change when a substance forms from its elements under standard conditions. ✘

This definition is almost correct, but the candidate forgot to mention the amount of substance. The correct definition is that enthalpy of formation is the enthalpy change when one mole of a substance forms from its elements under standard conditions.

(b) **(i)** Write an equation for a reaction with an enthalpy change that is equal to the enthalpy of formation of $SO_3(g)$. [1]

$S(s) + O_2(g) \rightarrow SO_3(g)$ ✘

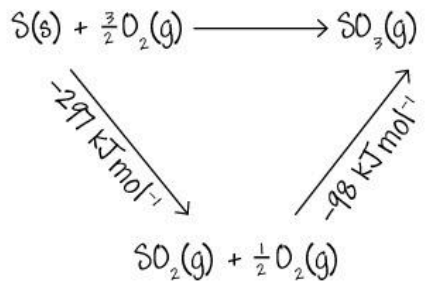
The candidate has correctly shown that SO_3 is formed from its elements in their standard states. However, the equation is not balanced. The correct equation is

$$S(s) + \tfrac{3}{2}O_2(g) \rightarrow SO_3(g)$$

(ii) Calculate the enthalpy change of formation of $SO_3(g)$ from the data in the table.

You will need to construct an energy cycle for the reaction. [3]

Substance	Enthalpy of combustion /kJ mol^{-1}
S(s)	−297
SO_2(g)	−98



✔✔

$\Delta H = -297 - -98$ ✔

$= -199\ kJ\ mol-1$ ✘

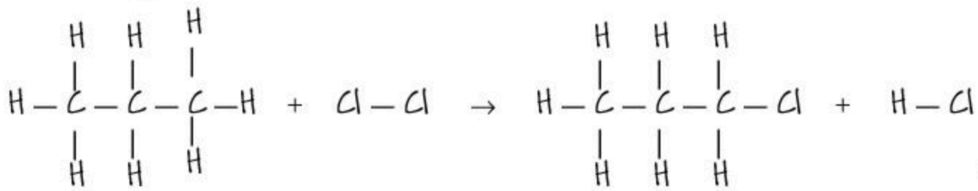
The candidate should have followed the direction of the arrows as shown in the diagram above. This gives a value for ΔH of $-297\ kJ\ mol^{-1} + -98\ kJ\ mol^{-1} = -395\ kJ\ mol^{-1}$.

(iii) State the name of the law you used in part **ii**. Hess' Law ✔ [1]

2 This question is about the reaction

$$C_3H_8(g) + Cl_2(g) \rightarrow C_3H_7Cl(g) + HCl(g)$$

(a) Calculate the enthalpy change of the reaction shown in the equation above using average bond energy values from the data booklet. [3]



✔

Bond	Bond energy /kJ mol^{-1}	Is the bond broken or made in the reaction?
C–H	410	broken
Cl–Cl	242	broken
C–Cl	340	made
H–Cl	431	made

✓

The candidate has made an excellent start to this question. The equation showing displayed formulae is useful, and the table summarises all the necessary data. The candidate now needs to do the final calculation, as shown below.

enthalpy change = sum of bond energies of bonds that are broken − sum of bond energies of bonds that are made

$= (410 + 242)\,\text{kJ mol}^{-1} - (340 + 431)\,\text{kJ mol}^{-1}$

$= -119\,\text{kJ mol}^{-1}$

(b) Calculate the enthalpy change of the reaction shown in the equation above using the enthalpy of formation values in the table below. [3]

Substance	Enthalpy of formation /kJ mol^{-1}
propane	−84.7
1-chloropropane	−136.8
hydrogen chloride	−92.3

ΔH_r = sum of ΔH_f of products − sum of ΔH_f of reactants

$\Delta H_r = (-136.8\,\text{kJmol}^{-1} + -92.3\,\text{kJmol}^{-1}) - (-84.7)$

$\Delta H_r = -144.4\,\text{kJmol}^{-1}$ ✓✓✓

This answer is excellent. It is laid out correctly, and all the working is clearly shown.

(c) Compare the values calculated in parts **a** and **b** and suggest one reason for the difference. [1]

The value calculated from bond energies has a greater negative value.

This is correct, but the question asks for a reason. Suitable answers include that some of the bond energies used in the calculation are *average* bond energies. The actual bond energies in the compounds given might be different from the average values.

3 This question is about entropy and Gibbs free energy change.

(a) For each change below, predict whether the entropy change is positive or negative.

Give a reason for each prediction. [3]

(i) $2Ba(NO_3)_2(s) \rightarrow 2BaO(s) + 4NO_2(g) + O_2(g)$

Positive, because the number of moles of substances in the gas state increases. ✓

(ii) $NH_4Cl(g) \rightarrow NH_4Cl(s)$

Negative

This answer is correct, but no reason is given, so no mark can be awarded. The candidate needs to add that changing state from gas to solid means that there are fewer ways of spreading out the energy.

(iii) Heating helium gas from −67 °C to room temperature.

Positive, because at a higher temperature there are more ways of spreading out the energy. ✔

(b) Calculate the entropy change for the reaction shown by the equation in **(a)(i)**. [2]

Use the data in the table.

Substance	Standard molar entropy /J K^{-1} mol^{-1}
$Ba(NO_3)_2$ (s)	213.8
BaO(s)	70.4
NO_2(g)	240.0
O_2(g)	102.5

$\Delta S^\ominus = (2 \times 70.4) + (4 \times 240) + 102.5 - (2 \times 213.8)$

$\Delta S^\ominus = 775.7\ J\,K^{-1}\,mol^{-1}$ ✔✔

The candidate did the calculation correctly, and achieved the mark. However, the answer could be further improved by stating that the entropy change is equal to the sum of the standard molar entropies of the products minus the sum of the standard molar entropies of the reactant.

(c) Calculate the Gibbs free energy change for the reaction in **(a)(i)** at 298 K. [2]

Use the entropy value that you calculated in part **(b)**.

The enthalpy change of the reaction is +1238 kJ mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ ✔

$\Delta G^\ominus = +1238\ kJ\,mol^{-1} - (298 \times 775.7\ J\,K^{-1}\,mol^{-1})$

$\Delta G^\ominus = -229920.6\ kJ\,mol^{-1}$ ✘

The candidate was not consistent in his use of units. If he had converted the units of $\Delta S^\ominus$ to kJ K^{-1} mol^{-1} then he would have calculated the correct answer of 1006.8 kJ mol^{-1}.

(d) Predict whether or not the reaction in part **(a)(i)** is spontaneous. [1]

Justify your prediction.

The reaction is spontaneous because the value of $\Delta G^\ominus$ is negative. ✔ (ecf)

The candidate gained an 'error carried forward' mark here, because his answer is consistent with the answer given in part **c**. In fact, though, since the correct value of $\Delta G^\ominus$ is positive, the reaction is not spontaneous.

Exam-style questions

1 Which statement is true for an endothermic reaction? [1]

A The system transfers energy to the surroundings.

B The temperature increases at first.

C The sign of ΔH is negative.

D The system gains energy.

2 Which equation has an enthalpy change equal to the enthalpy change of combustion of carbon monoxide? [1]

A $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

B $CO(g) + O(g) \rightarrow CO_2(g)$

C $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(s)$

D $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

3 What is $\Delta H_r^\ominus$ for the reaction below? [1]

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

Use the enthalpy of formation data shown in the table below.

Remember

The enthalpy of formation of an element in its standard state is 0.

Remember

The enthalpy of a reaction is the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants.

Substance	Enthalpy change of formation /kJ mol^{-1}
$C_3H_8(g)$	–104
$CO_2(g)$	–394
$H_2O(l)$	–286

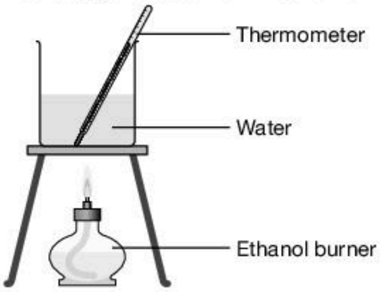
A $-576\,kJ\,mol^{-1}$

B $-784\,kJ\,mol^{-1}$

C $-2222\,kJ\,mol^{-1}$

D $-2430\,kJ\,mol^{-1}$

4 A student used burning ethanol to heat 80.0 g of water in the apparatus shown below.



The mass of ethanol burned was 1.00 g.

The temperature of the water increased from 22 °C to 86 °C.

(a) Write an equation for the combustion of ethanol, including state symbols. [1]

(b) Calculate the amount of energy transferred to the water. [2]

Exam tip

The value of the specific heat capacity of water is given in the data book.

(c) Use your answer to **(b)** and the value of M_r for ethanol to estimate the enthalpy of combustion of ethanol. [2]

(d) The accepted value for the enthalpy of combustion of ethanol is $-1371\,kJ\,mol^{-1}$.

Suggest why the value you estimated in **(c)** is not the same as the accepted value. [1]

5 This question is about lattice energy.

(a) Write an equation whose enthalpy change is equal to the lattice energy of magnesium chloride. [1]

(b) Draw a Born–Haber cycle for magnesium chloride. [4]

(c) Use your Born–Haber cycle, the data below, and data from the data booklet, to calculate the lattice energy of magnesium chloride. Show all your working. [4]

Enthalpy of formation of $MgCl_2(s)$	$-642\,kJ\,mol^{-1}$
Enthalpy of atomisation of Mg(s)	$+150\,kJ\,mol^{-1}$
Enthalpy of atomisation of chlorine	$+122\,kJ\,mol^{-1}$
Electron affinity of Cl(g)	$-349\,kJ\,mol^{-1}$

6 Electrochemistry

AS 6.1–6.3 pages 118–121;
6.7–6.9 pages 126–130
A 6.4–6.6 pages 121–126;
20.1–20.15 pages 371–395

Key points

- ☐ Calculate oxidation numbers
- ☐ Explain redox processes
- ☐ Use the relationship $F = Le$
- ☐ Predict substances made in electrolysis and calculate their amounts
- ☐ Describe how to find the value of L by electrolysis
- ☐ Define *standard electrode potential* and *standard cell potential*
- ☐ Describe how to use the standard hydrogen electrode to measure standard electrode potentials
- ☐ Calculate standard cell potentials
- ☐ Use standard cell potentials to deduce the direction of electron flow in a cell and predict the feasibility of a reaction
- ☐ Use half-equations to construct redox equations
- ☐ Use the Nernst equation to predict how the value of an electrode potential varies with ion concentration.

Redox reactions

In some redox reactions, electrons transfer completely from one substance to another.

Key terms

Oxidation: the loss of electrons.

Reduction: the gain of electrons.

Oxidising agents: agents that accept electrons.

Reducing agents: agents that donate electrons.

Remember

OIL RIG – **o**xidation **i**s **l**oss and **r**eduction **i**s **g**ain (of electrons).

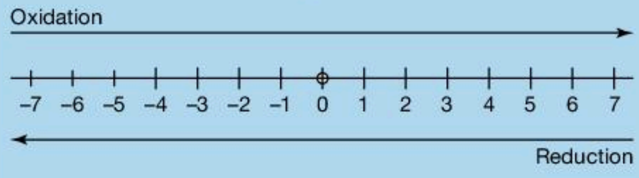
In some redox reactions, electrons are not completely transferred from one substance to another. In these reactions, **oxidation numbers** show which substances are oxidised and reduced. If the oxidation number of an atom increases in a chemical reaction, the atom is oxidised. If the oxidation number decreases, the atom is reduced.

Key term

Oxidation number: the oxidation number of an atom or ion describes its relative state of oxidation or reduction.

Exam tip

You can use a number line to help work out whether oxidation number increases or decreases (Figure 6.1).



▲ **Figure 6.1** Showing oxidation and reduction on a number line

Remember

To find the oxidation numbers of the atoms in a compound, assume that the compound is ionic, and work out the charge on each atom.

Remember

- The oxidation number of an element alone is 0.
- The oxidation number of hydrogen in all compounds is +1, except in metal hydrides, when it is –1.
- The oxidation number of oxygen in all compounds is –2, except in peroxides and OF_2.
- The oxidation number of chlorine is –1, except in its compounds with oxygen or fluorine.
- The oxidation number of Group 1 elements is +1
- The oxidation number of Group 2 elements is +2.

Worked example

Identify the substances that are oxidised and reduced in the reactions below.

a) $2Fe + 3Cl_2 \rightarrow 2FeCl_3$

b) $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

Answer

a) Fe loses electrons to form Fe^{3+} in the product, so Fe is oxidised. Cl gains electrons to form Cl^- in the product, so Cl is reduced.

b) Let x be the oxidation number of Cr in $Cr_2O_7^{2-}$, and calculate x from

$2x + (7 \times -2) = -2$

So $x = +6$

The oxidation number of chromium changes from +6 in the reactant to +3 in the product, so chromium is reduced.

The oxidation number of iodine changes from −1 to 0, so iodine is oxidised.

Maths skills

Solving for *x*

To solve for x in an equation, rearrange so that all terms that include x are on one side of the equation, and all the other terms are on the other side. This means that in answer **b**,

$2x+(7\times-2)=-2$ becomes
$2x=-2-(7\times-2)$

Simplify each side:

$2x=-2--14$
$2x=+12$

Finally, divide both sides by 2 to solve for x:

$x=+6$

Electrolysis

Calculating amounts of substance made in electrolysis

In electrolysis, an electrical current passes through a substance and breaks it down; electricity makes a chemical reaction happen. The amount of each product depends on the quantity of electricity (the electrical charge) and the number of electrons that are transferred.

The electrical charge is calculated from this equation:

$$\text{electrical charge (coulombs, C)} = \text{current (amps, A)} \times \text{time (seconds, s)}$$
$$Q = It$$

The charge on one mole of electrons is 96 500 C mol^{-1}, or 9.65×10^4 C mol^{-1}. This is the Faraday constant. It is equal to $L \times e$ where L is the Avogadro constant and e is the charge on an electron.

Common error

Some students forget that the unit of time in the equation $Q=It$ is the second.
If time is given in minutes, multiply by 60. If time is given in hours, multiply by 3600 (60×60).

Remember

$F=Le$. The values of L and e are given in the data booklet.

Worked example

A current of 1.8 A passes through a solution of copper(II) chloride for 45 minutes. What mass of copper is deposited at the cathode?

Answer

The reaction that occurs at the cathode is $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ so 2 mol of electrons are required to deposit 1 mol of solid copper. So the charge to deposit 1 mol of copper is 2 faradays, which is equal to $2 \times 96\,500\,C\,mol^{-1} = 193\,000\,C\,mol^{-1}$

The electrical charge in the experiment, $Q = I \times t$

$$Q = 1.8\,A \times (45\,min \times 60\,s\,min^{-1})$$
$$Q = 4860\,C$$

So the amount (in mol) of copper deposited $= \dfrac{4860C}{193\,000\,C\ mol^{-1}}$

$$= 0.025\,mol$$

The mass of 0.025 mol of copper $= 0.025\,mol \times 63.5\,g\,mol^{-1}$

$$= 1.6\,g\ (2\ s.f.)$$

Key terms

Anode: the positive electrode during electrolysis.

Cathode: the negative electrode during electrolysis.

Predicting products of electrolysis

For a molten electrolyte:

- Negative ions go to the **positive electrode (anode)** where they lose electrons.
- Positive ions go to the **negative electrode (cathode)** and gain electrons.

Worked example

Write half-equations for the reactions that occur at the cathode and anode in the electrolysis of molten lead bromide. For each electrode, explain whether oxidation or reduction has occurred.

Answer

At the cathode $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$. Lead ions gain electrons, so this is reduction.

At the anode $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$. Bromide ions lose electrons, so this is oxidation.

★ Exam tip

The question includes the word *explain*. This means that you need to write down how you know that reduction occurs at the cathode, and so on.

Water is present in an aqueous solution. This makes it harder to predict the products of electrolysis:

- At the cathode, the product is
  - a metal if the metal is below hydrogen in the redox series (e.g. Cu and Ag)
  - hydrogen if the metal is above hydrogen in the redox series (e.g. Ca and Na).
- At the anode, the product is
  - a halogen if the solution contains halide ions
  - oxygen if the solution does not contain halide ions.

The products also depend on the concentration of the solution. For example:

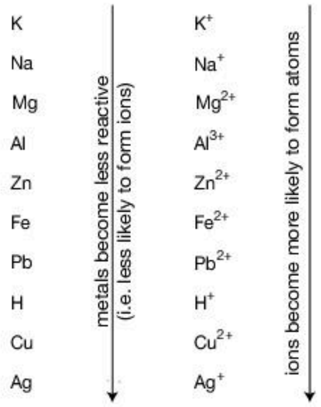
- For dilute solutions of halides, both oxygen and the halogen are produced.
- For concentrated solutions of Pb^{2+}, Fe^{2+} and Zn^{2+}, the metal may be produced instead of, or as well as, hydrogen.

The products of electrolysis differ for inert and non-inert electrodes. In the electrolysis of copper(II) sulfate with inert electrodes, oxygen evolves at the anode, but with copper electrodes, the reactions at the electrodes are:

- **cathode** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- **anode** $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Remember

Positive ions are called cations, because they are attracted to the cathode. Negative ions are called anions, because they are attracted to the anode.

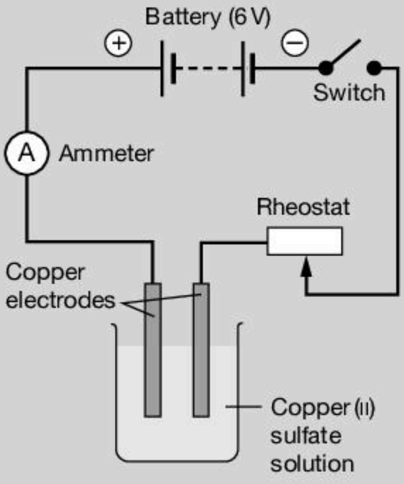


▲ **Figure 6.2** The redox series, also called the electrochemical series, showing the reactivity of atoms and ions

Practical skills

You can calculate a value for the Avogadro constant L in an electrolysis experiment:

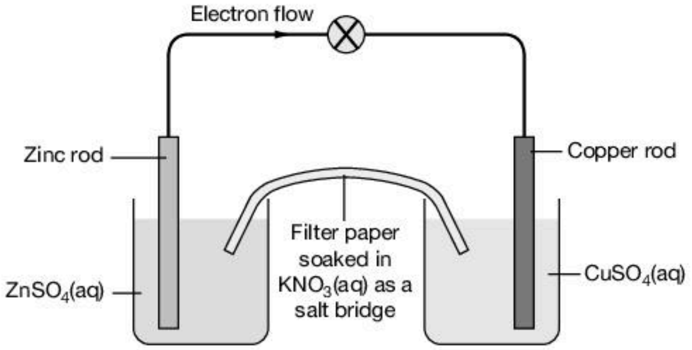
1. Find the mass of a clean, dry copper cathode.
2. Set up the apparatus in Figure 6.3.
3. Pass a known current for a known time.
4. Remove, clean and dry the cathode.
5. Find the mass of the cathode, and calculate the increase in mass.
6. Use your values from **1** and **5** to calculate the amount of copper deposited, in moles.
7. Use data from **3** and the equation $Q = It$ to calculate Q.
8. Use your answers from **6** and **7** to calculate the charge required to deposit 1 mol of copper. This is the value of $2F$, where F is the Faraday constant. (The value is $2F$ because 2 mol of electrons are required to deposit 1 mol of copper.)
9. Use the equation $F = Le$, your answer from **8**, and the value of e from the data booklet to calculate L.



▲ **Figure 6.3** Finding the amount of charge required to deposit 1 mol of copper

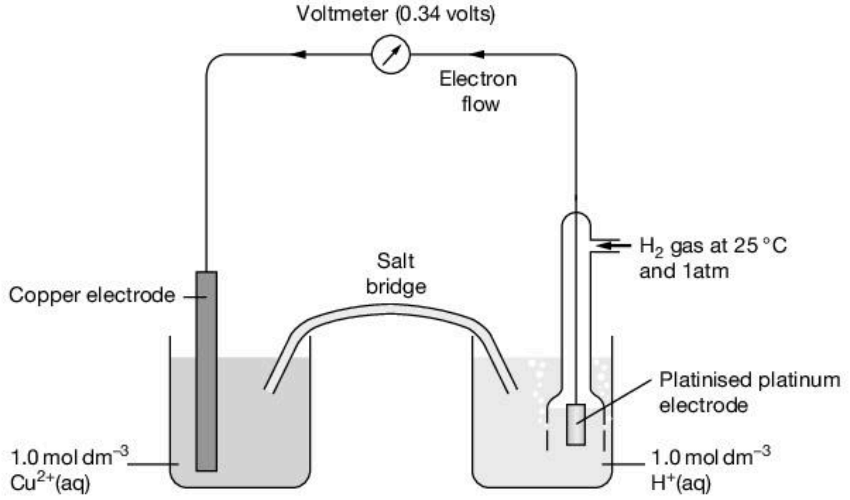
Standard electrode potentials

In an electrochemical cell, chemical reactions generate an electric current. An electrochemical cell is made up of two half-cells. Half of a redox reaction occurs in each half-cell.

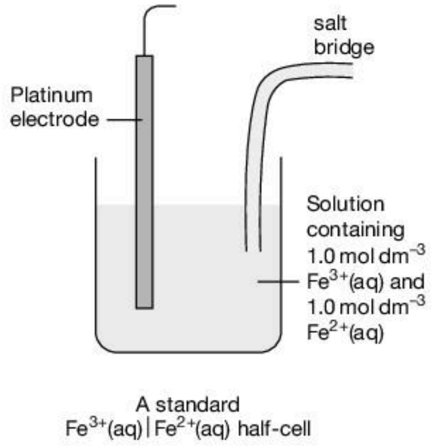


▲ **Figure 6.4** An electrochemical cell, made up of two half-cells

The **standard electrode potential** of a half-cell is measured by joining it to a standard hydrogen half-cell.



▲ **Figure 6.5** This electrochemical cell is made up of a standard $Cu^{2+}(aq)|Cu(s)$ half-cell joined to a standard hydrogen electrode; it is used to measure the standard electrode potential of the $Cu^{2+}(aq)|Cu(s)$ half-cell.



◀ **Figure 6.6** This half-cell is made up of ions of the same element, iron, in different oxidation states. Since the concentrations of both ions are 1.0 mol dm^{-3}, the cell is a standard $Fe^{3+}(aq)|Fe^{2+}(aq)$ half-cell.

Key terms

The **standard electrode potential $E^{\ominus}$** of a half-cell is the electromotive force (emf) that results when an electrode is joined to a standard hydrogen electrode in standard conditions.

The **standard cell potential** is the potential difference (voltage) that is produced when two standard half-cells are joined to make an electrochemical cell.

Remember

Standard conditions are $T = 298$ K, pressure = 100 kPa, solution concentration = 1 mol dm^{-3}.

Standard electrode potentials are also called standard redox potentials.

Standard electrode potentials are for equilibria, so half-reactions can go in either direction.

Calculating and using standard cell potential values

The data booklet has two tables of standard electrode potential data. The second table gives values of $E^\ominus$ in decreasing oxidising power. A few lines of the second table are shown in Table 6.1.

▼ **Table 6.1** Standard electrode potentials of half-cells

	Oxidising agent		**Reducing agent**		**$E^\ominus$/V**
increasing strength of oxidising agent ↑	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	increasing strength of reducing agent ↓	+0.34
	$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$		0.00
	$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$		–0.76

If a half-reaction has a high positive value for $E^\ominus$, the reaction is likely to happen spontaneously. For the species shown in Table 6.1:

- $Cu^{2+}(aq)$ is the strongest oxidising agent – it has the greatest tendency to accept electrons.
- Zn is the strongest reducing agent – it has the greatest tendency to donate electrons.

You can use standard electrode potentials to calculate a standard cell potential. For example, for the cell in Figure 6.4, $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$, the half-reactions below occur:

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^- \qquad E^\ominus = +0.76\,V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.34\,V$$

Remember

You need to change the sign of the standard electrode potential if the reaction happens in the reverse direction to that shown in the data table.

For the cell overall, the reaction is $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ and the standard cell potential, $E^\ominus_{cell}$ is $+0.76\,V + 0.34\,V = +1.10\,V$

In the circuit, electrons flow from the zinc electrode into the connecting wire. They then move through the wire to the copper electrode. Here, copper ions accept electrons. The copper ions are reduced to make copper atoms.

If the value of $E^\ominus_{cell}$ is positive, the reaction shown by the overall equation is likely to happen. If the value of $E^\ominus_{cell}$ is negative, the reaction will not happen.

Worked example

Use the data booklet to write down values of $E^\ominus$ for the half-cells below. Then deduce the relative reactivity of the Group 17 elements as oxidising agents. Explain your deduction.

$$F_2(g)|\ 2\ F^-(aq)$$
$$Cl_2(g)|\ 2\ Cl^-(aq)$$
$$Br_2(g)|\ 2\ Br^-(aq)$$
$$I_2(g)|\ 2\ I^-(aq)$$

Answer

The values of $E^\ominus$, from top to bottom above, are +2.87 V, +1.36 V, +1.07 V, +0.54 V.

The values get less positive down the group, from fluorine to iodine. This shows that the tendency to accept electrons from other species decreases down the group, so the strength of the elements as oxidising agents decreases.

Writing redox equations from half-equations

You can use two half-equations to write an equation for an overall redox equation

Worked example

Write an equation for the reaction of aqueous solutions containing V^{2+} with Cu^{2+} ions. Calculate the standard cell potential for the reaction.

Answer

From the data booklet:

$V^{2+} + 2e^- \rightarrow V \qquad E^\ominus = -1.20\,V$

$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\ominus = +0.34\,V$

Adding curved arrows:

$V^{2+} + 2e^- \rightarrow V \qquad E^\ominus = -1.20\,V$

$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^\ominus = +0.34\,V$

The overall equation is:

$V + Cu^{2+} \rightarrow Cu + V^{2+} \qquad E^\ominus = +0.34\,V + +1.20\,V$

$E^\ominus = +1.54\,V$

Exam tip

To write redox equations from half-equations, write the half-equation with the more negative value of $E^\ominus$ above. Then draw anticlockwise arrows to write the equation.

The variation of electrode potential with concentration

For a metal ion | metal system, if the concentration of aqueous ions in solution increases, the value of the electrode potential becomes more positive. This happens because the ions are more likely to be reduced if there are more of them in a given volume of solution.

The Nernst equation is used to calculate electrode potentials at different concentrations:

$$E = E^\ominus + \frac{(0.059)}{z}\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

Remember

Z is the number of electrons transferred. *E* is the electrode potential under non-standard conditions, and $E^\ominus$ is the electrode potential under standard conditions. The oxidised species is the one with fewer electrons.

Worked example

Calculate *E* for the $Cl_2(g)|Cl^-(aq)$ half-cell when the concentration of chloride ions is $0.1\,mol\,dm^{-3}$

Answer

$$E = +1.36V + \frac{0.059}{1}\log\frac{[Cl_2]}{[Cl^-]}$$

$$E = +1.36V + 0.059\log\frac{1}{0.1}$$

$$E = +1.36V + 0.059\log 10$$

$$E = +1.419V$$

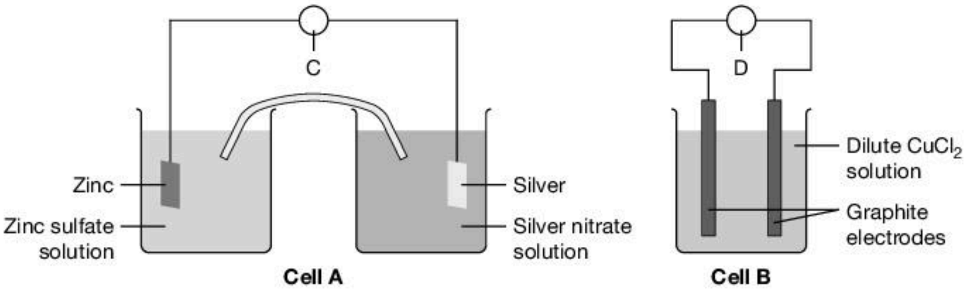
Advantages of new types of batteries and fuel cells

Cells and batteries enable us to store – and use – the energy from chemical reactions.

- Hydrogen–oxygen fuel cells produce just one waste product, water.
- Rechargeable batteries save money over time because you do not need to keep buying new batteries. They also reduce the use of finite resources.

Raise your grade

1 The diagrams below show an electrochemical cell and an electrolysis cell.



(a) (i) Explain how the functions of an electrochemical and an electrolysis cell are different. [2]

In an electrolysis cell, an electrical current passes through a substance and breaks it down. ✓ But an electrochemical cell is different. ✗

The candidate has gained one of the two marks, but has not stated how the function of electrochemical cell is different. To gain the second mark, she needs to state that, in an electrochemical cell, chemical reactions generate an electric current.

(ii) Name the pieces of apparatus at **C** and at **D** in the diagrams above. [2]

C is a voltmeter ✓ and D is mains electricity. ✗

D is not mains electricity, since mains electricity has an alternating current. Electrolysis requires a direct current from a power pack or battery.

(b) (i) Predict the products formed at the cathode and anode in cell **B** above. [2]

Cathode – copper ✓

Anode – chlorine gas ✗

The candidate is correct in stating that one of the products at the anode is chlorine gas. Since the solution is dilute, oxygen gas is also formed at the anode.

(ii) Write a half-equation for the reaction that occurs at the cathode in cell **B**. [1]

$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ ✗

The candidate is correct in stating that copper ions move to the cathode. However, the charge on the copper ion in $CuCl_2(aq)$ is +2, so the correct half-equation is

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

(iii) Describe how to measure the mass of product deposited at the cathode in cell **B**. [1]

Find the mass of the clean dry cathode before and after the experiment. ✗

The candidate is correct so far, but needs to add that the mass of product deposited is the difference in mass of the cathode before and after the experiment.
This value can be found by doing the following calculation:

mass of product = mass of cathode at end of experiment – mass of cathode at start

(c) A current of 2.0 A flows for 1 hour and 10 minutes through cell **B**.

(i) Calculate the electrical charge, Q. [2]

$Q = It$ ✓

$Q = 2.0 \times 70$ ✗

$Q = 140\,C$

The candidate has not converted the time to seconds. The correct calculation is

$Q = 2.0\,\text{A} \times (70\,\text{min} \times 60\,\text{s min}^{-1})$

$Q = 8400\,\text{C}$

★ Exam tip

Include units in calculations. This means you are less likely to make mistakes.

(ii) Do a calculation to predict the mass of product deposited at the cathode. [3]

96500 C deposits one mole of Cu. ✓ ecf

So 140 C deposits $\dfrac{140\,C}{96500\,C\ \text{mol}^{-1}}$

$= 0.0014\,\text{mol}$ ✓ ecf

This has a mass of $0.0014\,\text{mol} \times$

$63.5\,\text{g mol}^{-1} = 0.089\,\text{g}$ ✓ ecf

The candidate has used correct working throughout, in spite of basing her calculations on previous errors. For this reason she achieves the full three marks. 'Ecf' means 'error carried forward'.

The correct answer is:

$96\,500 \times 2 = 193\,000$ C deposits one mole of Cu, since each mole requires 2 mol of electrons.

The correct value of Q is 8400 C, so the amount of Cu deposited is $= \dfrac{8400\ \text{C}}{193000\ \text{C mol}^{1}} = 0.0044\,\text{mol}$

This has a mass of $0.0044\,\text{mol} \times 63.5\,\text{g mol}^{-1} = 0.28\,\text{g}$

(iii) In an experiment, the mass of product measured in **(b) (iii)** was less than the mass calculated in **(c) (ii)**. Suggest why. [1]

Some of the copper might have fallen off the cathode. ✓

(d) Cell **A** shows the electrochemical cell made up of $Zn|Zn^{2+}(aq)$ and $Ag^{+}(aq)|Ag$.

(i) Write half-equations for the reactions that occur in cell B. [2]

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ ✓

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ ✓

(ii) Write an equation for the overall redox reaction that occurs in cell B. [1]

$Zn(s) + Ag^{+}(aq) \rightarrow Ag(s) + Zn^{2+}(aq)$ ✗

The equation is not balanced. To balance the equation, the candidate must include multipliers in the silver half-equation, as follows:

$Zn(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Zn^{2+}(aq)$

(iii) Calculate the value of the standard cell potential for cell **A** [2]

cell potential $= +0.76\,V + 0.80\,V = 1.56\,V$ ✓✓

(e) (i) Write down the Nernst equation. [1]

$$E = E^{\ominus} + \frac{(0.059)}{z}\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$$ ✓

(ii) Calculate the value of E for the $Ag^{+}(aq)|Ag(s)$ half-cell when the concentration of silver ions in the solution is 0.01 mol dm^{-3}. [2]

$E = 0.80\,V + \dfrac{0.059}{1}\log 0.01$

$E = 0.80\,V - 0.118\,V$

$E = 0.682\,V$ ✓✓

Exam-style questions

1 Which list correctly gives the oxidation numbers of chromium in the correct order for the compounds below? [1]

	$CrCl_2$	K_2CrF_6	$K_2[Cr(CO)_5]$	K_2CrO_4
A	−2	+6	+3	+4
B	+2	+4	−2	+6
C	+2	+5	+5	+2
D	−2	+2	+3	+4

2 Which list correctly gives the oxidation numbers of vanadium in the correct order for the species below? [1]

	Na_3VO_4	NH_4VO_3	MgV_2O_6	$Mg_2V_2O_7$	V_2O_4
A	+4	+3	+6	+7	+4
B	+3	+4	+2	+2	+2
C	+1	+1	+2	+2	+2
D	+5	+5	+2	+5	+4

3 Which element is reduced in the reaction below? [1]

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

A manganese

B iron

C hydrogen

D oxygen

4 In an electrolysis experiment, an electric current passes through an electrolyte, sodium sulfate solution. Inert electrodes are used.

(a) Predict the product formed at

(i) the cathode [1]

(ii) the anode. [1]

(b) (i) Write a half-equation for the reaction that occurs at the cathode. [1]

(ii) Explain whether the reaction that occurs at the cathode is an oxidation or reduction reaction. [1]

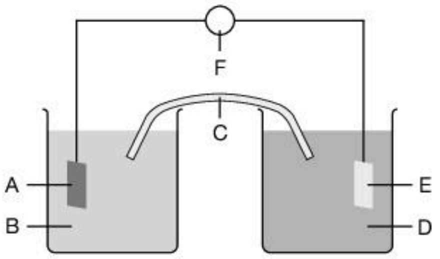
(c) A current of 2.3 A is passed through the cell for 50 minutes.

(i) Calculate the electrical charge, Q. [2]

(ii) Predict the amount of molecules of product made at the cathode, in mol. [2]

(iii) Calculate the volume of product made at the cathode under room conditions. Give your answer in dm^3. [2]

5 The diagram shows the apparatus for measuring the value of $E^\ominus$ for the cell made up of $Zn(s)|Zn^{2+}(aq)$ and $Fe^{3+}(aq)|Fe^{2+}(aq)$.



(a) State what each letter, A to F, represents. [6]

(b) (i) State what is meant by the symbol $E^\ominus$. [1]

(ii) State the conditions for measuring $E^\ominus$ for any half-cell. [1]

(c) (i) Use the data booklet to give the value of $E^\ominus$ for the $Zn(s)|Zn^{2+}(aq)$ half-cell. [1]

(ii) Predict how the value of E for the $Zn(s)|Zn^{2+}(aq)$ half-cell would change if the concentration of $Zn^{2+}(aq)$ were increased. Explain your reasoning. [1]

(d) Calculate the value of the standard cell potential for the cell shown in the diagram. [3]

7 Equilibria

AS 7.1–7.4 pages 132–138; 7.7–7.16 pages 141–156; 12.6–12.7 pages 237–241; 12.11 pages 245–247
A 7.5 pages 139–140; 21.1–21.13 pages 398–418

Key points

☐ Explain what reversible reactions and dynamic equilibria are.
☐ Use Le Chatelier's principle.
☐ State whether changes in conditions affect equilibrium constants.
☐ Deduce and use expressions for equilibrium constants.
☐ Explain the conditions used in the Haber and Contact processes.
☐ Use the Brønsted–Lowry theory of acids and bases.
☐ Explain the differences between strong and weak acids and bases.
☐ Explain and use pH, K_a, pK_a, K_w.
☐ Calculate $[H^+(aq)]$ and pH values for strong and weak acids and strong bases.
☐ Explain the choice of indicator for an acid–base titration.
☐ Describe and explain changes in pH during acid–base titrations.
☐ Explain how buffer solutions control pH, and describe and explain their uses.
☐ Calculate the pH of buffer solutions.
☐ Use the concept of solubility product and calculate its value from concentration data.
☐ Show understanding of the common ion effect.
☐ State the meaning of *partition coefficient* and calculate and use its value for a two-solvent system.

Dynamic equilibrium

In a **closed system**, a **reversible reaction** will achieve **dynamic equilibrium**. When the reaction reaches dynamic equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction. This means that, at dynamic equilibrium, large-scale properties remain constant, even though molecular-scale processes continue. A dynamic equilibrium may be achieved from either direction.

Le Chatelier's principle states that if a closed system at equilibrium is subject to a change in conditions, the system adjusts itself in order to minimise the effects of the change.

Worked example

For the equilibrium below, predict the effect on the position of the equilibrium of adding a few drops of:

a) dilute sulfuric acid

b) dilute sodium hydroxide solution.

Explain your predictions.

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

Key terms

Closed system: a system that is separate from the surroundings. Materials and energy cannot be transferred between a closed system and the surroundings.

Reversible reaction: a reaction whose direction can be changed if the conditions are changed.

Dynamic equilibrium: a state of balance in which the rate of the forward reaction is equal to the rate of the backward reaction.

Le Chatelier's principle: this states that if a closed system at equilibrium is subject to a change, the system adjusts itself and so minimises the effects of the change.

Answer

a) The mixture becomes more orange. This is because sulfuric acid contains H^+ ions. Adding H^+ ions shifts the equilibrium to the right, so minimising the effects of the change.

b) The mixture becomes more yellow. The OH^- ions in sodium hydroxide react with, and remove, H^+ ions. The equilibrium shifts to the left, so minimising the effects of the change.

Practical skills

You can carry out this experiment in the laboratory. Wear eye protection and protective gloves. Put 10 drops of dilute yellow potassium dichromate(VI) solution in a test tube. Add a few drops of dilute sulfuric acid, place a bung on the test tube, and shake. The mixture becomes orange. Then add dilute sodium hydroxide solution. The mixture becomes yellow again. You can do this several times, as the equilibrium shifts from right to left and back again.

Le Chatelier's principle predicts the effects of changing temperature and pressure, as well as concentration.

Catalysts do not affect the position of equilibrium for any reversible reaction.

Remember

Increasing temperature shifts an equilibrium in the *endothermic* direction.

Decreasing temperature shifts an equilibrium in the *exothermic* direction.

Worked example

For the equilibrium below, predict the effect on the position of the equilibrium of:

a) decreasing the pressure **b)** decreasing the temperature.

Explain your predictions.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196\,\text{kJ}\,\text{mol}^{-1}$$

Answer

a) The equilibrium shifts towards the left. This is because there are more moles of gas on the left. Increasing the number of moles of gas increases the gas pressure, so minimising the effects of the change.

b) The equilibrium shifts towards the right. This is because the forward reaction is exothermic. The effects of the decrease in temperature are minimised by shifting the equilibrium in the direction that transfers heat to the surroundings.

Exam tip

When explaining predictions about changes in pressure, state which side of the equation has the greater number of moles of gas.

The equilibrium constant

The **equilibrium constant** gives the exact position of an equilibrium for a given temperature.

For the equation: $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant, $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Key term

Equilibrium constant: the equilibrium constant gives the exact position of an equilibrium for a given temperature, and is represented by the symbol K_c.

Equilibrium constants are also given in terms of **partial pressures, p,** for reactions in the gas phase.

For the equation: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2\,(p_{O_2})}$$

Remember

For a given equilibrium:

- Values of K_c and K_p change if temperature changes.
- Values of K_c and K_p do not change if pressure or concentration change.

Worked example

At a certain temperature, 0.050 mol of PCl_5 was placed in a 1.0 dm^3 reaction vessel. The equilibrium below was established. The amount of PCl_5 present in the equilibrium mixture was 4.20×10^{-3} mol.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

a) Deduce an expression for K_c.

b) Calculate the concentrations of PCl_3 and Cl_2 at equilibrium.

c) Calculate K_c. Include the correct units in your answer.

Answer

a) $K_c = \dfrac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$

b) At equilibrium, $[PCl_3] = [Cl_2] = 0.0500\text{ mol dm}^{-3} - 4.20 \times 10^{-3}\text{ mol dm}^{-3}$
$= 0.0458\text{ mol dm}^{-3}$

c) $K_c = \dfrac{(0.0458\text{ mol dm}^{-3}) \times (0.0458\text{ mol dm}^{-3})}{4.20 \times 10^{-3}\text{ mol dm}^{-3}}$

$K_c = 0.499\text{ mol dm}^{-3}$

Remember

The units of K_c depend on the expression for that particular reaction.

Maths skills

Cancelling units

To work out the units of an equilibrium constant, include all units in the equilibrium constant equation.

- In the worked example above, the units for K_c cancel out as shown. This means that, for this reaction, the units of K_c are mol dm^{-3}.

$$K_c = \frac{(0.0458\text{ mol dm}^{-3}) \times (0.0458\ \cancel{\text{mol dm}^{-3}})}{4.20 \times 10^{-3}\ \cancel{\text{mol dm}^{-3}}}$$

- In the worked example below, all the units for K_c cancel out. For this reaction, K_c has no units.

Worked example

At a certain temperature 0.100 mol of ethanoic acid was mixed with 0.100 mol of ethanol in a 1 dm^3 reaction vessel. The equilibrium below was established.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The value of K_c is 4.6 at the temperature of the reaction. Calculate the concentration of each substance present in the reaction mixture.

Answer

The equilibrium constant expression is

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

	$CH_3COOH(l)$	+	$C_2H_5OH(l)$	$\rightleftharpoons$	$CH_3COOC_2H_5(l)$	+	$H_2O(l)$
Amount at start:	0.100 mol		0.100 mol		0		0
Amount at equilibrium:	$(0.100 - x\,\text{mol})$		$(0.100 - x\,\text{mol})$		$x\,\text{mol}$		$x\,\text{mol}$

Substituting into the equilibrium constant expression gives:

$$4.6 = \frac{x \times x}{(1-x)(1-x)}$$

$$4.6 = \frac{x^2}{(1-x)^2}$$

Solving for x gives:

$$\sqrt{4.6} = \frac{x}{1-x}$$

$$0.68 = x$$

So at equilibrium: $[CH_3COOC_2H_5] = [H_2O] = x = 0.68\,\text{mol dm}^{-3}$
and $[CH_3COOH] = [C_2H_5OH] = (1 - 0.68) = 0.32\,\text{mol dm}^{-3}$

Important industrial processes

The **Haber process** makes ammonia from nitrogen and hydrogen:

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

The **Contact process** produces sulfur trioxide, which is used to manufacture sulfuric acid.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196\,\text{kJ mol}^{-1}$$

Choosing conditions for industrial processes involves balancing two key factors:

- ensuring that the position of equilibrium favours the desired product
- ensuring that equilibrium is achieved as quickly as possible.

Worked example

Explain why the Contact process is carried out at a temperature of 450 °C and a pressure of 1 atm, and why a vanadium(V) oxide catalyst is used.

Answer

There is a greater number of moles of gas molecules on the left than on the right. This means that high pressures favour the production of sulfur trioxide. However, a low pressure is chosen because the extra yield at high pressure is not worth the extra expense.

The forward reaction is exothermic. This means that low temperatures favour the production of sulfur trioxide. However, a higher temperature is chosen because the rate of reaction at lower temperatures is too slow. At 450 °C equilibrium is achieved quickly with a reasonably high yield of the desired product.

The catalyst does not affect the position of the equilibrium, but it ensures that equilibrium is reached quickly.

Acids and bases

A **Brønsted–Lowry acid** is a proton donor, and a **Brønsted–Lowry base** is a proton acceptor. Equations for the dissociation constants of acids show **conjugate acid–base pairs**.

In an acid–base equilibrium, there are two conjugate acid–base pairs.

Worked examples

1 Identify the conjugate acid–base pair in the equilibrium below, stating which species is the acid, and which is the base:

$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

Answer

The conjugate acid–base pair is $HCl(aq)$ and $Cl^-(aq)$. HCl is the acid and $Cl^-(aq)$ is the base.

2 In the equilibrium below, explain why water is identified as acid 2, and the ethanoate ion (CH_3COO^-) is base 1.

$$\underset{\text{acid 1}}{CH_3COOH(aq)} + \underset{\text{base 2}}{OH^-(aq)} \rightleftharpoons \underset{\text{acid 2}}{H_2O(l)} + \underset{\text{base 1}}{CH_3COO^-(aq)}$$

Answer

In the reverse direction:

- Water is an acid because it donates protons.
  Water is acid 2 because it is the conjugate acid of base 2 (the hydroxide ion).
- The ethanoate ion is a base because it accepts protons.
  It is base 1 because it is the conjugate base of acid 1 (ethanoic acid).

★ Exam tip

In the exam, Roman numerals may be used to identify conjugate acid–base pairs:

acid-I, base-I; acid-II, base-II

A strong acid or base is fully dissociated in solution. However, a weak acid is only partly dissociated in solution. The equilibrium is towards the left for a weak acid.

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

✗ Common error

Some students confuse strong with concentrated, and dilute with weak:

- A concentrated solution has a large amount of acid or base dissolved in 1 dm^3 of solution.
- A strong acid or base is fully dissociated in solution.
- A dilute solution has a small amount of acid or base dissolved in 1 dm^3 of solution.
- A weak acid or base is only partly dissociated in solution.

Acid calculations

The pH of a solution is related to the hydrogen ion concentration by the expression:

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

The pH scale is logarithmic. This means that the concentration $[H^+(aq)]$ in a solution of pH 1 is 100 times greater than $[H^+(aq)]$ in a solution of pH 3.

Maths skills

Using the log button

To calculate pH, use the **log** button on your calculator to find $\log_{10}$ of the value of $[H^+(aq)]$. Then change the sign of the answer.

To find $[H^+(aq)]$ when you know the pH, use the expression $[H^+(aq)] = 10^{-pH}$. Start by putting the pH value into your calculator, change its sign and press the 10^x button (check the calculator booklet if necessary).

The **acid dissociation constant K_a** shows the extent of dissociation of an acid. The higher the value of K_a, the greater the dissociation of an acid. Values of K_a are often converted to pK_a values since these are easier to compare.

$$pK_a = -\log_{10} K_a$$

Worked example

Write an expression for K_a for propanoic acid. The equilibrium is

$$CH_3CH_2COOH(aq) \rightleftharpoons H^+(aq) + CH_3CH_2COO^-(aq)$$

Answer

$$K_a = \frac{[H^+(aq)][CH_3CH_2COO^-(aq)]}{[CH_3CH_2COOH(aq)]}$$

The **ionic product of water K_w** is the equilibrium constant for the dissociation of water. The value of K_w at 298 K is $1 \times 10^{-14}\,mol^2\,dm^{-6}$.

Since $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

Then $K_w = [H^+(aq)]\,[OH^-(aq)]$

Worked examples

1 Calculate the pK_a value for a solution with a K_a value of $6.7 \times 10^{-6}\,mol\,dm^{-3}$.

Answer

$$pK_a = -\log_{10} K_a$$
$$pK_a = -\log_{10} 6.7 \times 10^{-6}$$
$$pK_a = 5.2 \text{ (2 sig. fig.)}$$

2 Calculate the pH of $0.0320\,mol\,dm^{-3}$ propanoic acid CH_3CH_2COOH at 298 K. The value of $K_a = 1.34 \times 10^{-5}\,mol\,dm^{-3}$.

Answer

Start by calculating $[H^+(aq)]$.

$$K_a = \frac{[H^+(aq)][CH_3CH_2COO^-(aq)]}{[CH_3CH_2COOH(aq)]}$$

$$K_a = \frac{[H^+(aq)]^2}{[CH_3CH_2COOH(aq)]}$$

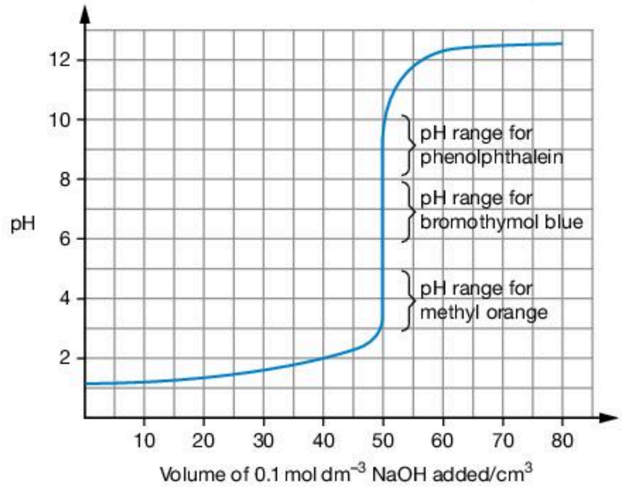
$$[H^+(aq)]^2 = K_a\,[CH_3CH_2COOH(aq)]$$
$$= 1.34 \times 10^{-5}\,mol\,dm^{-3} \times 0.0320\,mol\,dm^{-3}$$
$$[H^+(aq)] = 6.55 \times 10^{-4}\,mol\,dm^{-3}$$

Then calculate pH from the expression $pH = -\log_{10}[H^+(aq)]$

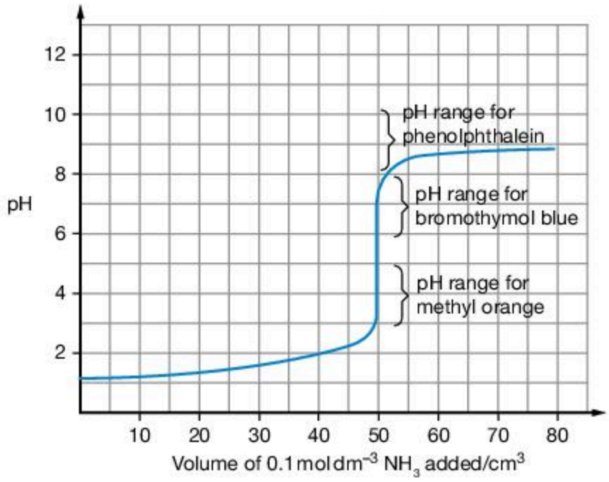
$$pH = -\log_{10} 6.55 \times 10^{-4}$$
$$pH = 3.18 \text{ (3 sig. fig.)}$$

Acid–base titrations

In an acid–base titration, the indicator chosen must have a distinct colour change at the end point. Its colour change must occur in the vertical section of a pH titration curve (see Figures 7.1 and 7.2). Figure 7.2 shows why phenolphthalein is not a suitable indicator for titrations of strong acids with weak bases.



▲ **Figure 7.1** For a strong acid–strong base titration, the three indicators shown are suitable.



▲ **Figure 7.2** A titration curve obtained by adding ammonia solution to hydrochloric acid.

Buffer solutions

Key term

Buffer solution: a buffer solution resists changes in pH on addition of acid or alkali.

A **buffer solution** resists changes in pH when an acid or alkali is added to it. A buffer solution is a mixture of a weak acid and its conjugate base. For the general acid HA and its conjugate base MA:

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

- On adding acid, the extra H^+ ions react with the conjugate base, and are removed. By Le Chatelier's principle, the equilibrium shifts to the left.
- On adding an alkali, the OH^- ions react with H^+ ions, and so are removed. This shifts the equilibrium to the right. More H^+ ions are now available to react with any extra OH^- that is added.

Worked example

Calculate the pH of a buffer solution made by mixing 0.01 mol dm^{-3} ethanoic acid with 0.2 mol dm^{-3} sodium ethanoate. The value of K_a for ethanoic acid is 1.7×10^{-5} mol dm^{-3}.

Answer

Start by calculating $[H^+(aq)]$:

$$K_a = \frac{[H^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

$$[H^+(aq)] = \frac{K_a[CH_3COOH(aq)]}{[CH_3COO^-(aq)]} = \frac{1.7\times10^{-5}\ \text{mol dm}^{-3}\times0.01\ \text{mol dm}^{-3}}{0.2\ \text{mol dm}^{-3}}$$

$$[H^+(aq)] = 8.5\times10^{-7}\ \text{mol dm}^{-3}$$

Then calculate pH from the expression $pH = -\log_{10}[H^+(aq)]$.

$$pH = -\log_{10} 8.5 \times 10^{-7}$$
$$pH = 6.1 \text{ (2 sig. fig.)}$$

Solubility product

The **solubility product** of a sparingly soluble salt A_xB_y is given by the expression below:

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Common error

Some candidates confuse solubility product and solubility. Make sure you know the difference between them.

Remember

The concept of solubility product applies only to sparingly soluble salts. Some undissolved solid must be present in contact with the solution.

Worked examples

1 Write down an expression for the solubility product of lead(II) iodide, PbI_2, and deduce its units.

Answer

At equilibrium:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

So $K_{sp} = [Pb^{2+}(aq)][I^-(aq)]^2$

The units are $mol\,dm^{-3} \times mol^2\,dm^{-6}$. So overall the units are $mol^3\,dm^{-9}$.

2 A saturated solution of lead iodide has a concentration of $1.65 \times 10^{-3}\,mol\,dm^{-3}$ at 20 °C. Calculate the solubility product of lead iodide at this temperature.

Answer

$[Pb^{2+}] = 1.65 \times 10^{-3}\,mol\,dm^{-3}$
$[I^-] = 2 \times 1.65 \times 10^{-3}\,mol\,dm^{-3}$
$= 3.3 \times 10^{-3}\,mol\,dm^{-3}$

$K_{sp} = [Pb^{2+}][I^-]^2$
$K_{sp} = [1.65 \times 10^{-3}\,mol\,dm^{-3}][3.3 \times 10^{-3}\,mol\,dm^{-3}]^2$
$K_{sp} = 1.80 \times 10^{-8}\,mol^3\,dm^{-9}$

Common error

Candidates sometimes forget that the concentration of an ion might be different from that of the salt. For PbI_2, the concentration of I^- ions is twice that of Pb^{2+} ions.

If lead iodide solution is mixed with potassium iodide solution, the solubility of lead iodide is less than it is in pure water. This is because the extra iodide ions shift the position of the equilibrium below to the left.

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

This is an example of the **common ion effect**.

Key term

Common ion effect: the solubility of a salt XY is reduced in the present of ions of X or Y from another source.

Partition coefficients

For a solute that dissolves in two different solutes that do not mix, the ratio of the concentrations of the solute in the two solvents is constant.

Key term

The **partition coefficient** of solute X in two immiscible solvents A and B at constant temperature is defined by this equation:

$$\frac{[X\,(\text{solvent A})]_{eqm}}{[X\,(\text{solvent B})]_{eqm}} = \text{a constant}$$

Raise your grade

1 The reaction of steam with ethene is used in industry to produce ethanol C_2H_5OH. The equation for the equilibrium reaction is: $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$

(a) Write an expression for the equilibrium constant K_p for the reaction above in terms of partial pressures. [1]

$$K_p = \frac{p_{C_2H_4(g)}\,p_{H_2O(g)}}{p_{C_2H_5OH(g)}} \quad ✗$$

The candidate has given the equilibrium expression for the reverse reaction. The correct answer is

$$K_p = \frac{p_{C_2H_5OH(g)}}{p_{C_2H_4(g)}\,p_{H_2O(g)}}$$

(b) Assuming the partial pressures at equilibrium are measured in atm, give the units of K_p. [1]

atm ✓ e.c.f.

This answer is consistent with the answer given by candidate in part **a**, so the mark has been awarded. The correct answer is atm^{-1}.

(c) The enthalpy change for the forward reaction is −45 kJ mol^{-1}.

(i) Predict the enthalpy change for the backward reaction. [1]

+45 kJ mol^{-1} ✓

(ii) Explain whether temperature should be increased or decreased to increase the yield of ethanol. [2]

The temperature should be decreased to increase the yield of ethanol. ✓✗

The answer is correct, but the candidate has not given an explanation for his answer. The candidate should add that the forward reaction is favoured at lower temperatures because, by Le Chatelier's principle, the system will respond by shifting the equilibrium to the right, so transferring more heat.

(d) Explain whether pressure should be increased or decreased to increase the yield of ethanol. [2]

There is a greater number of moles of gas molecules on the left ✓ so pressure should be decreased to increase the yield of ethanol. ✗

The candidate has correctly referred to the number of moles of gas molecules on each side of the equilibrium expression. However, the pressure should be increased to maximise the yield of ethanol. By Le Chatelier's principle, the system will respond by shifting the equilibrium to the right, so reducing the pressure.

(e) In an industrial plant that produces ethanol from ethene and steam, the reaction is carried out at a temperature of 300 °C and 70 atm pressure. Suggest reasons for these conditions, referring to your answers to question parts **c** and **d** as well as your knowledge of equilibrium reactions and rates of reaction. [4]

My answer to part **c** suggests that the temperature should be lower to maximise yield. However, at low temperatures the reaction is likely to reach equilibrium too slowly to produce a good yield in a reasonable time. ✓✓

My answer to part d suggests that the pressure should be low, but it is not. ✗

The candidate needs to state that high pressures increase the yield of ethanol. The pressure is quite high, but higher pressures are not chosen because of the increased expense and greater risk of operating at high pressures.

2 Chlorine gas was bubbled through a mixture of water and tetrachloromethane at 298 K. The mixture was shaken until equilibrium was reached. The layers of solution separated, and the concentration of chlorine in both solvents was measured. The results are in the table.

Experiment number	Concentration of chlorine at equilibrium /mol dm^{-3}	
	in CCl_4	in H_2O
1	0.900	0.0900
2	0.810	0.0790
3	0.690	0.0707

(a) Explain what is meant by the term *partition coefficient*. [1]

Solubility in one solvent relative to another. ✗

This answer is not precise enough. A good answer to this question would include the equation and statement that follows:

The partition coefficient of solute X in two immiscible solvents A and B is

$$\frac{[\text{X (solvent A)}]_{\text{eqm}}}{[\text{X (solvent B)}]_{\text{eqm}}} = \text{a constant}$$

(b) Calculate the mean value of the partition coefficient for chlorine in the three experiments above. [2]

$$\text{Partition coefficient} = \frac{0.900\ \text{mol dm}^{-3}}{0.0900\ \text{mol dm}^{-3}} = 10.00\ ✓$$

The candidate has calculated this value correctly. However, he also needs to calculate the values for Experiments 2 and 3, and find the mean of these three values.

The other two values are

$$\text{Partition coefficient} = \frac{0.810\ \text{mol dm}^{-3}}{0.0790\ \text{mol dm}^{-3}} = 10.25$$

$$\text{Partition coefficient} = \frac{0.690\ \text{mol dm}^{-3}}{0.0707\ \text{mol dm}^{-3}} = 9.76$$

$$\text{Mean} = \frac{10.00 + 10.25 + 9.76}{3} = 10.00$$

(c) Predict the concentration of chlorine in water if its concentration in tetrachloromethane is 0.510 mol dm^{-3}. [2]

$$\frac{0.510\ \text{mol dm}^{-3}}{x\ \text{mol dm}^{-3}} = 10.00$$

Solving for x gives a concentration of 0.0510 mol dm^{-3} ✓✓

The candidate has achieved the marks and shown his working clearly.

Exam-style questions

Choose your answer to questions 1, 2 and 3 by selecting on the basis of:

A	B	C	D
1, 2 and 3 are correct.	1 and 2 only are correct.	2 and 3 only are correct.	1 only is correct.

1 Which of these statements are correct for a system in dynamic equilibrium?

(1) The rate of the backward reaction is equal to the rate of the forward reaction.

(2) Large-scale properties remain constant.

(3) Molecular-scale properties remain constant.

2 Which statements must be true for the equilibrium below?

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

(1) Increasing the pressure shifts the equilibrium to the left.

(2) Increasing the concentration of oxygen shifts the equilibrium to the right.

(3) Using a suitable catalyst shifts the equilibrium to the right.

3 The equation below represents the Haber process.

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

The conditions chosen for the Haber process are 400 °C and 100 atm pressure, and an iron catalyst is used. Which statements help to explain this choice of conditions?

(1) There are more moles of gas on the left than on the right, so as pressure increases the position of the equilibrium moves to the right.

(2) The reaction is exothermic, so as temperature increases the position of the equilibrium moves to the right.

(3) Equilibrium is reached more quickly at low temperatures than at high temperatures.

4 0.1 mol of COF_2 was placed in 1 dm^3 reaction vessel at 1000 °C. The equilibrium below was established.

$$2COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$$

(a) Describe the processes that occur when dynamic equilibrium is established. [2]

(b) Write an expression for the equilibrium constant K_c for the reaction. [1]

(c) The equilibrium mixture was found to contain 0.037 mol of carbon dioxide. Calculate K_c. [3]

(d) Deduce the value of K_c for the equilibrium shown by the equation below:

$$CO_2(g) + CF_4(g) \rightleftharpoons 2COF_2(g)$$ [1]

(e) Predict the effect on the position of equilibrium of adding more carbon dioxide to the reaction vessel, and explain your prediction. [2]

5 A buffer solution was made by dissolving 2.88 g of sodium benzoate (C_6H_5COONa) in 1 dm^3 of 0.01 mol dm^{-3} benzoic acid. K_a for benzoic acid = 6.3×10^{-5} mol dm^{-3}.

(a) Calculate the concentration of benzoate ions in the solution, assuming that all benzoate ions are from sodium benzoate. [2]

(b) Calculate the value of $[H^+]$ for the buffer solution. [2]

(c) Calculate the pH of the buffer solution. [2]

(d) Explain why the pH of the buffer solution changes very little on addition of

(i) a solution containing H^+ ions [2]

(ii) a solution containing OH^- ions. [2]

6 **(a)** Explain the term *pH*. [1]

(b) State the difference between a weak base and a strong base. [2]

(c) Potassium hydroxide is a strong base. Calculate the pH of a solution of potassium hydroxide of concentration 22.4 g dm^{-3}. [5]

8 Reaction kinetics

AS 8.1–8.8 pages 159–172;
8.10 pages 173–174;
22.8 pages 434–436
A 14.8 pages 296–298;
22.1–22.8 pages 421–435;
29.4 pages 538–540

Key points

- ☐ Explain what *rate of reaction* means.
- ☐ Explain what *activation energy* means.
- ☐ Explain the effect of concentration on reaction rate.
- ☐ Explain the effect of temperature on reaction rate.
- ☐ Explain what *catalysts* are, and describe the difference between heterogeneous and homogeneous catalysts.
- ☐ Explain what enzymes are.
- ☐ Explain the meaning of *rate equation, order of reaction, rate constant, half-life, rate-determining step.*
- ☐ Construct and use rate equations to work out the order of a reaction.
- ☐ Use the half-life of first-order reactions in calculations.
- ☐ Calculate values of rate constants.
- ☐ For a multi-step reaction, suggest reaction mechanisms and the order of reaction.
- ☐ Explain the effect of temperature change on rate constant and reaction rate.
- ☐ Outline how homogeneous, heterogeneous and enzyme catalysts work.

The effect of concentration on reaction rates

The **rate of a reaction** indicates the speed of a reaction:

$$\text{Reaction rate} = \frac{\text{change in amount of substance}}{\text{time taken}}$$

A reaction can only occur if reactant particles collide. For reactions in solution, collisions are more frequent at higher concentrations. This means that, usually, increasing the concentration of one or more reactants increases the reaction rate.

Key term

Rate of a reaction: the rate of change in the amount or concentration of a particular reactant.

The effect of temperature on reaction rates

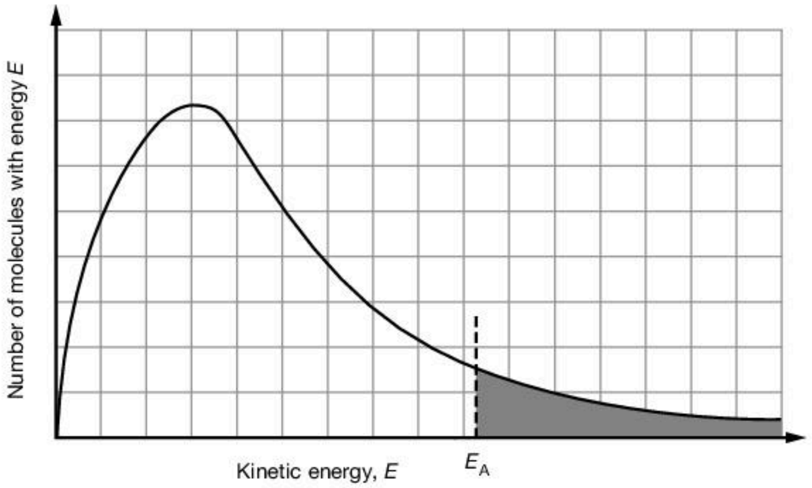
Increasing the temperature increases the rate of a reaction for two reasons:

- At higher temperatures, particles move more quickly, so their collisions are more frequent.
- Colliding particles only react if they collide with enough energy. Increasing the temperature results in a greater proportion of successful collisions.

The Boltzmann distribution shows the distribution of the kinetic energies of gas particles at a given temperature. Particles with energy equal to or greater than the **activation energy, E_A** have enough energy to react at that temperature (see Figure 8.1).

Key term

Activation energy: the activation energy of a reaction is the minimum energy needed for the reaction to happen.



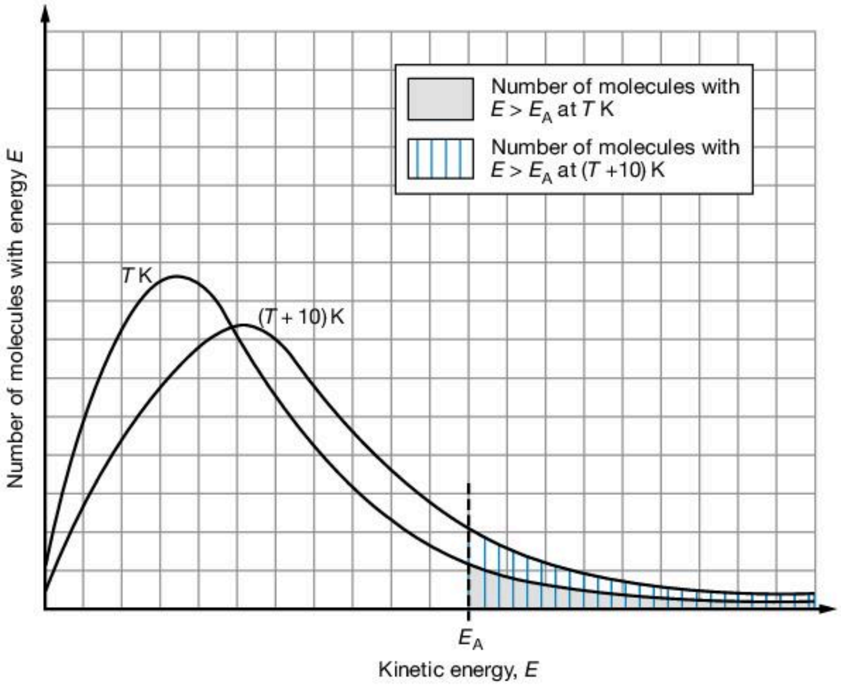
▲ **Figure 8.1** Distribution of the kinetic energies for gas molecules at a given temperature

Worked example

Use the Boltzmann distribution to explain why, for an increase in temperature of 10 K, the reaction rate approximately doubles.

Answer

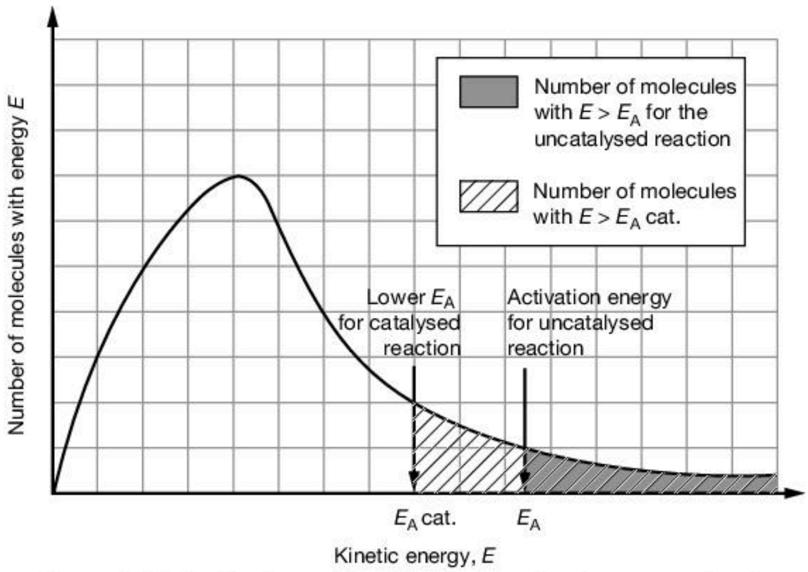
Figure 8.2 shows the Boltzmann distribution at two temperatures, T K and $(T + 10)$ K The number of particles that have enough energy to react (with $E > E_A$) approximately doubles for a 10 K temperature increase.



▲ **Figure 8.2** Distribution of the kinetic energies for gas molecules at T K and $(T + 10)$ K

The effect of catalysts on reaction rate

A **catalyst** works by changing the mechanism of a reaction so that the activation energy is lower. This means that a greater number of particles have enough energy to react.



▲ **Figure 8.3** Distribution of the kinetic energies for gas molecules, with the activation energy shown for catalysed and uncatalysed reactions

Key terms

A **catalyst** is a substance that increases the rate of a chemical reaction. It is not changed in the reaction.

A **heterogeneous catalyst** is in a different phase from the reactants and products.

A **homogeneous catalyst** is in the same phase as the reactants and products.

An **enzyme** is a biological catalyst. Enzymes are proteins, and usually catalyse specific reactions only.

Rate equations

Relationships between reaction rates and reactant concentrations can only be found by experiment. **Rate equations** show these relationships.

For the reaction A + B → products:

- Rate = $k[\mathrm{A}]^m\,[\mathrm{B}]^n$
- k is the **rate constant**.
- m is the **order of the reaction** with respect to A, and n is the order of reaction with respect to B. The values of m and n can be 0, 1 or 2. They are found by experiment.
- The overall order of the reaction is $m + n$.

✗ Common error

Some students think that the values of m and n can be derived from the chemical equation for the reaction. They cannot.

Remember

If a reaction is zero order with respect to one reactant, then the concentration of that reactant does not affect the reaction rate. The reactant does not appear in the rate equation.

Worked example

A reaction is first order with respect to A and zero order with respect to B. Write the rate equation for the reaction.

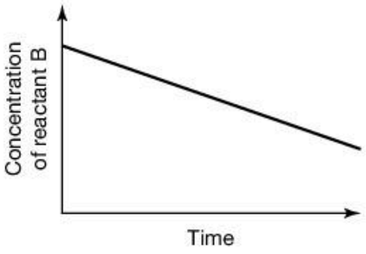
Answer

Rate = $k[\mathrm{A}]$

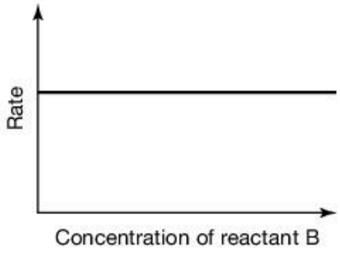
Remember

If a reaction is first order with respect to one reactant, you do not need to include the number '1' in the rate equation. In this case, the rate of reaction is directly proportional to the concentration of this reactant.

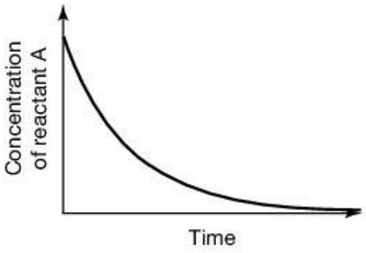
Deducing the order of a reaction



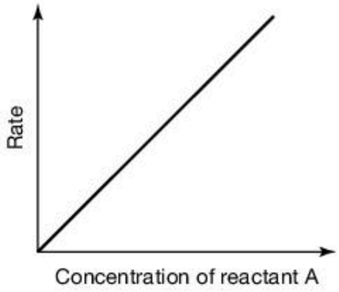
▲ **Figure 8.4** Concentration–time graph for a reaction that is zero order with respect to reactant B



▲ **Figure 8.5** Rate–concentration graph for a reaction that is zero order with respect to reactant B



▲ **Figure 8.6** Concentration–time graph for a reaction that is first order with respect to reactant A



▲ **Figure 8.7** Rate–concentration graph for a reaction that is first order with respect to reactant A

✗ Common error

Students sometimes confuse concentration–time graphs and rate–time graphs. Make sure you check the axis labels carefully.

Worked example

Substances A and B react together.

a) Use the data in Table 8.1 to show that the reaction is first order with respect to A and zero order with respect to B.

b) Calculate the rate constant for the reaction.

▼ **Table 8.1** Results from reacting A and B

Run	Initial [A] / mol dm^{-3}	Initial [B] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.1	0.1	1.4×10^{-3}
2	0.2	0.1	2.8×10^{-3}
3	0.1	0.2	1.4×10^{-3}

Answer

a) When [B] is constant, and [A] doubles, the rate also doubles. This shows that the reaction is first order with respect to A. When [A] is constant, and [B] doubles, the rate does not change. This shows that the reaction is zero order with respect to B.

b) rate = k[A]

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

$$k = \frac{1.4 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{0.1\ \text{mol dm}^{-3}} = 1.4 \times 10^{-2}\ \text{s}^{-1}$$

★ Exam tip

You can often deduce the rate equation directly from data, as here, or you may be given a graph like those above.

Maths skills

Cancelling units

You can cancel the units that are the same both above and below the line in an equation.

The rate of a first-order reaction can also be deduced from **half-life** data. For a first-order reaction, the half-life is independent of concentration. Whatever the concentration of the reactant, the half-life does not change.

Key terms

Initial rate of a reaction: the instantaneous reaction rate at the very start of the reaction.

Half-life: the half-life of a reactant is the time taken for the concentration of the reactant to be halved.

Worked example

The decomposition of dinitrogen pentoxide is first order in certain conditions:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The rate constant for the reaction is $4.5 \times 10^{-5}\,s^{-1}$ at 300 K

a) Calculate the half-life of the reaction.

b) If the concentration of N_2O_5 is $0.010\,mol\,dm^{-3}$ at the start of the reaction, calculate its concentration at two half-lives.

Answer

a) For a reaction with constant half-life:

$$k = \frac{\ln 2}{\text{Half-life}}$$

Rearranging:

$$\text{Half-life} = \frac{\ln 2}{k}$$

Substituting values into the equation:

$$\text{Half-life} = \frac{0.693}{4.5 \times 10^{-5}\ s^{-1}}$$

$$\text{Half-life} = 1.54 \times 10^{4}\,s$$

b) At one half life $[N_2O_5]$ $= \dfrac{0.01\,mol\,dm^{-3}}{2}$

$= 0.005\,mol\,dm^{-3}$

At two half lives $[N_2O_5]$ $= \dfrac{0.005\,mol\,dm^{-3}}{2}$

$= 0.0025\,mol\,dm^{-3}$

Rate equations and reaction mechanisms

You can use the rate equation for a reaction to predict its mechanism. You can also predict the order of reaction that results from a given mechanism.

Remember

$\log_e x$ or $\ln x$ is the natural logarithm of x. You can use a calculator to find its value.

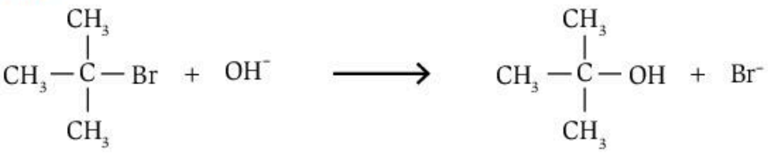
Half-life has the symbol $t_{\frac{1}{2}}$.

Worked example

The rate of the reaction shown by the equation below has this rate equation:

$$\text{Rate} = k[(CH_3)_3CBr]$$

Predict the mechanism of the reaction, and state the **rate-determining step**.



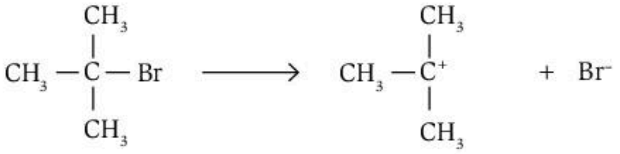
$$CH_3-C(CH_3)(CH_3)-Br + OH^- \longrightarrow CH_3-C(CH_3)(CH_3)-OH + Br^-$$

Key term

Rate-determining step: the rate-determining step of a reaction is the slowest step of its reaction mechanism. It has the highest activation energy.

Answer

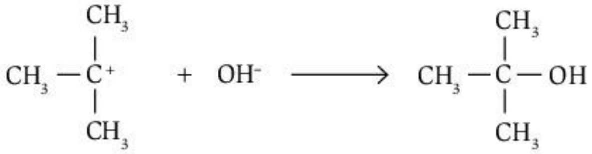
The rate equation shows that only one substance, $(CH_3)_3CBr$, is involved in the rate-determining step. This suggests that the reaction has two steps. First, the C—Br bond in $(CH_3)_3CBr$ bond breaks to form two ions:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + Br^-$$

Step 1

Then the carbocation reacts with the hydroxide ion:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + OH^- \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

Step 2

Step 1 is the rate-determining step since it happens more slowly than Step 2, in which two oppositely charged ions join together.

Experimental techniques for studying rates

The only way to find out about reaction rates is by experiment:

- measuring volumes of gas evolved in given times, for example in the reaction hydrochloric acid with magnesium
- using a colorimeter to measure the change in colour as a coloured product is made, or as a coloured reactant is used up
- sampling and titration, by:
    - removing small samples of the reacting mixture
    - quenching the reaction in these samples by flooding with solvent
    - doing a titration to find the concentration of one of the reactants or products in the reacting mixture.

More about catalysts

Heterogeneous catalysis is used in the Haber process and in catalytic converters. In both situations, gas molecules are adsorbed on the surface of the metal catalyst. This weakens the bonds in the gas molecules, and helps to orientate the molecules so that they can react.

As an example of homogeneous catalysis, oxides of nitrogen in the atmosphere catalyse the oxidation of sulfur dioxide to form sulfur trioxide.

Transition metals have a variable oxidation state, so they can catalyse redox reactions. For example, Fe^{2+} or Fe^{3+} ions catalyse this reaction:

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

In the catalysed reaction, Fe^{3+} quickly oxidises I^- to I_2 and $S_2O_8^{2-}$ quickly oxidises Fe^{2+} back to Fe^{3+}:

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$
$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

Enzymes each catalyse a specific reaction. Enzyme reactions have a lock-and-key mechanism. They work best at certain conditions of pH and temperature.

Link

There is more about the reactions that occur in catalytic converters in Unit 15.

Link

There is more about this catalysis reaction in Unit 13.

Link

Heterogeneous and homogeneous catalysts and enzymes are defined earlier in this unit.

Raise your grade

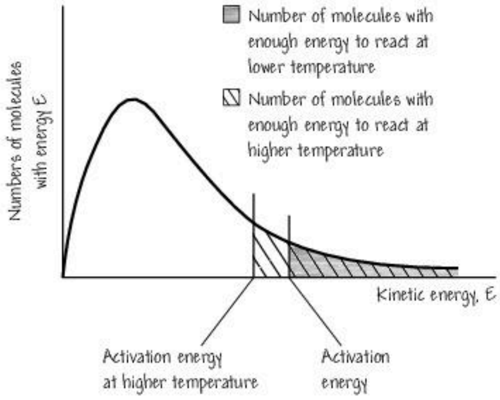
1 The reaction below occurs in aqueous solution:

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

(a) (i) Predict the effect on the rate of reaction of increasing the temperature. [1]

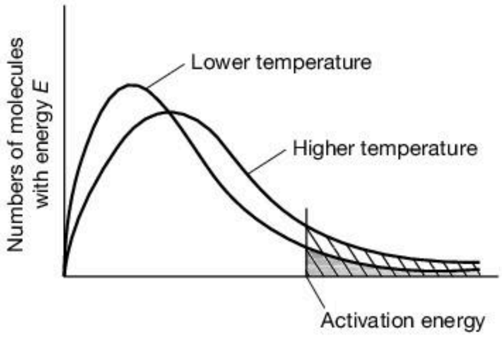
Increases ✓

(ii) Explain your answer to part **(i)** in terms of the Boltzmann distribution. Include a labelled sketch graph in your answer. [3]



✓✗✗

The candidate achieves 1 mark for correctly sketching the Boltzmann distribution graph. However, he has drawn a graph showing the effect of using a catalyst, not increasing the temperature, so does not achieve the other two marks. The correct graph is shown below. The key for the graph below is the same as for that above.



(b) The data in the table show the reaction rate for different initial concentrations of chlorine dioxide and hydroxide ions. The three experiments were carried out at 273 K.

Experiment number	Initial [ClO_2 (aq)] / mol dm^{-3}	Initial [OH^- (aq)] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	4.00×10^{-3}	3.60×10^{-4}	7.00×10^{-6}
2	8.00×10^{-3}	3.60×10^{-4}	2.80×10^{-5}
3	8.00×10^{-3}	7.20×10^{-4}	5.60×10^{-5}

(i) Explain how the data show that the reaction is first order with respect to hydroxide ions. [2]

When the concentration of hydroxide ions doubles the rate of reaction doubles. ✓✗

The answer is incomplete. The candidate needs to qualify his answer by adding the words in bold below:

When the concentration of hydroxide ions doubles, **and the concentration of ClO_2 is constant (as in Experiments 2 and 3)**, the reaction rate doubles.

(ii) Deduce the order of reaction with respect to chlorine dioxide. Explain your answer. [2]

When the concentration of ClO_2 doubles, and the concentration of OH^- is constant, the rate of reaction is four times greater. The reaction is second order with respect to chlorine dioxide. ✔✔

(iii) Write the rate equation for the reaction. [1]

Rate = $[ClO_2]^2[OH^-]$ ✘

The candidate forgot to include the rate constant in the equation. The correct answer is:

Rate = $k\,[ClO_2]^2[OH^-]$

(iv) State the overall order of the reaction. [1]

The overall order is $2 + 1 = 3$ ✔

(v) Calculate the value of the rate constant at the temperature of the reaction. Include the correct units in your answer. [2]

Rate = $k\,[ClO_2]^2[OH^-]$

$$k = \frac{\text{rate}}{[ClO_2]^2[OH^-]}$$

$$= \frac{7.00\times10^{-6}}{(4\times10^{-3})^2(3.6\times10^{-4})} \checkmark$$

$$= 1.21\times10^{-3} \times$$

The correct answer is 1.21×10^{3}. Since the candidate showed his working correctly, he achieved one of the two available marks for the calculation.

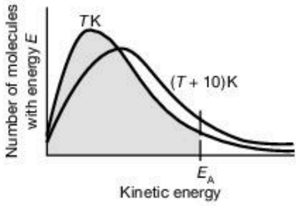
The candidate should have included the units in this working, and given the units of the rate constant as $dm^6\,mol^{-2}s^{-1}$, as shown below.

$$k = \frac{7.00\times10^{-6}\,mol\,dm^{-3}s^{-1}}{(4\times10^{-3}\,mol\,dm^{-3})^2\times3.6\times10^{-4}\,mol\,dm^{-3}}$$

$$k = 1.21\times10^{3}\,dm^{6}\,mol^{-2}\,s^{-1}$$

Exam-style questions

1 What does the shaded area show?



A The number of molecules that have enough energy to react at *T* K.

B The number of molecules that have enough energy to react at (*T* + 10) K.

C The number of molecules that do not have enough energy to react at *T* K.

D The number of molecules that do not have enough energy to react at (*T* + 10) K.

Choose your answer to questions 2, 3 and 4 by selecting on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

2 Which statements **explain** how changes in conditions affect changes in reaction rates?

1 As temperature increases, reaction rate increases.

2 At higher temperatures, particles move more quickly.

3 At higher concentrations of solution, particles collide more frequently.

3 Which statements about catalysts are correct?

1 Catalysts work best at high temperatures.

2 A heterogeneous catalyst is in a different state from the reactants.

3 Enzymes are proteins.

4 Which statements explain how catalysts speed up reactions?

1 A catalyst provides a reaction mechanism with a lower activation energy than for the uncatalysed reaction.

2 A catalyst results in a greater proportion of reactant molecules having enough energy to react.

3 A catalyst increases the energy of the reactant particles.

5 The table shows initial rate data for the reaction of hydrogen with nitrogen monoxide at 975 K.

$$2NO(g) + 2H_2(g) \rightarrow 2H_2O(g) + N_2(g)$$

Run	Initial [NO(g)] / mol dm^{-3}	Initial [H_2(g)] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.045	0.020	16×10^{-7}
2	0.0225	0.020	4×10^{-7}
3	0.045	0.010	8×10^{-7}

(a) Determine the order of reaction with respect to NO and with respect to H_2. [2]

(b) Write the rate equation for the reaction. [1]

(c) Calculate the value of the rate constant for the reaction at 975 K. [2]

(d) Calculate the initial reaction rate for the initial concentration values below:

$[NO(g)] = 0.050\,\text{mol dm}^{-3}$
$[H_2(g)] = 0.025\,\text{mol dm}^{-3}$ [2]

(e) Sketch the following graphs:

(i) a concentration–time graph with respect to hydrogen [1]

(ii) a rate–concentration graph with respect to hydrogen. [1]

(f) The reaction can be catalysed by solid palladium.

(i) State whether the catalyst is heterogeneous or homogeneous. [1]

(ii) Suggest how the palladium might catalyse the reaction. [2]

6 The reaction shown below is first order with respect to benzenediazonium chloride:

$$C_6H_5N_2Cl(aq) \rightarrow C_6H_5Cl(aq) + N_2(g)$$

(a) Suggest how the reaction could be followed experimentally. [1]

(b) The half-life of the reaction is 2.4×10^3 s at 300 K.

Calculate the rate constant of the reaction at this temperature. [2]

(c) Predict the number of molecules that are involved in the rate-determining step. Explain your prediction. [1]

9

Chemical periodicity

AS 9.1–9.11 pages 176–199; 4.14 pages 85–86

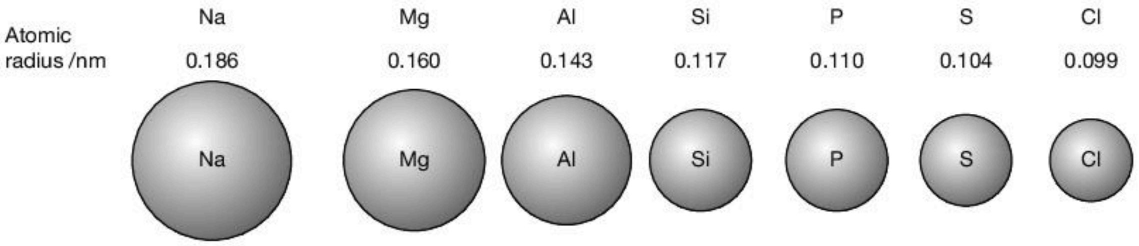
Key points

☐ Describe and explain periodicity of physical properties of the Period 3 elements, including:
  ○ atomic and ionic radius
  ○ melting point
  ○ electrical conductivity
  ○ first ionisation energy.
☐ Explain the properties of ceramics.
☐ Describe the reactions of the Period 3 elements with
  ○ oxygen
  ○ chlorine.
☐ State and explain the variation in oxidation number of the oxides and chlorides.
☐ Describe and explain the reactions with water of Period 3
  ○ oxides (including their acid/base nature)
  ○ chlorides.
☐ Interpret the variations and trends in chemical reactions in terms of bonding and electronegativity.
☐ Suggest the type of chemical bonding in chlorides and oxides from their properties.
☐ Predict the properties of an element in a given group using knowledge of periodicity.
☐ Deduce the nature, position in the periodic table, and identity of unknown elements from their properties.

Periodicity of physical properties

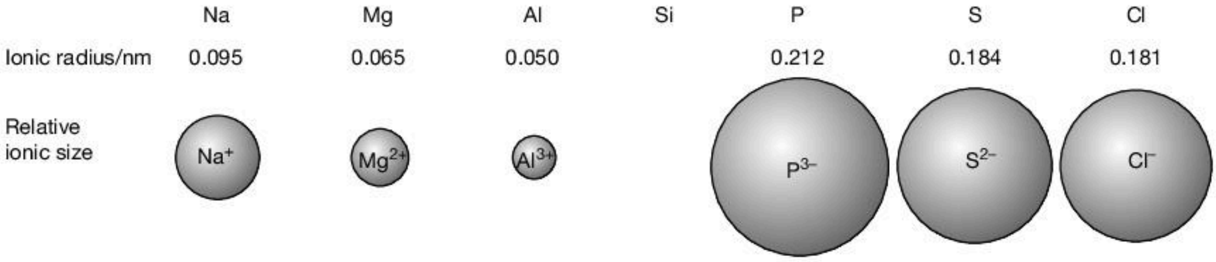
Atomic and ionic radius

Atomic radius decreases from left to right of Period 3. This is because nuclear charge increases, but electrons are added to the same shell. From left to right, the electrons are attracted more strongly by the increasing positive charge.



▲ **Figure 9.1** Atomic radius decreases from left to right of Period 3

The diagram below shows the variation in ionic radius for the Period 3 elements.



▲ **Figure 9.2** The variation in ionic radius for the Period 3 elements

Worked example

a) Explain why positive ions are smaller than the atoms they are made from, and why negative ions are bigger.

b) Explain the difference in size between Na^+ and Al^{3+}.

Answer

a) A positive ion is smaller than the atom it was made from because the ion has a greater number of positively charged protons than negatively charged electrons. The electrons are attracted more strongly by the nucleus, and so pulled in more closely. If the positive ion has lost all its outer electrons, it is smaller because the remaining electrons are in shells that are closer to the nucleus.

A negative ion is bigger than the atom it was made from because each extra electron results in an increase in repulsion between the clouds of negative charge.

b) The Al^{3+} ion is smaller than the Na^+ ion. This is because both ions have the same number of electrons, but the Al^{3+} ion has the greater nuclear charge. The Al^{3+} ion therefore attracts its electrons more strongly, and pulls them in more closely.

★ **Exam tip**

Before explaining the difference in size between the two ions, you need to describe the difference in size.

Melting point and electrical conductivity

Table 9.1 shows melting point data for the Period 3 elements. The structure and bonding of the elements explain this property.

▼ **Table 9.1** Melting points for Period 3 elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Melting point /°C	98	650	660	1410	44	119	−101	−189

The metals in Period 3 are good conductors of electricity because they have mobile, delocalised electrons to carry electrical charge. The other elements do not have mobile electrons.

Worked example

Explain the difference in melting point between sodium and aluminium.

Answer

The melting point of aluminium is higher than the melting point of sodium. In both elements a structure of positive ions and delocalised electrons is held together by electrostatic forces of attraction. The stronger the attractive forces, the higher the melting point. Since aluminium has three delocalised electrons per atom, and sodium has just one delocalised electron per atom, the strength of the attractive forces is greater in aluminium.

★ **Exam tip**

When you explain melting point, make sure you include three points:

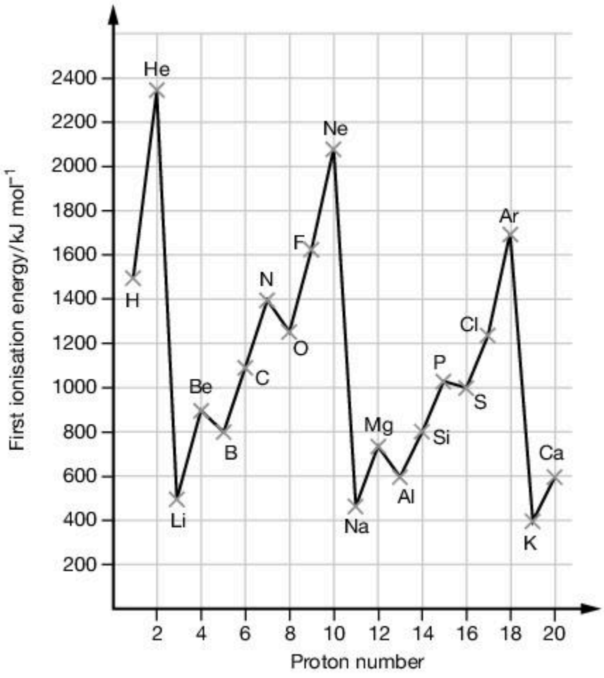
- the type of attractive forces involved
- the fact that stronger attractive forces result in higher melting points
- an explanation of the underlying reason, for example the number of delocalised electrons.

Remember

Silicon, phosphorus, oxygen and chlorine all have covalent bonds. Silicon is bonded in a giant covalent structure, with each atom joined to four others. When silicon melts, these strong covalent bonds must be broken. Phosphorus, oxygen and chlorine have small molecules (P_4, O_2 and Cl_2). When they melt, only the weak van der Waals forces between molecules are disrupted.

First ionisation energy

Figure 9.3 shows the **first ionisation energy** for the elements from hydrogen to calcium.



▲ **Figure 9.3** The variation in ionisation energy for the elements from hydrogen to calcium

Key term

First ionisation energy: the energy required to remove one mole of electrons from one mole of atoms in the gas state to make one mole of ions in the gas state, each with a single positive charge.

Common error

Students frequently give incomplete definitions for ionisation energy. Make sure you remember all parts of the definition.

Remember

First ionisation energy is the energy for the process shown by the general equation for:

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

In general, first ionisation energy increases from left to right of a period. This is because nuclear charge increases from left to right, but the outer electrons are in the same shell, so the shielding is the same for all elements. The greater nuclear charge attracts the outer electrons more strongly, and pulls them in more closely.

Remember

Four factors affect ionisation energy:

- the charge on the nucleus
- the distance between the nucleus and outer electrons
- the amount of shielding between the nucleus and outer electrons
- whether or not the electron is part of a pair.

Worked example

Give the electronic configurations of magnesium and aluminium. Then explain why the first ionisation energy of aluminium is less than that of magnesium.

Answer

Magnesium: $1s^2\ 2s^2\ 2p^6\ 3s^2$

Aluminium: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

The electron from aluminium is removed from a 3p orbital, but the electron from magnesium is removed from a 3s orbital. The 3p electron is slightly further from the nucleus than the 3s electrons. Also, the 3p electron is screened from the nucleus by the 3s electrons. Both these factors mean that less energy is required to remove the first electron from an aluminium atom than is required to remove the first electron from a sodium atom.

Common error

Students sometimes explain different ionisation energies by stating that a full or half-full shell is more stable than other configurations. This explanation is incorrect, and will gain no marks.

The physical properties of ceramics

Magnesium oxide, aluminium oxide and silicon dioxide are examples of ceramics. Ceramics have giant structures, with strong bonds between their atoms and/or ions. This means that ceramics are hard and strong, but brittle. They are electrical insulators.

Worked example

Explain why ceramics have high melting points, and why they do not conduct electricity.

Answer

Magnesium oxide and aluminium oxide have strong electrostatic forces of attraction between oppositely charged ions in a giant ionic structure. Silicon dioxide has strong covalent bonds between its atoms in a giant covalent structure. This means that a large amount of energy is needed to break the bonds when a ceramic melts, so it has a high melting point. A ceramic does not conduct electricity because it does not have charged particles that are free to move.

Periodicity of chemical properties

Reactions with oxygen and chlorine

- Sodium and magnesium react vigorously with oxygen and chlorine.
- Aluminium powder burns in oxygen. Bigger pieces of aluminium react more slowly because of the layer of relatively unreactive Al_2O_3 on the surface. Aluminium foil burns in chlorine.
- Silicon, phosphorus and sulfur react slowly with oxygen and chlorine.

Worked example

Write equations for the reactions of:

a) Na, Al, P and S with oxygen

b) Al, Si and P with chlorine.

Answer

a)
$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$
$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$
$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$
$$S(s) + O_2(g) \rightarrow SO_2(g)$$

b)
$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$
$$Si + 2Cl_2 \rightarrow SiCl_4$$
$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

Exam tip

When you write an equation, check that it is properly balanced.

Remember

Phosphorus exists as P_4 molecules in the solid state.

Remember

Aluminium chloride sublimes, forming $Al_2Cl_6(g)$.

Common error

Some students think that SO_3 is formed directly in the reaction of sulfur with oxygen. It is not! The compound is formed by passing a mixture of SO_2 and oxygen or air over a catalyst such as a vanadium(V) catalyst at 450 °C. The equation for the reaction is:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Oxidation numbers

The Period 3 elements have different **oxidation numbers** from each other in their compounds.

Key term

Oxidation number: a number given to an atom or ion to describe its relative state of oxidation or reduction.

Worked example

Copy and complete the table. Then explain the variation in oxidation numbers in the oxides and chlorides.

Compound	Oxidation number of Period 3 element
Na_2O	
MgO	
Al_2O_3	
P_4O_{10}	
SO_2	
SO_3	

Compound	Oxidation number of Period 3 element
$NaCl$	
$MgCl_2$	
Al_2Cl_6	
$SiCl_4$	
PCl_5	

Answer

Compound	Oxidation number of Period 3 element
Na_2O	+1
MgO	+2
Al_2O_3	+3
P_4O_{10}	+5
SO_2	+4
SO_3	+6

Compound	Oxidation number of Period 3 element
NaCl	+1
$MgCl_2$	+2
Al_2Cl_6	+3
$SiCl_4$	+4
PCl_5	+5

For both oxides and chlorides, the maximum oxidation number is the same as the number of electrons in the outer shell involved in bonding. In SO_2, only four outer electrons are involved in bonding, so the oxidation number of sulfur in this compound is +4.

Remember

The more electronegative element in a compound has the negative oxidation number.

- In all Period 3 oxides, the oxidation number of oxygen is –2.
- In all Period 3 chlorides, the oxidation number of chlorine is –1.

The oxides and hydroxides of Period 3 elements

Table 9.2 shows how the oxides of the Period 3 elements react with water, as well as whether the oxides are acidic, basic or **amphoteric**.

Key term

Amphoteric: an amphoteric substance is one that can act as both an acid and a base.

▼ **Table 9.2** The reactions of Period 3 oxides and water

Formula of oxide	Structure and bonding	Nature of oxide	Reaction of oxide with water
Na_2O	Ionic	Alkaline	Reacts to make NaOH
MgO	Ionic	Basic	Reacts to make $Mg(OH)_2$
Al_2O_3	Ionic	Amphoteric	None
SiO_2	Giant covalent	Weakly acidic	None
P_4O_{10}	Simple molecular	Acidic	Reacts to make H_3PO_4
SO_3	Simple molecular	Acidic	Reacts to make H_2SO_4

Electronegativity increases from sodium to sulfur. This explains the change in bonding in the oxides, from ionic on the left of the period, to simple molecular on the right of the period.

Worked example

Write equations for the following reactions:

a) sodium oxide with water

b) aluminium oxide with hot dilute hydrochloric acid

c) aluminium oxide with hot concentrated sodium hydroxide solution.

Answer

a) $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

b) $Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

c) $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$

Exam tip

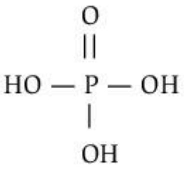
Practise writing equations for reactions of the oxides with dilute acids and sodium hydroxide solution. Always check that your equations are balanced.

Remember

In general, an oxide reacts with an acid to make a salt and water.

The hydroxides show a similar trend:

- Sodium and magnesium hydroxides are basic.
- Aluminium hydroxide is amphoteric.
- H_4SiO_4, H_3PO_4 and H_2SO_4 all include covalently bonded hydroxide groups (see Figure 9.4). They are acidic, since they donate H^+ ions in solution. Their acidity increases from left to right of Period 3.



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH$$

▲ Figure 9.4 Undissociated phosphoric(v) acid

Reactions of Period 3 chlorides with water

Table 9.3 shows the bonding in the Period 3 chlorides, as well as what happens when they are added to water.

▼ Table 9.3 Properties of Period 3 chlorides

Formula of chloride	Structure and bonding	What happens when the chloride is added to water
$NaCl$	Ionic	Dissolves to make solution of pH 7
$MgCl_2$		Forms weakly acidic solution of pH ≈ 6.5
Al_2Cl_6	• Simple molecular in gas state • Ionic in solid state	$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$ $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$
$SiCl_4$	Simple molecular	Violent, exothermic reaction: $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$
PCl_3 and PCl_5		Violent, exothermic reaction: $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(g)$
SCl_2		Slow reaction to make a mixture of compounds including hydrochloric acid.

The bonding in sodium chloride and magnesium chloride is ionic because of the large difference in electronegativity between the metal and chlorine. Chlorides in which both elements have similar electronegativity values exist as simple molecules.

Exam tip

You need to be able to give equations for the reactions in Table 9.3, and suggest pH values for the solutions formed. In an excess of water, the reactions of $SiCl_4$ and PCl_5 do not make fumes of HCl gas. Instead, hydrochloric acid is formed in solution.

Raise your grade

1 The table gives some data for the Period 3 elements.

	Na	Mg	Al	Si	P	S	Cl	Ar
First ionisation energy /kJ mol^{-1}	494	736	577	786	1060	1000	1260	1520
Atomic radius /nm	0.186	0.160	0.143	0.117	0.110	0.104	0.009	0.190
Ionic radius /nm	0.095	0.065	0.050	0.041	0.212	0.184	0.181	

(a) Define the term *first ionisation energy*. [1]

The energy to make ions. ✗

This definition is incomplete. The correct definition is that first ionisation energy is the energy required to remove one mole of electrons from one mole of atoms in the gas state to make one mole of ions in the gas state, each with a single positive charge.

(b) Describe and explain the general trend in first ionisation energy from left to right of Period 3. [3]

From left to right, first ionisation energy increases overall. ✓✗ ✗

The candidate gained one of the three marks for describing the trend, but she did not explain the trend.

The explanation for the general increase in first ionisation energy is that the increasing nuclear charge and decreasing atomic radius result in a stronger force of attraction between the nucleus and outer electron.

★ Exam tip

Read questions carefully, and make sure you answer all parts.

(c) **(i)** Give the electronic configurations of phosphorus and sulfur. [1]

$1s^2\ 2s^22p^3$ and $1s^2\ 2s^22p^4$ ✗

The candidate has mistakenly given the electronic structures of the elements that are above phosphorus and sulfur in the periodic table. The correct electronic configurations are

Phosphorus: $1s^2\ 2s^22p^6\ 3s^23p^3$

Sulfur: $1s^2\ 2s^22p^6\ 3s^23p^4$

(ii) Explain the difference in first ionisation energy for phosphorus and sulfur. [2]

The first ionisation energy for sulfur is less than the first ionisation energy for phosphorus. This is because a sulfur atom has two 3p electrons in the same orbital. ✗ ✗

This answer is correct so far, but the candidate needs to complete the explanation by adding that the two electrons in the same 3p orbital repel each other. This results in less energy being required to remove one electron from a sulfur atom than from a phosphorus atom. A phosphorus atom does not have paired electrons in any of its p orbitals.

(d) Describe and explain the trend in atomic radius from left to right of Period 3. [2]

The atomic radius decreases from left to right of Period 3. This is because the positive nuclear charge increases from left to right, and electrons are added to the same shell. ✓✗

Again, this answer is correct so far. However, the candidate needs to add that the increasing nuclear charge attracts electrons in the outer shell more strongly.

(e) Describe and explain the difference in atomic and ionic radius for aluminium. [2]

The difference is because the ion has a greater number of positively charged protons than negatively charged electrons, so the electrons are attracted more strongly and pulled in more closely. ✓✗

This explanation is clear and correct. However, the candidate lost a mark because she forgot to describe the difference in radius – the ionic radius is less than the atomic radius.

2 This question is about the elements of Period 2.

The letters given below are not the chemical symbols of the elements they represent.

(a) A Period 2 element **T** forms several oxides. Their formulae are $\mathbf{T}_2$O, **T**O, $\mathbf{T}$O$_2$, $\mathbf{T}_2$O$_4$ and $\mathbf{T}_2$O$_5$.

(i) What is the oxidation number of **T** in $\mathbf{T}_2$O? [1]

1 ✗

It is vital to include the sign when giving oxidation numbers, so the correct answer is +1.

(ii) Give the formula of the compound in which **T** has the highest oxidation number. [1]

TO_2 ✗

The oxidation number is TO_2 is +4, but the oxidation number in T_2O_5 is +5.

(b) A Period 2 element **X** reacts vigorously with water to form an alkaline solution. Its chloride has the formula **X**Cl.

(i) Predict the group number of element **X**. [1]

Group 1. ✓

(ii) Justify the prediction you made in part **(ii)**. [2]

The oxidation number of the element must be +1, since the formula of the chloride is XCl. ✓✗

This justification is correct, but there are two marks for the question, so the candidate needs to make two points.

The second point is that the Group 1 element in Period 3 (sodium) reacts vigorously with water to make an alkaline solution, so it is likely that the Group 1 element in Period 2 reacts in a similar way.

Exam-style questions

Choose your answers to questions 1 and 2 by selecting on the basis of:

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

Exam tip

When answering this type of multiple choice question, read through each statement and tick the ones that are correct. Then work out whether the answer is A, B, C or D.

1 A student investigated an oxide of a Period 3 element. She wrote down her observations.

The compound was solid at room temperature. On adding to water some of it reacted slowly to form an alkaline solution. There was a reaction when the compound was added to dilute hydrochloric acid, which resulted in the formation of a colourless solution.

What can be deduced from the student's observations? [1]

1 The compound is a metal oxide.

2 The solution formed in the reaction with hydrochloric acid would conduct electricity.

3 The products of the reaction with hydrochloric acid were sodium chloride and water.

2 Which properties do sulfur and phosphorus have in common? [1]

1 Their melting points are higher than 25 °C.

2 Their ionic radii are greater than their atomic radii.

3 Their chlorides react vigorously with water, producing fumes of a gas that turns damp red litmus paper blue.

3 This question is about the Period 3 elements shown below:

Na Mg Al Si P S Cl Ar

(a) Name the element with the highest melting point, and explain why its melting point is so high. [2]

(b) Give the names of three Period 3 elements that conduct electricity, and explain why they conduct. [2]

(c) Write equations for the reactions below. Include state symbols in your answers.

(i) magnesium with oxygen [1]

(ii) sodium oxide with water [1]

(iii) aluminium oxide with sodium hydroxide [1]

(iv) silicon chloride with water. [1]

✗ Common error

Some students forget to include state symbols in equations. If you are asked to include them, remember to include them!

(d) **(i)** Aluminium oxide is a ceramic.

Give the names and formulae of two other Period 3 oxides that are ceramics. [2]

(ii) Ceramic materials are hard, strong and brittle.

State and explain two other physical properties of the ceramic materials that you named in part **i**. [4]

Exam tip

There are four marks for this question, so make sure that your answer is detailed enough.

4 **(a)** Define the term *electronegativity.* [1]

(b) Describe the trend in electronegativity across Period 3. [1]

(c) Use ideas about electronegativity to explain the different types of bonding in sodium chloride and silicon chloride. [2]

5 This question is about the elements of Period 2 and Period 4. The letters given are not the chemical symbols of the elements they represent.

(a) A Period 2 element **Y** reacts with chlorine to make a compound that is liquid at room temperature. Element **Y** also reacts with oxygen to make an acidic oxide.

Predict whether element **Y** is in Group 1, 2, 14 or 18 and justify your prediction. [2]

(b) A Period 4 element **Z** is in Group 2.

(i) Predict one physical of element **Z**. [1]

(ii) Explain why element **Z** has the property you predicted in part **i**. [1]

(iii) Predict the formula of **Z** chloride. [1]

(iv) Predict one physical property and one chemical property of **Z** chloride. [2]

10 Group 2

AS 10.1–10.7 pages 202–212
A 10.5 pages 206–209

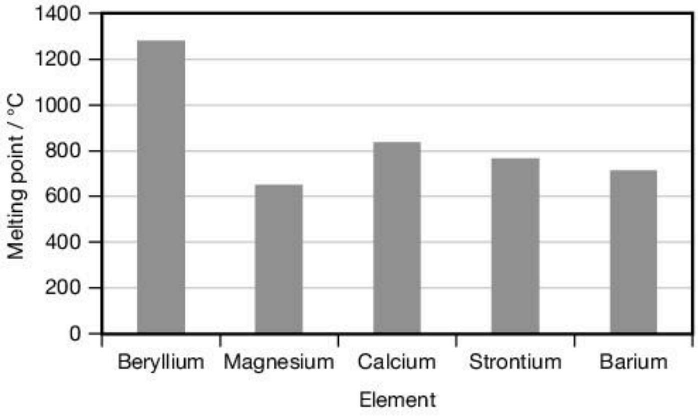
Key points

- ☐ Describe the reactions of the Group 2 elements with oxygen, water and dilute acids.
- ☐ Describe the reactions of the oxides, hydroxides and carbonates with water and dilute acids.
- ☐ Describe thermal decomposition reactions of nitrates and carbonates.
- ☐ Interpret and make predictions from patterns in physical and chemical properties.
- ☐ Describe patterns in solubility.
- ☐ Explain patterns in thermal decomposition reactions.
- ☐ Explain patterns in solubility.
- ☐ Describe and explain uses of calcium compounds in agriculture.

Physical properties of the Group 2 elements

The Group 2 elements have low melting and boiling points compared with those of the transition elements. This is because the delocalised s electrons in the metallic lattice are attracted only weakly to the nuclei of the metal ions.

Figure 10.1 shows the melting points of the Group 2 elements. Overall, the trend is that melting point decreases down the group. The melting point for magnesium does not fit the trend.



▲ **Figure 10.1** The melting points of Group 2 elements

Remember

A Group 2 element has two electrons in its outer shell, in an s orbital. The electronic configuration of magnesium, for example, is $1s^2 2s^2 2p^6 3s^2$. The two outer electrons are delocalised in the metal lattice.

Link

There is more about metallic structure and bonding in Unit 3 Chemical bonding, and Unit 4 States of matter.

Reactions of the Group 2 elements

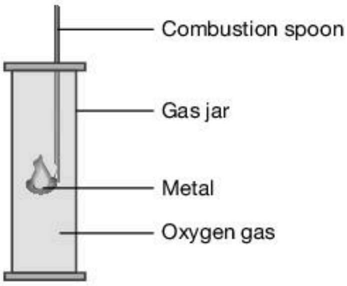
When Group 2 metals burn in oxygen, the products are oxides or peroxides:

- Mg and Ca make oxides, such as MgO.

  $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

- Sr and Ba make oxides and peroxides, such as BaO_2.

  $Ba(s) + O_2(g) \rightarrow BaO_2(s)$



Beryllium does not burn in oxygen, but tarnishes in air forming a layer of oxide on its surface.

The Group 2 elements react with water. The reactions get more vigorous going down the group: magnesium reacts only with water in the gas state as steam, the other Group 2 elements also react with liquid water.

$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

$$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$$

The Group 2 elements also react with dilute acids to give a salt and hydrogen gas. The reactions get more vigorous going down the group. For example, magnesium reacts with hydrochloric acid to make magnesium chloride and hydrogen gas:

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

Chemical tests

You can test for hydrogen by placing a lighted splint in a small sample of the gas. The splint goes out with a squeaky pop.

Remember

- Hydrochloric acid makes chloride salts.
- Nitric acid makes nitrate salts.
- Sulfuric acid makes sulfate salts.

Worked example

A student burns a freshly cut sample of calcium in air.

a) Describe what he would see.

b) Write an equation for the reaction.

c) Explain whether the calcium is oxidised or reduced in the reaction.

Answer

a) The silver-coloured calcium would burn with a red flame. A white solid would be made.

b) $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$

c) Calcium loses electrons, so it is oxidised: $Ca \rightarrow Ca^{2+} + 2e^-$

Exam tip

You need to be able to describe what you would see in the reactions of each Group 2 element with oxygen and air, water and dilute acids. Don't forget to include the appearance of the reactant and product.

The behaviour of Group 2 oxides and hydroxides in water

CaO, SrO and BaO react vigorously and exothermically with cold water. The products are hydroxides:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

MgO reacts slowly with cold water, and BeO does not react with water.

The hydroxides do not react with water. Their solubility increases down the group.

Link

There is more about exothermic and endothermic reactions in Unit 5, Chemical energetics.

Worked example

Table 10.1 shows the solubilities of the Group 2 hydroxides in water.

▼ **Table 10.1** Solubilities of Group 2 hydroxides

Compound	Solubility /mol per 100 g of water at 298 K
$Mg(OH)_2$	0.20×10^{-4}
$Ca(OH)_2$	15.3×10^{-4}
$Sr(OH)_2$	33.7×10^{-4}
$Ba(OH)_2$	150×10^{-4}

a) Describe the trend shown in Table 10.1.

b) Use data from the table to predict and explain the trend in pH when one spatula measure of each hydroxide is added to a test tube of distilled water.

Answer

a) Going down the group, the solubility of the hydroxides increases.

b) pH increases down the group because the concentration of dissolved OH^- increases with increasing solubility of the hydroxide.

The reactions of Group 2 compounds with dilute acids

Group 2 oxides, hydroxides and carbonates react with dilute nitric and hydrochloric acids to make salts. For example:

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

$$Ca(OH)_2(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$$

$$MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + CO_2(g) + H_2O(l)$$

The reactions with sulfuric acid produce small amounts of sulfates. Since most Group 2 sulfates are insoluble, they form precipitates which coat the surface of the solid reactant. The reaction then stops.

Worked example

A student adds Group 2 elements, and compounds of Group 2 elements, to dilute acids. Her observations are in the table.

Group 2 element or compound	Acid	Observations	Observation on bubbling gas produced through limewater	Observation on placing lighted splint in gas produced
X	A	white precipitate seen on surface of solid X	no change	no change
Y	B	bubbles vigorously	precipitate formed	no change
Z	C	bubbles vigorously	no change	squeaky pop

a) i) Which letter might represent magnesium? Explain your decision.

ii) Write an equation for the reaction of magnesium with dilute hydrochloric acid.

b) Which letter might represent calcium carbonate? Explain your decision.

c) Which letter might represent sulfuric acid? Explain your decision.

★ Exam tip

Exam questions often ask you to *explain* your answer. This means that you need to write down a reason for a decision or observation.

Answer

a) i) Z is magnesium. The metal reacts vigorously with the acid, and the squeaky pop shows that hydrogen gas is produced.

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

b) Y is calcium carbonate. It reacts vigorously with the acid, and the limewater test shows that carbon dioxide gas is produced.

c) A is sulfuric acid. It reacts with X to make a small amount of a sulfate, which forms a precipitate that coats the surface of X so that no more X can react.

Thermal decomposition reactions of nitrates and carbonates

All the Group 2 carbonates decompose on heating to make the metal oxide and carbon dioxide gas. For example:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

The Group 2 nitrates also decompose on heating. The products are the metal oxide, nitrogen dioxide and oxygen gas.

$$2Sr(NO_3)_2(s) \rightarrow 2SrO(s) + 4NO_2(g) + O_2(g)$$

Going down the group, you need to heat the carbonates and nitrates more strongly to make them decompose.

Remember

Group 2 nitrates decompose to make three products – a metal oxide, nitrogen dioxide and oxygen. Nitrogen dioxide gas is brown.

Remember

You can work out formulae from the charges on the ions. The total charge must be equal to zero.

Worked example

A student heats a sample of calcium compound in a hot Bunsen flame. A brown gas is produced.

a) Give the name and formula of the calcium compound.

b) Name the type of reaction that occurs when the compound is heated.

c) Write an equation for the reaction, including state symbols.

d) Describe how the student could test for the other gas (the one that is not brown) that is produced in the reaction.

Answer

a) calcium nitrate, $Ca(NO_3)_2$

b) thermal decomposition

c) $2Ca(NO_3)_2(s) \rightarrow 2CaO(s) + 4NO_2(g) + O_2(g)$

d) glowing splint relights

Explaining trends in thermal decomposition

The carbonates and nitrates of the Group 2 elements become more stable down the group.

As the metal ion, X^{2+}, gets bigger, its charge density decreases.

- An X^{2+} ion with a high charge density, such as Mg^{2+}, polarises the outer electrons in CO_3^{2-}. This distorts the CO_3^{2-} ion, making it less stable. This means that, on heating, the CO_3^{2-} ion decomposes to form a small O^{2-} ion which bonds strongly to X^{2+}.

- An X^{2+} ion with a low charge density, such as Ba^{2+}, polarises the outer electrons in CO_3^{2-} much less. This explains why $BaCO_3$ does not decompose on heating in a Bunsen flame.

Worked example

Explain why magnesium nitrate decomposes at a lower temperature than strontium nitrate.

Answer

The Mg^{2+} ion has a higher charge density than the bigger Sr^{2+} ion. This means that Mg^{2+} polarises and destabilises NO_3^- ions more than Sr^{2+} ions do. On heating, the NO_3^- ion in $Mg(NO_3)_2$ decomposes to form a small O^{2-} ion which bonds strongly to Mg^{2+}.

Sr^{2+} has a lower charge density than Mg^{2+}. It distorts the NO_3^- ion less, so the decomposition temperature of $Sr(NO_3)_2$ is higher than the decomposition temperature of $Mg(NO_3)_2$.

Exam tip

In any question that involves making comparisons, describe both situations and then explain the difference.

Solubility of hydroxides and sulfates

Table 10.1 shows that the Group 2 hydroxides become *more* soluble going down the group.

The trend for the sulfates is different. They become *less* soluble going down the group (see Table 10.2).

▼ **Table 10.2** Solubilities of Group 2 sulfates

Compound	Solubility /mol per 100 g of water at 298 K
$MgSO_4$	3600×10^{-4}
$CaSO_4$	11×10^{-4}
$SrSO_4$	0.62×10^{-4}
$BaSO_4$	0.009×10^{-4}

Explaining trends in solubility

Solubility is determined by the relative magnitude of

- lattice energy (the energy released when gaseous ions form a solid lattice)
- hydration energy (the energy released when gaseous ions are surrounded by water molecules).

The size of the X^{2+} ion affects both these energies. Going down the group, X^{2+} gets bigger. This makes both lattice energy and hydration energy get smaller and less negative.

- For sulfates, the change in hydration energies is *less* significant than the change in lattice energies. This is because the lattice energy values are relatively high because of the strong attraction between X^{2+} and SO_4^{2-} ions.
- For hydroxides, the change is hydration energies is *more* significant than the change in lattice energies. This is because the lattice energy values are relatively small owing to the single negative charge on the OH^- ion.

Using Group 2 compounds

Different crops thrive in soils of different pH. In agriculture, $Ca(OH)_2$ and $CaCO_3$ powders are used to increase soil pH, making it less acidic.

Raise your grade

1 This question is about the reactions of calcium and magnesium with water.

(a) A student adds a small sample of calcium to a large beaker of water.

(i) Describe what he would see as time progresses. [2]

Bubbles

The answer is correct, but more detail is required. The candidate should state that the reacting mixture bubbles vigorously. As the reaction continues, the piece of calcium will get smaller. The reaction will finish when all the calcium has been used up.

(ii) Write an equation for the reaction. [1]

$Ca + H_2O \rightarrow CaOH + H_2$ ✗

This answer is incorrect. The formula of the calcium ion is Ca^{2+} and the formula of the hydroxide ion is OH^-. This means that the formula of calcium hydroxide is $Ca(OH)_2$. The correct equation is $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

(iii) Write a half-equation to show that calcium is oxidised in the reaction. [1]

$Ca \rightarrow Ca^{2+} + 2e^-$ ✓

The candidate has given the correct equation, and shown that, in oxidation, each calcium atom loses two electrons to make a Ca^{2+} ion.

(iv) Use ideas about electronic configurations to explain why calcium is oxidised in many of its reactions. [2]

The electronic configuration of calcium is $1s^2 2s^2 2p^6 3s^2$. ✗ Calcium atoms achieve greater stability by losing the s^2 electrons resulting in an ion (Ca^{2+}) with a full outer shell. ✓

The candidate's explanation is correct and clear. However, she has given the electronic configuration for a magnesium atom instead of for a calcium atom. The electronic configuration of a calcium atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$.

(b) The student adds a small piece of magnesium ribbon to cold water.

(i) Describe what he would see. [1]

Vigorous bubbles. ✗

Calcium bubbles vigorously in cold water, but magnesium slowly forms very tiny bubbles.

(ii) Explain the difference in reactivity between magnesium and calcium. [4]

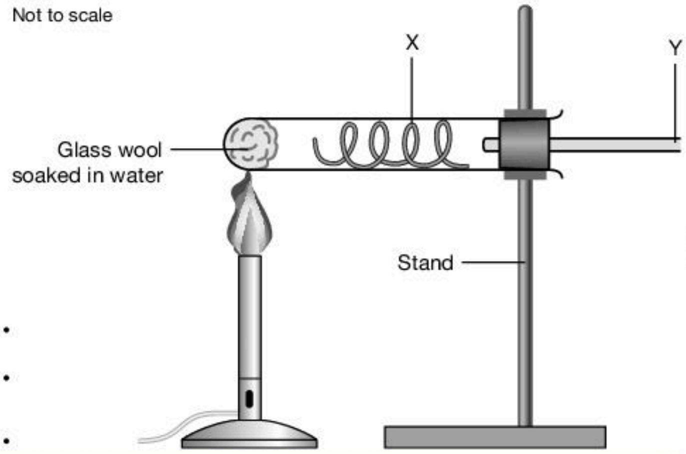
The outer electrons in magnesium are closer to the nucleus. ✓✗

The answer is correct so far, but incomplete. There are four marks available for the question, so greater detail is required. A complete answer would include these points:

- In most of their reactions, calcium and magnesium atoms lose/donate the two electrons from their outer s orbital.
- These electrons are more strongly attracted to the nucleus in magnesium than in calcium because they are nearer the nucleus in a magnesium atom…
- ... and because there is less shielding by inner electrons in a magnesium atom.
- For these reasons, the outer s electrons are more easily lost from the calcium atom than from the magnesium and so calcium is more reactive than magnesium.

(c) The student heats some magnesium ribbon with steam in the apparatus shown.

(i) Describe the appearance of the substances in the boiling tube at X before, during and after the reaction.



[3]

Before – silver coloured

metal strip ✔

During – bright white flame ✔

This answer is correct so far, but the answer is incomplete. The candidate needs to add that after the reaction a white powder is present at X.

(ii) Write an equation for the reaction of magnesium with steam. [1]

$Mg(s) + H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g)$ ✘

There are two errors in this equation. The first is that the water should be shown as being in the gas state: $H_2O(g)$

The second is that the reaction with steam forms MgO, not $Mg(OH)_2$. The correct equation is therefore: $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$

(iii) Write an equation for the reaction that occurs at Y. [1]

$H_2 + O_2 \rightarrow H_2O$ ✘

The candidate realises that the hydrogen formed burns at Y to make water, but the equation is not balanced. The equation for the reaction is: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

(d) The mass of the magnesium ribbon at the start of the reaction was 2.43 g.

(i) Calculate the change in mass of the boiling tube and its contents as a result of the reaction. Assume that water is present in excess, and that all the magnesium reacts. [4]

$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$

1 mol 1 mol 1 mol 1 mol ✔

2.43 g of magnesium is 2.43 g $\div$ 24.3 g mol^{-1} = 0.1 mol

So 0.1 mol of water is used.

This has a relative mass of

0.1 × 18 = 1.8 g ✔

So the change in mass is

2.43 − 1.8 = 0.63 g ✘

The candidate made a good start to this question, and achieved two marks by showing his working so far. To complete the question, the candidate needs to add:

Total mass of reactants, which are all in the boiling tube at the start, is:

$$2.43 + 1.8\ g = 4.23\ g$$

By the law of conservation of mass, the total mass of products = 4.23 g.

The MgO remains in the test tube. Its mass is $0.10 \times (24.3 + 16.0) = 4.03$ g.

The mass of hydrogen is therefore 4.23 g − 4.03 g = 0.20 g.

Since hydrogen is the only substance that leaves the boiling tube, the total mass decreases by 0.20 g.

(ii) Calculate the volume of the gas product of the reaction at room temperature and pressure. Assume that 1 mol of gas occupies 24.0 dm^3 under these conditions. [2]

1 mol of gas occupies 24 dm^3. ✔

So 0.1 mol occupies 0.1×24 dm^3 = 2.4 dm^3. ✔

This answer is correct and the candidate has shown all working clearly. It gains full marks.

Exam-style questions

Choose your answers to questions 1 and 2 by selecting on the basis of:

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

1 Which statements about Group 2 carbonates are correct? [1]

1 They react with dilute hydrochloric acid to make a salt and carbon dioxide only.

2 Barium carbonate decomposes on heating to make barium oxide and carbon dioxide.

3 Calcium carbonate is added to soil to increase its pH.

2 Which statements about the reactions of barium are correct? [1]

1 It reacts rapidly with cold water to make barium hydroxide and hydrogen gas.

2 It burns in excess oxygen to make barium peroxide and barium oxide.

3 It reacts with hydrochloric acid to make barium chloride and hydrogen.

3 Radium is a radioactive element at the bottom of Group 2.

(a) A scientist adds a small piece of radium to water.

(i) Predict what the scientist would see. [1]

(ii) Give a reason for your prediction. [1]

(b) A scientist heats a small piece of radium in air.

(i) Predict the two products formed. [1]

(ii) Write two equations, each showing the formation of one of the products named in part **i**. [2]

(c) Predict whether radium hydroxide is more or less soluble in water than barium hydroxide. Give a reason for your prediction. [1]

4 This question is about calcium and strontium and their compounds.

(a) Write the electron configuration of Ca^{2+}. [1]

(b) Explain why the radius of Ca^{2+} is smaller than the radius of Ca. [1]

(c) Explain why the radius of Sr is bigger than the radius of Ca. [1]

(d) Calcium reacts with chlorine.

Draw a dot-and-cross diagram to show the electron transfer that occurs. [1]

(e) Write balanced equations for the following reactions:

(i) strontium and water [1]

(ii) strontium oxide and dilute hydrochloric acid [1]

(iii) strontium carbonate and dilute nitric acid. [1]

5 A student heats 3.28 g of anhydrous calcium nitrate strongly in a test tube.

(a) Describe what the student would see. [1]

(b) Describe how the student could test for one of the gases produced. [1]

(c) Write an equation for the reaction, including state symbols. [1]

(d) Assume that all the calcium nitrate reacted.

(i) Calculate the mass of solid product remaining in the test tube. [3]

(ii) Calculate the total volume of gaseous products produced at room temperature and pressure. Assume that 1 mol of gas occupies 24.0 dm^3 under these conditions. [3]

(e) The student then heated a sample of barium nitrate in a test tube.

Describe and explain how the reaction is similar to, and different from, the reaction that occurs on heating calcium nitrate. [3]

11 Group 17

AS 11.1–11.9 pages 215–228

Key points

- ☐ Describe and explain the physical properties of the halogens.
- ☐ Describe and explain the reactions of the halogens and their hydrides.
- ☐ Describe and explain the reactions of the halide ions.
- ☐ Describe and explain the reactions of chlorine with sodium hydroxide.
- ☐ State and explain some uses of the halogens and their compounds.

Physical properties of the elements

The Group 17 elements exist as diatomic molecules, such as Cl_2. Table 11.1 shows their colours and states at room temperature.

▼ **Table 11.1** Colours and states of the halogens

Element	Colour and state at room temperature	Boiling point /°C
Fluorine	yellow gas	−188
Chlorine	pale green gas	−35
Bromine	red-brown liquid	59
Iodine	shiny dark grey solid	183

Common error

Some candidates explain the boiling point trend in terms of molecular mass or size. Make sure you learn the full explanation.

Volatility decreases down the group. This is because, going down the group:

- the number of electrons increases
- the magnitude of instantaneous and induced dipoles increases
- van der Waals forces become stronger
- more energy is needed to overcome the intermolecular forces
- boiling point increases.

Link

There is more about van der Waals forces in Unit 3, Chemical bonding.

Chemical properties of the elements

The elements often act as oxidising agents. In these reactions each halogen atom gains one electron to form a halide ion. Fluorine is the strongest oxidising agent because it has the strongest tendency to gain an electron.

Remember

OIL RIG – oxidation **i**s **l**oss (of electrons) and **r**eduction **i**s **g**ain. So an oxidising agent removes electrons and a reducing agent donates electrons.

Worked example

Use your knowledge of electron configurations to explain why the Group 17 elements act as oxidising agents.

Answer

Halogen atoms have 7 electrons in their outer valence shell. For example, the electronic configuration of fluorine is $1s^22s^22p^5$. When a halogen acts as an oxidising agent, its atoms each gain one electron. This gives a stable electron configuration such as $1s^22s^22p^6$.

Chemical properties of the halogen hydrides

The halogens react with hydrogen to form hydrides, for example:

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

The reactions get less vigorous going down the group:

- Fluorine reacts explosively with hydrogen in the cold.
- Chlorine and hydrogen explode in the presence of sunlight or a flame.
- Bromine vapour and hydrogen react with a gentle explosion.
- Iodine and hydrogen react partially to establish an equilibrium:

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

The relative thermal stabilities of the hydrogen halides change down the group, as shown in Table 11.2.

▼ **Table 11.2** Thermal stabilities of hydrogen halides

Compound	Observations on placing a hot glass rod in a sample of the compound
HF	no change
HCl	no change
HBr	traces of red-brown gas
HI	large amounts of violet gas formed

Worked example

a) Write an equation to show the thermal decomposition reaction of HI.

b) Describe the trend in heat stability of the halogen hydrides.

c) Use data from Table 11.3 to explain the trend you described in part **b**.

▼ **Table 11.3** Bond energies of the halogens

Compound	Bond energy/kJ mol^{-1}
HF	562
HCl	431
HBr	366
HI	299

Answer

a) $2HI(g) \rightarrow H_2(g) + I_2(g)$

b) Going down the group, the halogen hydrides become less stable.

c) Since the H–X bond energy decreases down the group, the energy needed to break the H–X bond decreases. This means that activation energies and thus stability decrease down the group.

Chemical tests

Reactions of the halide ions

You can use silver nitrate solution to test for halide ions.

- Pour around 1 cm^3 of the halide solution into a test tube.
- Add a few drops of dilute nitric acid solution.
- Add two or three drops of aqueous silver nitrate and note your observations.
- Add around 1 cm^3 of aqueous ammonia.

Table 11.4 shows how to interpret the results.

▼ **Table 11.4** Testing for the halides

Solution	Observation on adding dilute silver nitrate solution	Observation on adding dilute ammonia solution
NaCl	white precipitate	precipitate dissolves
NaBr	cream precipitate	precipitate partially dissolves
NaI	yellow precipitate	precipitate does not dissolve

The equations below summarise the reactions for chloride ions:

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

$$AgCl(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

Worked example

A few drops of acidified silver nitrate solution are added to a solution of a potassium halide. A yellow precipitate forms.

a) Give the name and formula of the halide ion in the solution.

b) Write an ionic equation for the reaction that occurs when silver nitrate is added.

c) Describe and explain how you could use ammonia solution to confirm the identity of the halide.

Answer

a) Iodide, I^-

b) $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

c) Add ammonia solution to the precipitate. The precipitate does not dissolve, confirming that the salt is an iodide.

★ **Exam tip**

It is usually best to give the ionic equation to show the formation of precipitates.

✗ **Common error**

Students often name halide ions incorrectly:

Cl^- is a chloride ion, not a chlorine ion.

Br^- is a bromide ion, not a bromine ion.

Table 11.5 summarises how solid halides react with concentrated sulfuric acid.

▼ **Table 11.5** Reactions of halides with concentrated sulfuric acid

Halide	Reaction on adding concentrated H_2SO_4
NaF	HF made
NaCl	HCl made
NaBr	HBr made first, then red-brown $Br_2(g)$, SO_2 and H_2O
NaI	HI made first, then purple $I_2(g)$, SO_2 and H_2O

All the solid halides react to make hydrogen halide gases, for example:

$$Cl^-(s) + H_2SO_4(l) \rightarrow HCl(g) + HSO_4^-(s)$$

HCl and HF do not react further. However, concentrated sulfuric acid oxidises HBr and HI to form the elements, for example:

$$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(g) + 2H_2O(l) + SO_2(g)$$

The reactions of chlorine with sodium hydroxide

Chlorine reacts with dilute sodium hydroxide solution at 15 °C to form a mixture of chloride and chlorate(I) ions:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + OCl^-(aq) + H_2O(l)$$

At 70 °C, the chlorate(I) ion then decomposes to make chloride and chlorate(V) ions:

$$3OCl^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-(aq)$$

Worked example

Use oxidation numbers to show that chlorine is both oxidised and reduced in the reaction shown by the equation below:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + OCl^-(aq) + H_2O(l)$$

Answer

Cl_2 is oxidised to OCl^-, since the oxidation number changes from 0 to +1.

Cl_2 is reduced to Cl^-, since the oxidation number changes from 0 to −1.

Exam tip

Make sure you learn the products of the reactions, and practise balancing the equations.

Remember

The I in chlorate(I) and the V in chlorate(V) give the oxidation number of chlorine in the ions.

Common error

Some students get these two reactions confused. Make sure you learn the products of the reactions with cold dilute NaOH, and with hot concentrated NaOH.

Uses of the halogens and their compounds

Small amounts of chlorine make water safe to drink. Chlorine reacts with water to make a mixture of chloric(I) acid, HClO, and hydrochloric acid, HCl:

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HClO(aq) + HCl(aq)$$

Chloric(I) acid molecules pass through bacteria cell walls. Inside the cell, they oxidise molecules involved in the cell's metabolism. This kills the organism.

The halogens and their compounds have many other uses, some of which are shown in Table 11.6.

▼ **Table 11.6** Uses of halogens and their compounds

Substance	Uses
Bleach (mixture of NaCl and NaOCl, made by reacting Cl_2 with cold, dilute NaOH)	• killing bacteria • cleaning • bleaching paper to make it white
PVC (polyvinyl chloride), a polymer	• pipes • flooring • electric cable covering
Halogenated hydrocarbons	• solvents • refrigerants • aerosols

Link

There is more about the uses of chlorine compounds in Unit 16, Halogen derivatives.

Raise your grade

1 The halogens are reactive non-metal elements.

(a) All the halogens form halides.

(i) Give the formula of sodium bromide. [1]

NaBr ✔

(ii) Describe the trend in the reactivities of sodium halides with concentrated sulfuric acid. Include the names of the halogen-containing compounds formed. [2]

Going down the group they get more reactive. ✔✘

This answer is incomplete. Since the question has two marks, more detail is required. The candidate needs to add that the acid reacts with sodium fluoride to make hydrogen fluoride, and with sodium chloride to make hydrogen chloride. He also needs to point out that the reactions with NaBr and NaI produce both the hydrogen halide and the elements.

(iii) Write equations and use them to help you to explain how potassium bromide, KBr, reacts with concentrated sulfuric acid to make an acidic gas and a red-brown gas. [3]

$KBr(s) + H_2SO_4(l) \rightarrow HBr(g) + KHSO_4(s)$ ✔

$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(g) + SO_2(g)$ ✘

The candidate has correctly given the first equation, showing that the acid reacts with KBr to make HBr. He then needs to add that the HBr formed in this reaction is oxidised by H_2SO_4 to make Br_2, and give the correct equation for this reaction:

$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(g) + 2H_2O(l) + SO_2(g)$

(iv) Explain why the red-brown substance is formed as a gas, not as a liquid. [2]

The red-brown substance is bromine. You might expect it to form as a liquid, since bromine is liquid at room temperature. ✔✘

The candidate has made a good start to his answer. However, he needs to add an explanation for the bromine being in the gas state. The explanation is that the reaction with sulfuric acid is exothermic. Some of the energy transferred during the reaction is used to heat up the products, including bromine. This results in bromine being formed in the gas state.

(b) The halogens have different colours, and exist in different states at room temperature.

(i) A halogen has a melting point of –7 °C and a boiling point of 59 °C.

What is its state and colour at room temperature? [2]

Liquid state ✔ purple. ✘

The candidate has correctly used the melting and boiling point data to deduce that the halogen is in the liquid state. The halogen that is in the liquid state at room temperature is Br_2, which is red-brown.

(ii) The table shows enthalpy of vaporisation data for the Group 17 elements.

Halogen	**Enthalpy of vaporisation /kJ mol^{-1}**
Fluorine	+3.3
Chlorine	10
Bromine	+15
Iodine	+30

Describe the trend shown in the table. [1]

It gets bigger. ✗

This explanation is inadequate. The candidate needs to point out that the enthalpy of vaporisation increases (or gets more endothermic) *down the group*.

(iii) Explain this trend. [3]

It is because the van der Waals forces get stronger down the group. ✓✗✗

The candidate has made a good start to this question. He needs to add an explanation for the increasing strength of the van der Waals forces, as given below.

Going down the group, the number of electrons in the halogen molecule increases. This results in larger instantaneous and induced dipoles, which results in stronger van der Waals forces between the molecules. The greater these intermolecular forces, the greater the energy required to overcome them, and the higher the enthalpy of vaporisation.

(c) A student has samples of KCl and KBr. He does not know which is which.

Describe and explain how the student could use chemical reactions to identify the salts. Describe the tests the student should do, and give the expected results. Include equations in your answer. [4]

Make solutions of KCl and KBr, and add silver nitrate solution. ✓ One goes white and the other is cream.

The candidate has started his answer correctly. He needs to add that KCl makes a white precipitate with acidified silver nitrate solution, and KBr makes a cream precipitate with the solution. This part of the answer needs an ionic equation, to show the formation of the precipitates:

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

The candidate needs to add that aqueous ammonia solution can be added to the precipitates to confirm their identity. The AgCl precipitate dissolves, but the AgBr precipitate dissolves only partly. Again, including an equation completes this part of the answer.

$$AgCl(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

Exam-style questions

Choose your answers to questions 1–3 by selecting on the basis of:

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

1 Which statements help to explain the change in boiling point down Group 17? [1]

 1 The number of electrons in the halogen molecule increases.

 2 Instantaneous and induced dipoles become stronger.

 3 The bond energy of the covalent bond in the halogen molecule decreases.

2 Which products are formed when chlorine reacts with cold aqueous sodium hydroxide solution? [1]

 1 water

 2 sodium chloride

 3 sodium chlorate(V)

3 Which statements help to explain how chlorine makes water safe to drink?

 1 Chlorine reacts with water to make chloric(V) acid.

 2 Chloric(I) acid molecules can pass through bacteria cell walls.

 3 Chloric(I) acid molecules oxidise molecules involved in cell metabolism.

4 The table shows melting point data for the halogens.

Halogen	Melting point /°C
Fluorine	−220
Chlorine	−102
Bromine	−7
Iodine	114

(a) Describe the trend shown in the table. [1]

(b) Describe in detail all the bonding in a solid halogen. [3]

(c) Use your answer to part **(b)** to help you to explain the trend in the table. [4]

5 The halogens have similar electron configurations.

(a) Give the electron configurations of the valence shells of chlorine and bromine. [2]

(b) The halogens are oxidising agents.

 (i) Write an equation for a reaction in which chlorine acts as an oxidising agent. [1]

 (ii) Explain why chlorine is a stronger oxidising agent than bromine. [1]

6 The halogens react with hydrogen.

(a) Fluorine reacts explosively with hydrogen.

 (i) Write an equation for the reaction. [1]

 (ii) Describe one property of the product formed. [1]

(b) Bromine does not react with hydrogen at room temperature.

 (i) State the conditions required for bromine to react with hydrogen. [1]

 (ii) Use data from the table to explain why the reaction of fluorine with hydrogen is more vigorous than the reaction of bromine with hydrogen, and why the reaction with fluorine is more exothermic. [4]

Bond	Bond energy /kJ mol^{-1}
F—F	158
Br—Br	198
H—F	562
H—Br	366

12 Transition elements

A 25.1–25.16 pages 461–483

Key points

☐ State what transition elements are

☐ State the electronic configurations of the first-row transition elements and ions

☐ Compare the properties of transition elements with calcium

☐ Predict oxidation states

☐ Describe and explain reactions of transition metals with ligands to form complexes

☐ Describe the shapes of complexes

☐ Predict the formula and charge of a complex ion

☐ Describe and explain ligand exchange

☐ Describe and explain the use of redox systems

☐ Predict the likelihood of redox reactions

☐ Explain why complexes are coloured

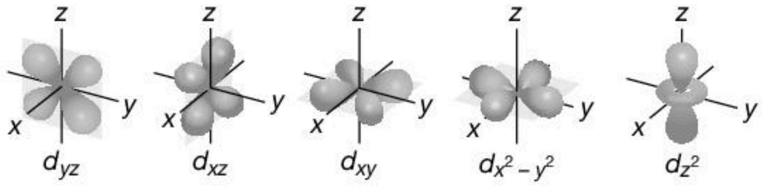
☐ Describe stereoisomerism in complexes

☐ Describe the use of cisplatin

☐ Use and interpret stability constants.

Electronic configurations of transition elements

Transition element atoms include electrons in d orbitals. There are five d orbitals, shown in Figure 12.1.



▲ **Figure 12.1** The five d orbitals

Key term

Transition element: an element that forms one or more stable ions with incomplete d orbitals.

★ Exam tip

To work out the electronic configuration of a d-block element ion, follow the steps below. This method gives the correct answer for all oxidation states.

1 Write down the electronic configuration for the atom.

2 Place all the 4s electrons into 3d orbitals, if 3d orbitals are available.

3 Check the charge on the ion, and remove the correct number of electrons.

Table 12.1 shows the electronic configurations of some d-block elements and their common ions.

▼ **Table 12.1** Electronic configurations of some d-block elements

Element	Symbol	Electronic configuration of atom	Common ion	Electronic configuration of ion
Scandium	Sc	$[\mathrm{Ar}]3d^{1}4s^{2}$	Sc^{3+}	$[\mathrm{Ar}]$
Titanium	Ti	$[\mathrm{Ar}]3d^{2}4s^{2}$	Ti^{3+} Ti^{4+}	$[\mathrm{Ar}]3d^{1}$ $[\mathrm{Ar}]$
Vanadium	V		V^{3+}	$[\mathrm{Ar}]3d^{2}$
Chromium	Cr	$[\mathrm{Ar}]3d^{5}4s^{1}$	Cr^{3+}	
Manganese	Mn	$[\mathrm{Ar}]3d^{5}4s^{2}$	Mn^{2+}	$[\mathrm{Ar}]3d^{5}$
Iron	Fe		Fe^{2+} Fe^{3+}	$[\mathrm{Ar}]3d^{6}$ $[\mathrm{Ar}]3d^{5}$
Cobalt	Co	$[\mathrm{Ar}]3d^{7}4s^{2}$	Co^{2+}	
Nickel	Ni	$[\mathrm{Ar}]3d^{8}4s^{2}$		$[\mathrm{Ar}]3d^{8}$
Copper	Cu		Cu^{+} Cu^{2+}	$[\mathrm{Ar}]3d^{10}$
Zinc	Zn	$[\mathrm{Ar}]3d^{10}4s^{2}$	Zn^{2+}	$[\mathrm{Ar}]3d^{10}$

✗ **Common error**

Not all d-block elements are transition elements. A transition element forms ions with incomplete d orbitals.

Worked example

Write down the electronic configurations and formulae of ions that are missing from Table 12.1. Then explain why zinc is not a transition element.

Answer

V is $[\mathrm{Ar}]3d^{3}4s^{2}$

Cr^{3+} is $[\mathrm{Ar}]3d^{3}$

Fe is $[\mathrm{Ar}]3d^{6}4s^{2}$

Co^{2+} is $[\mathrm{Ar}]3d^{7}$

The ion of nickel with the electronic configuration shown is Ni^{2+}

Cu is $[\mathrm{Ar}]3d^{10}4s^{1}$

Cu^{2+} is $[\mathrm{Ar}]3d^{9}$

Zinc is not a transition element because its ion does not have incomplete d orbitals. All the d orbitals in Zn^{2+} ion are filled.

In general, transition elements have higher melting points and densities than calcium, which is a typical s-block element.

Transition elements form compounds with more than one oxidation state. For example, compounds of manganese include MnO, $MnCl_3$, MnO_2, K_2MnO_4, $KMnO_4$.

All the transition elements from titanium to copper show the +2 oxidation state. The maximum oxidation state for most transition elements is equal to:

the number of 4s electrons + the number of unpaired 3d electrons

Worked example

a) Give the oxidation numbers of manganese in the manganese compounds listed above.

b) From which orbitals are electrons lost in the formation of Mn^{2+} and Cu^{2+} ions?

Answer

a) MnO +2 $MnCl_3$ +3 MnO_2 +4

K_2MnO_4 +6 $KMnO_4$ +7

b) The two 4s electrons are lost in the formation of Mn^{2+} ions.

In the formation of Cu^{2+}, one 4s and one 3d electron are lost.

Remember

The oxidation state of oxygen is usually −2 and the oxidation number of chlorine is usually −1. The oxidation state of Group 1 metals, such as potassium, is always +1.

Complexes

Ligands, shapes and formulae

Transition elements form **complexes** with molecules or ions, for example $[(Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$.

Water molecules and chloride ions are monodentate **ligands** since they form just one dative bond with the central positive ion. Bidentate ions form two dative bonds to the central cation, and polydentate ions form more than two dative bonds. The number of dative bonds is given by the **co-ordination number**.

Key terms

Complex: a molecule or ion formed by a central atom or ion, surrounded by one or more ligands.

Ligand: a species in a complex ion that contains a lone pair of electrons forming a dative bond to a central metal atom or ion.

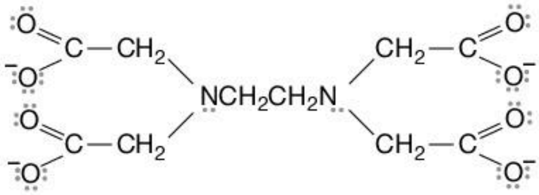
Co-ordination number: the co-ordination number of a metal ion in a complex is the number of dative bonds it forms with ligands.

Worked example

State whether each of the ligands below is monodentate, bidentate or polydentate.

a) $:NH_3$

b) EDTA



c) 1,2-diaminoethane

$H_2\underset{\cdot\cdot}{N}CH_2CH_2\underset{\cdot\cdot}{N}H_2$

Answer

a) monodentate

b) polydentate

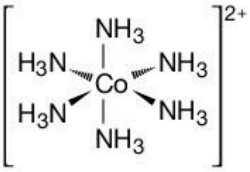
c) bidentate

Transition metal complexes have different shapes. They can be linear, octahedral, tetrahedral or square planar.

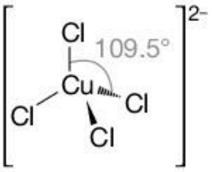
Worked example

Give the formula and shape of the complex ions shown below. Then state the co-ordination numbers of the central metal ion.

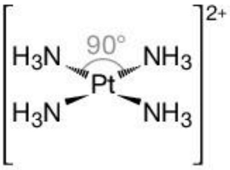
a)



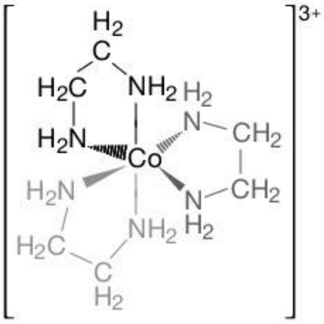
b)



c)



d)



Answer

a) $[Co(NH_3)_6]^{2+}$, octahedral. The co-ordination number is 6.

b) $[CuCl_4]^{2-}$, tetrahedral. The co-ordination number is 4.

c) $[Pt(NH_3)_4]^{2+}$, square planar. The co-ordination number is 4.

d) $[Co(NH_2CH_2CH_2NH_2)_3]^{3+}$, octahedral. The co-ordination number is 6.

Common error

Some candidates think that co-ordination number is equal to the number of molecules or ions around the central metal ion. The co-ordination number is actually the number of bonds the central ion forms with ligands. The two numbers are often, but not always, the same.

Remember

Most complexes with a co-ordination number of 4 have a tetrahedral arrangement of ligands. A few complexes with a co-ordination number of 4 are square planar.

Ligand exchange

In ligand exchange reactions, one ligand in a compound is replaced by another ligand.

For example, $[Cu(H_2O)_6]^{2+}$ is a pale blue solution. Adding a few drops of ammonia solution forms a pale blue precipitate of copper(II) hydroxide, $Cu(OH)_2$. Adding excess ammonia solution results in a dark blue solution, $[Cu(NH_3)_4(H_2O)_2]^{2+}$. The overall reaction is:

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

Worked example

Explain why adding excess concentrated hydrochloric acid to a pale blue solution containing $[Cu(H_2O)_6]^{2+}$ forms a green solution followed by a yellow solution. Include an equation in your answer.

Answer

There is a ligand exchange reaction, in which the six water ligands around the copper are replaced by four chloride ions to form the complex ion $[CuCl_4]^{2-}(aq)$:

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

The $[CuCl_4]^{2-}$ ion is yellow. The green solution contains a mixture of $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$ ions.

Redox systems

Ions of transition elements are involved in many redox systems.

Worked example

A solution containing Fe^{2+} was oxidised to Fe^{3+} by acidified $KMnO_4$ solution. A separate solution containing Fe^{2+} was then oxidised by acidified $Cr_2O_7^{2-}$. Give equations for both reactions.

Answer

The data booklet gives these half-equations for the first reaction:

1 $Fe^{3+} + e^- \rightarrow Fe^{2+}$

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

Reversing the direction of Equation 1 and multiplying by 5, then adding the two equations, gives the overall equation:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

The half-equations for the second reaction are:

1 $Fe^{3+} + e^- \rightarrow Fe^{2+}$

2 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Reversing the direction of Equation 1 and multiplying by 6, then adding the two equations, gives the overall equation:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

Exam tip

You do not need to remember these half-equations – they are given in the data booklet.

Exam tip

When you have written an equation by combining half-equations, check that the charges are balanced.

You can use electrode potential values to predict the likelihood of a redox reaction.

Worked example

Use electrode potential values to show that the equation in the first worked example above is likely to occur.

Answer

From the data booklet, the electrode potential values are:

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

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^\ominus = +1.52\,V$$

Drawing in curved arrows, then adding the values of $E^\ominus$ in the direction of the arrows gives:

$$+0.77\,V + +1.52\,V = +2.29\,V$$

The value of $E^\ominus$ for the overall equation is positive, so the reaction is likely to occur.

Remember

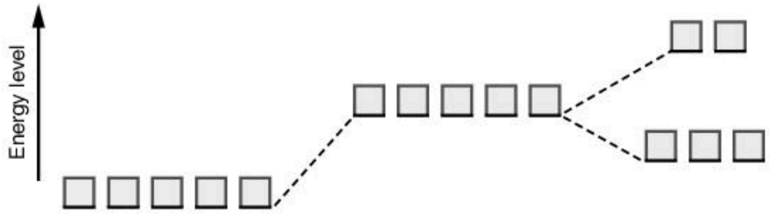
The equilibrium with the more positive electrode potential goes in the forward direction.

Link

Unit 6, Electrochemistry, shows how to use standard electrode potential values in calculations.

Colours of complexes

Transition metal complexes are coloured. This is because, in tetrahedral and octahedral complexes, the d orbitals split into two energy levels. The energy levels are **non-degenerate**.



(a) Five d orbitals in an isolated gaseous ion – degenerate orbitals

(b) Five d orbitals in an ion in a uniform electric field – degenerate orbitals

(c) Five d orbitals in an octahedral complex ion – non-degenerate orbitals

▲ **Figure 12.2** The effect of ligands on the energy levels of the five 3d orbitals of the central metal cation

Electrons in a complex move from a lower energy d orbital to a higher energy d orbital when they absorb the correct amount of energy from white light. That energy corresponds to light of a given frequency and colour. The colour seen is the colour of the light transmitted through the solution – it is white light without the light that has been absorbed by the electrons.

The energy gap in the d orbitals depends on the metal ion and its charge, as well as the ligand. For example, the energy gap between the two sets of d orbitals is bigger in $[Cu(NH_3)_4(H_2O)_2]^{2+}$ than in $[Cu(H_2O)_6]^{2+}$. This explains why the ammonia-containing complex is darker blue.

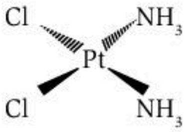
Stereoisomers in transition metal complexes

Complexes show two types of isomerism:

- **cis–trans isomerism**
- **optical isomerism**

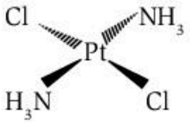
Worked example

State whether the formula below shows cis-platin or trans-platin. Explain your answer. Then draw the structure of the other isomer.



Answer

The formula shows cis-platin, since the two chloride ions are both on the same side of the central metal atom. Trans-platin has its ligands arranged like this, with the chloride ions opposite each other.



Cisplatin is an anti-cancer drug. It binds to DNA in cancer cells, which prevents them dividing.

Key term

Non-degenerate orbitals: orbitals at different energy levels.

Key terms

Isomers: compounds with the same molecular formula but different arrangements of atoms in space

Cis–trans isomers: pairs of square planar complexes with the same ligands arranged differently about the central ion.

Optical isomers: pairs of mirror-image complexes. The two isomers rotate plane-polarised light in opposite directions.

Link

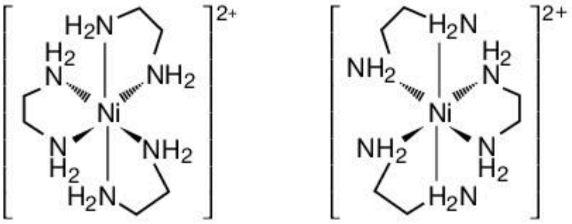
Cis–trans isomerism and optical isomerism in organic compounds are described in Unit 14, An introduction to organic chemistry.

If a complex ion has no plane of symmetry, it shows optical isomerism. Complexes that show optical isomerism occur in octahedral complexes with bidentate ligands. An example is shown below. This isomer rotates plane-polarised light in one direction. Its mirror image rotates plane-polarised light in the opposite direction.

Worked example

Draw the optical isomer of the complex ion shown below (left).

Answer



Stability constants

A ligand exchange reaction is an equilibrium reaction, so an equilibrium expression can be written for it. The equilibrium constant for a ligand exchange reaction is the **stability constant, K_{stab}**. The greater the value of K_{stab}, the more stable the complex ion.

Key term

Stability constant, K_{stab}, of a complex ion: the equilibrium constant for the formation of the complex ion in a solvent from its ions or molecules.

Exam tip

In stability constant expressions, the square brackets represent concentration. The charges on complex ions are written inside the square brackets.

Worked example

Write an expression for K_{stab} for the ligand exchange reaction below:

$[Ni(H_2O)_6]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Ni(NH_3)(H_2O)_5]^{2+}(aq) + H_2O(l)$

Answer

$$K_{stab} = \frac{Ni(NH_3)(H_2O)_5^{2+}}{Ni(H_2O)_6^{2+}\ [NH_3]}$$

Worked example

The values of K_{stab} for two ligand exchange equilibria are given below. Compare the two values and explain their significance.

$[Ni(H_2O)_6]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Ni(NH_3)(H_2O)_5]^{2+}(aq) + H_2O(l) \qquad K_{stab} = 630$

$[Ni(NH_3)_2(H_2O)_4]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Ni(NH_3)_3(H_2O)_3]^{2+}(aq) + H_2O(l) \qquad K_{stab} = 53.7$

Answer

The value for the first ligand exchange equilibrium is more than 10 times greater than that for the second equilibrium. This shows that the position of the equilibrium is more in favour of the products for the first reaction than for the second reaction. In both cases, the complex ion on the right is more stable than the complex ion on the left.

Remember

The concentration of water is not usually included in K_{stab} expressions because the reaction takes place in aqueous solution.

Raise your grade

1 Carboplatin is a drug used to treat cancer. The drug includes the transition element platinum. Its formula is $C_6H_{12}N_2O_4Pt$.

(a) (i) Define the term *transition element*. [1]

A transition element has outer electrons in d orbitals. ✗

This definition is incorrect. A transition element is an element in the d-block of the periodic table that forms one or more stable ions with incomplete d orbitals.

★ Exam tip

Learn definitions carefully.

(ii) Predict how the melting point and density of platinum compare to the melting point and density of calcium. [2]

They are higher. ✗

It is not clear what the candidate means. The correct answer is that both melting point and density are higher for platinum than for calcium.

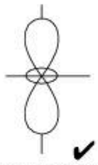
(iii) The outer electrons in a platinum atom are in 5d and 6s orbitals, with the arrangement $5d^9 6s^1$.

Predict the arrangement of the outer electrons in the Pt^{2+} ion. [1]

$5d^7 6s^1$ ✗

This answer is incorrect. Remember, to find the electronic configuration of a transition metal ion, start by placing all the electrons in the atom in the d orbitals (if enough d orbitals are available). Then remove the required number of electrons. This gives the correct answer, $5d^8$.

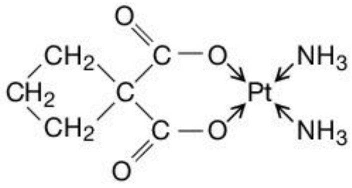
(iv) Sketch two d orbitals with different shapes.



✔

The candidate has correctly drawn the shape of one type of d orbital, but did not draw the shape of the other type. This is shown below.

(b) Carboplatin is a complex. Its structure is shown below. The complex has no overall charge.



(i) Write down the molecular formulae of the two different types of ligand in carboplatin, including their charge if appropriate. [2]

$C_6H_4O_4^{2-}$ ✗ and NH_3 ✔

The candidate has not counted all the hydrogen atoms in the ion shown on the left above. The formula should be $C_6H_6O_4^{2-}$.

(ii) Deduce the charge on the platinum ion in carboplatin. Explain your deduction. [2]

+2 ✓ ✗

The answer is correct, but does not give an explanation for the deduction. The candidate needs to add that the $C_6H_6O_2$ species is an ion with a charge of –2. The NH_3 molecules have no charge. Since there is no overall charge on the complex, the charge on the platinum ion must be +2.

(iii) Define the term *ligand*. [1]

A ligand is a species that contains a lone pair of electrons. ✗

This answer is correct so far, but the candidate needs to add that the lone pair of electrons forms a dative bond to a central metal atom or ion.

(iv) For each ligand in part **(iii)**, state whether it is monodentate, bidentate or polydentate. [2]

NH_3 is monodentate. ✓

$C_6H_6O_2^{2-}$ is bidentate. ✓

(v) Give the co-ordination number of platinum in carboplatin. [1]

3 ✗

The co-ordination number is 4. The co-ordination number is the number of dative bonds the central ion forms with ligands, not the number of ligands.

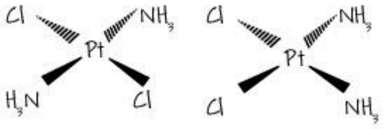
(vi) Describe the shape of the carboplatin complex ion with respect to platinum. [1]

tetrahedral. ✗

In fact the shape is square planar; most complexes of platinum are this shape.

(c) Another cancer drug is cisplatin, $Pt(NH_3)_2Cl_2$.

(i) Draw and name the structures of cisplatin and transplatin. [2]



cisplatin ✗ trans-platin ✗

The candidate has got these answers the wrong way round. Like ligands are next to each other in cis-isomers, and opposite each other in trans-isomers.

(ii) Describe one difference and one similarity between cisplatin and carboplatin. [2]

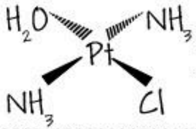
They are similar because they both have two ammonia molecule ligands.

They are different because carboplatin includes a bidentate ligand and cisplatin does not. ✓✓

This answer is perfect. In identifying the difference, the candidate has described how the situation is different in carboplatin and cisplatin.

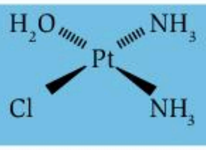
(d) In the body, cisplatin forms *cis*-$[PtCl(NH_3)_2(H_2O)]^+$. In cancer cells, the water ligand is displaced by bases in DNA.

(i) Predict the structure of *cis*-$[PtCl(NH_3)_2(H_2O)]^+$. [1]



✗

This answer is incorrect. Remember, in a cis-isomer, the two like ligands are next to each other, not opposite each other. One correct answer is shown below.



(ii) Explain why the charge of *cis*-$[PtCl(NH_3)_2(H_2O)]^+$ is +1. [1]

The complex contains one Pt^{2+} ion and one Cl^- ion.

The answer is correct so far, but the candidate needs to add that the other ligands (two ammonia molecules and one water molecule) are neutral.

(iii) Write an equilibrium expression for the formation of *cis*-$[PtCl(NH_3)_2(H_2O)]^+$ as a result of ligand exchange. [1]

$[PtCl_2(NH_3)_2] \rightleftharpoons [PtCl(NH_3)_2(H_2O)]^+ + Cl^-$ ✗

This equilibrium expression is almost correct, but it is not balanced. There should be a water molecule shown on the left of the ⇌ symbol. The correct expression is:

$$[PtCl_2(NH_3)_2]\,(aq) + H_2O\,(l) \rightleftharpoons [PtCl(NH_3)_2(H_2O)]^+(aq) + Cl^-\,(aq)$$

Notice that the correct expression also includes state symbols.

(iv) Define the term *stability constant*. [1]

Stability constant is the equilibrium constant for the formation of a complex ion. ✓

(v) Deduce an expression for the stability constant of the ligand substitution in **(iii)**. [1]

$$K_{stab} = \frac{PtCl(NH_3)_2(H_2O)^+ \quad Cl^-}{PtCl_2(NH_3)_2}$$ ✓

Exam-style questions

1 This question is about vanadium and its compounds. Vanadium is a transition element.

(a) Define the term *transition element*. [1]

(b) State the electronic configuration of the following species:

(i) V [1]

(ii) V^{3+} [1]

(c) Use your answer to part **(a)** to predict a common oxidation state of vanadium in its compounds, other than +3. Explain your prediction. [1]

(d) In acidic conditions, VO_2^+ takes part in the electrode reaction shown in the half equation below:

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

In aqueous solution VO_2^+ is yellow and VO^{2+} is blue.

(i) Give the oxidation states of vanadium in VO_2^+ and VO^{2+}. [2]

(ii) Explain whether vanadium is oxidised or reduced in the electrode reaction above. [1]

(iii) Deduce an equation for the reaction of VO_2^+ with Zn in acidic solution. [2]

(iv) Use $E^\ominus$ values from the data booklet to show that the reaction in part **(iii)** is likely to occur. [2]

(v) Predict the colour changes that occur in the reaction in part **(iii)**. [1]

(e) V^{2+} and V^{3+} form octahedral complexes in aqueous solution.

(i) Define the term *complex*. [1]

(ii) Name the ligand in the complex ion formed by V^{2+} in aqueous solution. [1]

(iii) Explain whether the ligand in part **(ii)** is monodentate, bidentate or polydentate. [2]

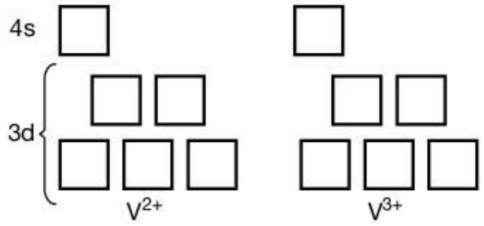
(iv) Predict the formula of the complex ion formed by V^{2+} in aqueous solution. [1]

(v) State the co-ordination number of V^{2+} in the complex in part **(iv)**. [1]

(vi) Sketch the structure of the complex ion in part **(iv)**. [1]

(f) Aqueous solutions of V^{2+} are violet and aqueous solutions of V^{3+} are green.

(i) Draw the electronic configurations of V^{2+} and V^{3+} on copies of the diagrams below. Represent an electron pair in an orbital with the symbol ⇅, or a single electron in an orbital with the symbol ↑. [2]



(ii) Use the diagrams you completed in part **(i)** to explain why V^{2+} and V^{3+} ions are coloured in aqueous solution. [3]

(g) Hydrated vanadium(III) chloride has the formula $[VCl_2(H_2O)_4]Cl{\bullet}2H_2O$ in the solid state.

(i) Deduce the overall charge on the vanadium-containing ion. [1]

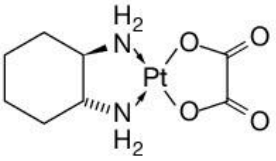
(ii) Predict the shape of the vanadium-containing ion. [1]

(iii) On dissolving in water $[V(H_2O)_6]^{3+}$ is formed.

Write an equilibrium expression to show the ligand exchange that occurs. Include state symbols. [1]

2 Oxaliplatin is a drug that is used to treat cancer.

(a) Oxaliplatin is a complex with the formula below.



(i) Define the term *complex*. [1]

(ii) Name the shape of the complex with respect to the central metal ion, Pt^{2+}. [1]

(iii) State the co-ordination number of the central metal ion. [1]

(iv) State and explain whether the 1,2-diaminocyclohexane ligand is monodentate, bidentate or polydentate. [1]

(c) The action of oxaliplatin in treating cancer is similar to that of cisplatin.

Suggest the action of oxaliplatin as an anti-cancer drug. [1]

13 Nitrogen and sulfur

AS 12.1–12.12 pages 231–248

Key points

- ☐ Explain why nitrogen is unreactive.
- ☐ Explain the reactions of ammonia and its salts.
- ☐ State why ammonia and its compounds are important.
- ☐ Explain how nitrate fertilisers damage the environment.
- ☐ Explain why oxides of nitrogen are pollutants, describe the problems they can cause and explain how they are removed from car exhausts.
- ☐ Describe how sulfur dioxide gets into the air.
- ☐ Explain how acid rain forms and describe its consequences.

Why nitrogen is unreactive

Nitrogen exists as molecules, N_2. The triple bond is strong – its bond energy is 944 kJ mol^{-1}. Since the N≡N triple bond must break in reactions involving nitrogen, its reactions have high activation energies. This is why nitrogen is unreactive.

✗ Common error

Some candidates explain the lack of reactivity of nitrogen by writing only about its large bond energy. This explanation is incomplete – you need to give the full explanation, as above.

Worked example

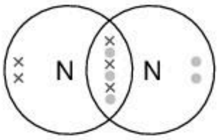
a) Give the electronic configuration of a nitrogen atom.

b) Draw a dot-and-cross diagram to show the bonding in a nitrogen molecule.

Answer

a) $1s^2 2s^2 2p^3$

b)



Ammonia and its compounds

Ammonia, NH_3, is an important compound. It is used to make:

- fertilisers, such as ammonium nitrate, NH_4NO_3, and ammonium sulfate, $(NH_4)_2SO_4$
- nitric acid, which is used to make fertilisers, explosives and dyes.

Ammonia is a base. It bonds with H^+ ions in many of its reactions to form ammonium ions, NH_4^+, as shown:

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

For example:

$$NH_3(aq) + HNO_3\ (aq) \rightarrow NH_4NO_3(aq)$$

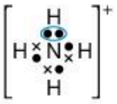
Worked example

a) Draw a dot-and-cross diagram of an ammonium ion.

b) On your diagram, circle the co-ordinate bond. Explain how the coordinate bond forms.

Answer

a)



b) The co-ordinate bond is formed from the lone pair of electrons on the nitrogen atom.

Common error

Some candidates forget to show the charge on complex ions such as this. Use square brackets to show that the charge is spread over the whole ion.

Exam tip

Exam questions may need you to refer to several areas of the syllabus. This question, whilst it appears to be about ammonium, requires you to use knowledge about chemical bonding.

Link

There is more about chemical bonding in Unit 3, Chemical bonding.

Ammonia is displaced from ammonium salts in reactions with bases. For example:

$$2NH_4Cl(s) + Ca(OH)_2(s) \rightarrow CaCl_2(s) + 2NH_3(g) + 2H_2O(l)$$

The ammonia produced makes damp red litmus paper turn blue.

Worked example

a) Write an equation to show the reaction of ammonium nitrate and sodium hydroxide solutions.

b) Describe how you could test for the gaseous product.

Answer

a) $NH_4NO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + NH_3(g) + H_2O(l)$

b) The gaseous product has a strong smell. You can test for it by holding a piece of damp red litmus paper in the gas. The litmus paper goes blue.

Remember

It is vital to balance chemical equations. Check that there are the same number of atoms of each element in the reactants and products.

Nitrate fertilisers

Nitrate fertilisers improve plant growth. They are soluble in water, so when it rains any extra fertiliser washes off the land into streams. In streams, rivers and lakes, the fertilisers cause **eutrophication**. Here's how:

- The fertiliser makes water plants grow well.
- Water plants cover the surface of the water, preventing light reaching plants underneath.
- The plants underneath die.
- Bacteria decompose the dead plants, so removing dissolved oxygen from the water.

Key term

Eutrophication: the enrichment of waterways with mineral nutrients that make water plants grow more than usual.

Common error

Candidates often do not include all the stages in explaining how eutrophication occurs. You need to give a full explanation to get maximum marks.

- Fish and other aquatic animals die, because there is not enough oxygen.

Oxides of nitrogen and sulfur

When a mixture of nitrogen and oxygen is ignited by a spark at high temperatures, the gases react to make nitrogen monoxide, NO. This happens in lightning storms and in car engines:

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

Fossil fuels contain sulfur impurities. On burning, sulfur reacts with oxygen:

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

In the air, reactions of NO and SO_2 make NO_2 and SO_3:

- NO and oxygen react to make NO_2:

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

- As soon as NO_2 forms, it reacts with SO_2 to make SO_3 and more NO:

  $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$

The NO formed in the reaction above reacts with more oxygen to make more NO_2. This means that NO acts as a catalyst in the reaction that makes SO_3.

Worked example

Use oxidation numbers to show which species are oxidised and reduced in the reaction of sulfur dioxide with nitrogen dioxide.

Answer

The equation for the reaction is:

$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

In the reaction, the oxidation number of sulfur increases from +4 in SO_2 to +6 in SO_3, so sulfur is oxidised.

The oxidation number of nitrogen decreases from +4 in NO_2 to +2 in NO, so nitrogen is reduced.

★ **Exam tip**

If you are asked to work out changes in oxidation number, start by writing an equation.

NO_2 and SO_3 are pollutants:

- They make health problems such as asthma worse.
- They dissolve in rain to make it acidic.

Acid rain has several impacts.

- It reacts with calcium carbonate, damaging limestone buildings.
- It makes lakes acidic, meaning that some water plants and animals cannot live.
- It kills trees.

Catalytic converters remove NO from car exhaust fumes. They may contain the metals platinum, palladium and/or rhodium. One of the reactions that occurs in a catalytic converter involves NO and CO:

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

Key term

Catalytic converter: a device that converts vehicle exhaust pollutants into less toxic substances. It contains metals that catalyse redox reactions, such as platinum, palladium and rhodium.

Raise your grade

1 Farmers add different substances to their soil.

(a) (i) State why a farmer might add ammonium sulfate to the soil. [1]

To improve plant growth. It contains a large amount of nitrogen, which is a vital plant nutrient. ✔

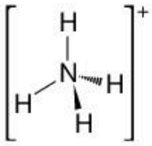
This is a good answer, since it mentions that nitrogen is an important nutrient as well as pointing that that the fertiliser improves plant growth.

(ii) Give the formula of ammonium sulfate. [1]

NH_4SO_4 ✘

The formula is incorrect. The charge on the ammonium ion is +1, and the charge on the sulfate ion is –2, so the formula of the compound is $(NH_4)_2SO_4$.

(iii) Draw the stereochemical structure of an ammonium ion, and give the H–N–H bond angle. [2]



✔

The bond angle is 105°. ✘

The bond angle is actually 109°. Since all the H atoms are equivalent, the bond angles will all be equal to the angle in a tetrahedron, which is 109°.

(b) Explain why a farmer might add calcium hydroxide powder to soil in which crop plants will be grown. [2]

So that the soil pH is suitable for growing the crops he wants to grow. ✔

Calcium hydroxide decreases soil pH. ✘

The first part of the answer is correct and clearly expressed. The second part of the answer is incorrect – calcium hydroxide is a base, so it increases soil pH, making it less acidic.

(c) Explain why the farmer should not add ammonium sulfate to the soil at the same time as adding calcium hydroxide. Include a chemical equation in your answer. [2]

The two substances react together, making foul-smelling ammonia gas. ✔✘

The candidate is correct, but she did not include a chemical equation in her answer.

The equation is: $(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2NH_3(g) + CaSO_4 + 2H_2O$

The candidate could also mention that, as well as the disadvantage of producing ammonia gas, the reaction also means that the substances are wasted, since they are not available for improving plant growth or changing soil pH.

(d) A farmer adds ammonium nitrate to the soil. Explain in detail how this substance results in fish dying if used in excess. [4]

It causes eutrophication which kills fish. ✓✗✗✗

The candidate achieves one mark for this answer. However, four marks are available, indicating that the candidate should answer the question in greater detail.

The candidate could add that excess fertiliser dissolves in rainwater, and runs into streams, rivers and lakes. This makes water plants grow well. The water plants cover the surface of the water, preventing light reaching plants underneath. The plants underneath die and decompose. The decomposition removes dissolved oxygen from the water, which is no longer available for fish and other aquatic animals. The animals die. This process is called eutrophication.

★ Exam tip

If several marks are available, a detailed answer is required. Try to make at least as many points in your answer as there are marks available.

2 This question is about acid rain.

Nitrogen and oxygen react in car engines.

(a) State one condition needed for the reaction. [1]

high temperature ✓

(b) Write an equation for the reaction of nitrogen and oxygen in car engines. [1]

$N_2(g) + O_2(g) \rightarrow NO(g)$ ✗

The formulae in the equation are correct, but the candidate has not balanced the equation. The balanced equation is below:

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

★ Exam tip

When you have written an equation, check that it is balanced.

(c) Describe how the product of the reaction of nitrogen and oxygen is removed from car exhausts. Include an equation in your reaction. [2]

It is reduced in a catalytic converter to make nitrogen gas. ✓✗

The answer is incomplete, since it does not include the equation below:

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

The candidate could also mention that catalytic converters contain metals such as platinum, palladium and/or rhodium.

(d) State one environmental problem caused by one of the products of the reaction in part **(c)**. In your answer, include the name of the product that causes this problem. [1]

Carbon dioxide causes global warming. ✓

Exam-style questions

1 Which compound or ion has no lone pairs of electrons in the valence shells of its atoms? [1]

A NH_3
B N_2
C N_2O_4
D NH_4^+

2 Which substance is **not** a product of the reaction between ammonium nitrate and calcium hydroxide? [1]

A calcium nitrate
B water
C ammonium hydroxide
D ammonia

3 What is the $H-N-H$ bond angle in ammonia? [1]

A 107°
B 109°
C 120°
D 180°

4 This question is about acid rain.

(a) State one source of each of the following gases in the atmosphere.

Include one equation in each answer.

(i) nitrogen monoxide, NO [2]

(ii) sulfur dioxide, SO_2 [2]

(b) Use oxidation numbers to help you to explain which substances are oxidised and which substances are reduced in the reactions in part **(a)**. [2]

(c) Use chemical equations to explain how NO and SO_2 take part in reactions in the atmosphere to make acid rain. [3]

(d) Use a chemical equation to help you to explain how acid rain damages limestone buildings. [2]

(e) Describe two problems caused by acid rain, in addition to damaging limestone buildings. [2]

5 A student performs a titration of ammonium hydroxide with sulfuric acid.

(a) Write an equation for the reaction that occurs. [1]

(b) The student follows the procedure below:

- Place $25.00\,cm^3$ of ammonium hydroxide solution in a conical flask.
- Add a few drops of methyl red indicator.
- Titrate with $0.05\,mol\,dm^{-3}$ sulfuric acid.
- Repeat until three titres that agree to within $0.10\,cm^3$ are obtained.

(i) The mean titre of sulfuric acid was $23.10\,cm^3$.

Calculate the amount of sulfuric acid, in mol. [2]

(ii) Calculate the amount of ammonium hydroxide in $25.00\,cm^3$ of solution. [1]

(iii) Calculate the concentration of the ammonium hydroxide solution. [1]

6 A student warms a sample of ammonium sulfate with sodium hydroxide solution.

(a) Write an equation for the reaction. [1]

(b) State one observation that the student will make during the reaction. [1]

(c) Describe how to test for the gas evolved in the reaction. [1]

(d) Calculate the volume of gas evolved at room temperature and pressure if the mass of ammonium sulfate used was 3.96 g. [3]

7 Nitrogen is unreactive, but it reacts with oxygen at the high temperatures of car engines to make nitrogen monoxide.

(a) Draw a dot-and-cross diagram to show the bonding in a nitrogen molecule. [1]

(b) Explain why nitrogen is unreactive. [1]

(c) Suggest why nitrogen reacts with oxygen at the temperature of car engines, but not at room temperature. Include a sketch of a labelled reaction pathway diagram to support your explanation. [2]

(d) Write an equation to show the reaction that occurs in a catalytic converter to remove nitrogen monoxide from car exhaust fumes. [1]

14 An introduction to organic chemistry

AS 13.1–13.6 pages 250–260
A 26.1–26.3 pages 486–490

Key points

☐ Interpret general, structural, displayed and skeletal formulae.

☐ Identify functional groups.

☐ Name organic compounds.

☐ Describe and identify different types of reaction.

☐ Describe and predict molecule shapes and bond angles.

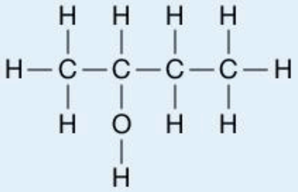
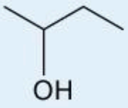
☐ Describe and explain
  ○ structural isomerism
  ○ geometrical isomerism
  ○ stereoisomerism.

☐ Name aromatic compounds with simple substituents.

Formulae

Table 14.1 shows different types of formulae for butan-2-ol.

▼ **Table 14.1** Formulae of butan-2-ol

Type of formula	Definition	Formula for butan-2-ol
Displayed	shows all the atoms and all the bonds between them	
Skeletal	shows carbon–carbon bonds and functional groups only	
Structural	shows how the atoms are joined together, and the positions of functional groups	$CH_3CHOHCH_2CH_3$
Molecular	shows the number of atoms of each element in one molecule of the compound	$C_4H_{10}O$

Remember

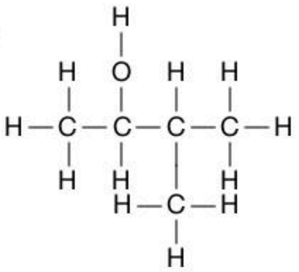
In a skeletal formula, there is a carbon atom at each end, at each bend and at each junction.

Worked example

Give the displayed, structural and molecular formula for 3-methylbutan-2-ol.

Answer

Displayed:



Structural: $CH_3CHOHCH(CH_3)CH_3$

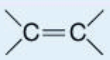
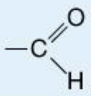
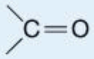
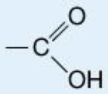
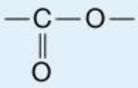
Molecular: $C_5H_{12}O$

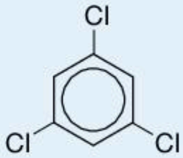
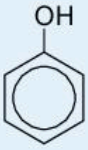
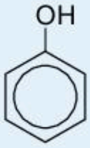
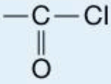
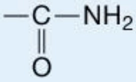
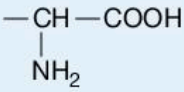
Functional groups

Key term

Functional group: the atom or group of atoms which gives an organic compound its properties. It has the same effect whatever the length or shape of the hydrocarbon skeleton it is joined to.

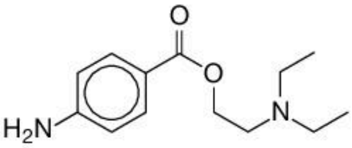
▼ **Table 14.2** Functional groups

Functional group	Name of homologous series	Example	
	alkenes	propene	$CH_2{=}CHCH_3$
–F or –Cl or –Br or –I	halogenoalkanes	1-bromopropane	$CH_3CH_2CH_2Br$
$-OH$	alcohols	propan-1-ol (a primary alcohol)	$CH_3CH_2CH_2OH$
		propan-2-ol (a secondary alcohol)	$CH_3CHOHCH_3$
		2-methylpropan-2-ol (a tertiary alcohol)	$CH_3C(CH_3)OHCH_3$
	aldehydes	propanal	CH_3CH_2CHO
	ketones	propanone	CH_3COCH_3
	carboxylic acids	propanoic acid	CH_3CH_2COOH
 $-\underset{\underset{O}{\Vert}}{C}-O-$	esters	propyl propanoate	$CH_3CH_2COOCH_2CH_2CH_3$
$-NH_2$	amines	propylamine	$CH_3CH_2CH_2NH_2$
$-C{\equiv}N$	nitriles	propanenitrile	CH_3CH_2CN

Functional group	Name of homologous series	Example	
	arenes	benzene	
	halogenoarenes (X = F, Cl, Br or I)	1,3,5-trichlorobenzene	
	phenols	phenol	
 $-\underset{\underset{\displaystyle O}{\Vert}}{C}-Cl$	acyl chlorides	propanoyl chloride	CH_3CH_2COCl
 $-\underset{\underset{\displaystyle O}{\Vert}}{C}-NH_2$	amides	propanamide	$CH_3CH_2CONH_2$
 $-\underset{\underset{\displaystyle NH_2}{\vert}}{CH}-COOH$	amino acids	glycine	H_2NCH_2COOH

Worked example

Procaine is a local anaesthetic. Its skeletal formula is shown below.



Name the functional groups in procaine.

Answer

Procaine has an amine group (NH_2), a benzene ring and an ester group (COO).

Exam tip

At AS level, you need to recognise the shape of the benzene ring in organic compounds, but you do not need to know about its properties or compounds.

Naming organic compounds

The name of an organic compound indicates the number of carbon atoms in its chain, and its functional group(s). Numbers in the name show the positions of functional groups.

Worked example

Give the names of the compounds below.

a) $CH_3CH{=}CHCH_2CH_3$

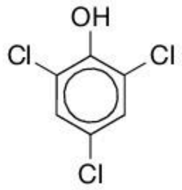
b) $CH_3CH_2COCH_2CH_3$

Common error

Students sometimes confuse prop- and pent- when naming compounds. Make sure you know which is which.

c) $CH_3CH_2CH_2CN$

d)



Answers

a) pent-2-ene

b) pentan-3-one

c) butanenitrile

d) 2,4,6-trichlorophenol

Describing organic reactions and their mechanisms

Breaking bonds

All reactions involve breaking bonds in reactants and making bonds to form products. A single bond consists of two shared electrons. There are two ways of breaking a single bond:

- In **homolytic fission**, one electron goes to each atom, or group of atoms. Each atom ends up with an unpaired electron. This atom, or group of atoms, is a reactive particle called a free radical. For example:

  $H\,\colon Br \rightarrow H\cdot \ + \ Br\cdot$

- In **heterolytic fission**, both shared electrons go to one atom, or group of atoms. This atom becomes a negatively charged ion. The other atom, or group of atoms, becomes a positively charged ion. For example:

  $H\,\colon Br \rightarrow H^+ + \colon Br^-$

Key terms

Homolytic fission: the breaking of a covalent bond to make two uncharged atoms or groups of atoms, each with an unpaired electron.

Heterolytic fission: the breaking of a covalent bond to make a positive ion and a negative ion.

Link

Free radicals take part in free radical substitution reactions. These are described in Unit 15, Hydrocarbons.

Electrophiles and nucleophiles

Many organic molecules have areas of positive or negative charge.

- A **nucleophile** has a lone pair of electrons. It is attracted to areas of positive charge in organic molecules that can accept electron pairs.
- An **electrophile** does not have enough electrons. It is attracted to areas of negative charge in organic molecules that can donate electron pairs.

Key terms

Nucleophile: this has a lone pair of electrons, and is attracted to areas of positive charge.

Electrophile: this is attracted to areas of negative charge.

Worked example

Decide whether each ion or molecule below can act as a nucleophile, an electrophile or both.

Br^- NH_3 CH_3^+ OH^- CH_3Cl H^+ H_2O

Answer

Electrophiles: CH_3^+ H^+

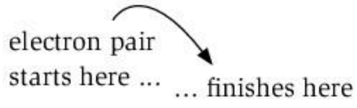
Nucleophiles: Br^- NH_3 OH^- H_2O

Both: CH_3Cl

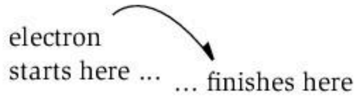
Representing reaction mechanisms

Different reactions proceed by different mechanisms. In the representation of a reaction mechanism

- Curly arrows show the movement of an electron pair:



- Curly half arrows show the movement of an unpaired electron:

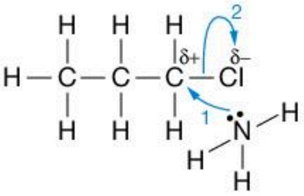


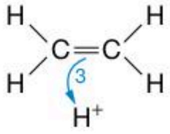
Remember

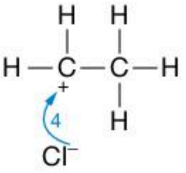
Curly arrows must start from a lone pair, or a bond, or the negative charge sign on an ion.

Worked example

Explain what each of the curly arrows below shows.







Answer

1. Lone pair of electrons from ammonia, NH_3, attacking the chlorine atom with the δ+ charge.
2. Pair of electrons from the C — Cl bond moving to the δ− chlorine atom.
3. Pair of electrons from the C = C double bond attacking the H^+ ion.
4. Lone pair of electrons from the Cl^- ion attacking the positively charged carbon atom in the ion.

Types of reaction

Organic molecules take part in different types of reaction. Some of these are shown in Table 14.3.

Chemical tests

The test for alkenes, in which bromine water is decolorised, is an example of an addition reaction. One bromine atom has been added to each of the carbon atoms that are joined by a double bond.

▼ **Table 14.3** Some reactions of organic molecules

Reaction type	Definition	Examples of compounds that take part in this type of reaction
Addition	the addition of atoms to a C=C or C=O bond, resulting in a C−C or C−O single bond	alkenes aldehydes
Substitution	the replacement of one atom or group in a molecule by another	halogenoalkanes alcohols
Elimination	the removal of atoms from two neighbouring carbon atoms that are joined by a single bond, resulting in a C=C double bond	halogenoalkanes alcohols
Hydrolysis	the reaction of an organic compound with water (or an acid or alkali) to make two or more products	esters
Condensation	the reaction of two molecules to make one big molecule and one small molecule, such as water	alcohols and carboxylic acids reacting together to make esters
Oxidation	often refers to the conversion of C−OH to C=O, or of C=O to COOH	alcohols aldehydes
Reduction	often refers to the conversion of C=O to C−OH	aldehydes ketones carboxylic acids

Worked example

Explain what is meant by the following terms:

a) electrophilic addition

b) nucleophilic substitution

c) elimination.

Answer

a) a reaction in which an electrophile attacks a C=C double bond and an atom joins to each carbon atom, resulting in a C—C single bond

b) a reaction in which a nucleophile attacks a carbon atom with a δ+ charge in an organic molecule. The nucleophile replaces one of the atoms, or a group of atoms, that was joined to the carbon atom

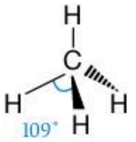
c) a reaction in which atoms from two neighbouring carbon atoms are removed resulting in a C=C double bond.

Link

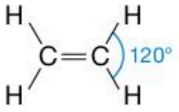
Units 15 to 21 explore these reaction types in greater detail.

Shapes of molecules

In alkanes, the bonds have a tetrahedral arrangement around each carbon atom. The bond angles are 109°:



In alkenes, the bonds are arranged in one plane. The bond angles are 120°.



In benzene, the bond angles are 120°.

Remember

Electron pair repulsion theory describes how electron pairs in molecules, including lone pairs and those in bonds, repel each other to get as far apart as possible.

Link

The bonding in ethane and ethene is discussed in terms of σ and π bonds on pages 23 and 24 in Unit 3, Chemical bonding.

Isomerism

There are different types of **isomer**, including structural isomers and stereoisomers.

Key term

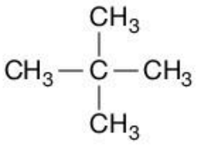
Isomers: compounds with the same molecular formula that have their atoms arranged in different ways.

Structural isomerism

In structural isomers, atoms are joined together differently:

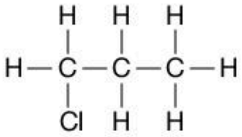
- **Chain isomerism** is the result of branching in the carbon chain, for example pentane and 2,2-dimethylpropane:

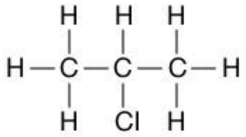
  $CH_3-CH_2-CH_2-CH_2-CH_3$

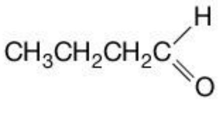
  $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

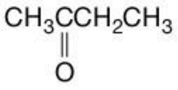
- In **positional isomers**, the functional groups are attached to different places in the same hydrocarbon chain. For example, 1-chloropropane and 2-chloropropane are positional isomers:

- **Functional group isomers** have the same molecular formula but different functional groups. For example butanal, butanone and but-2-enol are functional group isomers of C_4H_8O:

  $CH_3\underset{\underset{O}{\|}}{C}CH_2CH_3$

  $CH_3CH=CHCH_2OH$

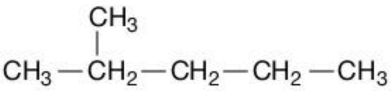
Common error

Candidates sometimes forget that there are different ways of drawing an unbranched carbon chain. A chain with a bend drawn in it may still be unbranched.

Worked example

Give the structural formulae of 2-methylpentane and 3-methylpentane. What type of structural isomerism do the two isomers show?

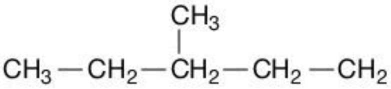
Answer



$CH_3-\overset{\overset{CH_3}{|}}{CH_2}-CH_2-CH_2-CH_3$

Exam tip

When drawing structural formulae, draw the carbon atoms in the main chain first. Then add functional groups or side chains.



$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH_2}-CH_2-CH_2$

This is an example of chain isomerism.

Stereoisomerism

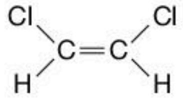
In **stereoisomers**, the atoms are joined together in the same order in both isomers, but the three-dimensional arrangement of atoms in space is different. There are two types: geometrical isomerism and optical isomerism.

Key term

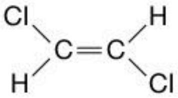
Stereoisomers: atoms joined together in the same way but arranged differently in three dimensions.

Geometrical (cis–trans) isomerism

Compounds with C=C double bonds may form geometrical isomers. Geometrical, or cis–trans, isomerism occurs because the π bond prevents rotation around the bond. For example, 1,2-dichlorethene has two geometrical isomers:



cis-1,2-dichloroethene



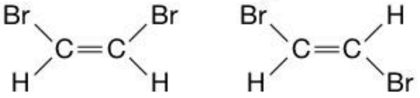
trans-1,2-dichlorethene

Remember

In the cis isomer the substituent atoms or groups are on the same side of the double bond. In the trans isomer the substituent atoms are on opposite sides of the double bond.

Worked example

Give the names of the geometrical isomers below.



Answer

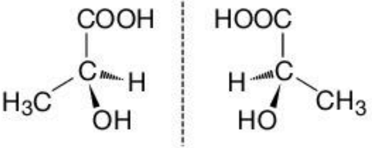
cis-1,2-dibromoethene and trans-1,2-dibromoethene.

Optical isomerism

Optical isomers are near-identical, with atoms in the same order, but have different three-dimensional shapes and rotate plane-polarised light in opposite directions.

A molecule has optical isomers if it has a carbon atom to which four different groups are attached. This carbon atom is a **chiral centre**. Optical isomers are mirror images of each other. The two forms are called enantiomers.

The formulae below show the two optical isomers of lactic acid.



Key term

Chiral centre: a carbon atom with four different groups attached to it.

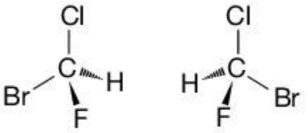
Remember

The symbol ▲ means that the group is coming out of the paper, towards you. The symbol ◁ means that the group is going into the paper, away from you.

Worked example

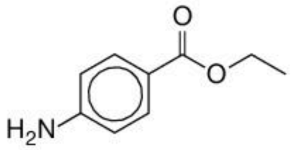
Draw the two optical isomers of bromochlorofluoromethane.

Answer

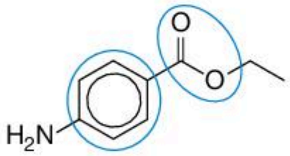


Raise your grade

1 Benzocaine is a local anaesthetic. The formula of the compound is given below.



(a) On a copy of the formula, circle and label the ester group and the benzene ring. [2]



✓✗

★ Exam tip

Read exam questions carefully, and follow all the instructions.

The candidate has correctly circled the two groups, but has not indicated which is which. For this reason the candidate has achieved one mark only. The group marked on the left is the benzene ring, and the group on the right is the ester.

(b) Give the molecular formula of benzocaine. [1]

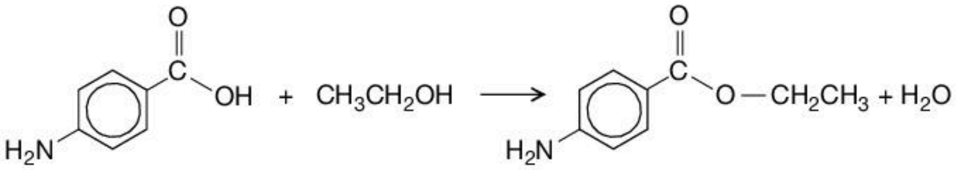
$C_8H_{11}NO_2$ ✗

The candidate is almost correct, but has shown only 8 carbon atoms, when in fact there are 9.

Remember

In a skeletal formula, there is a carbon atom at each end, at each bend and at each junction.

(c) Benzocaine is made in the reaction shown below.



Compound A Compound B

(i) Name one functional group in compound A, other than the benzene ring. [1]

acid ✗

The name of the functional group is incomplete – the functional group is a carboxylic acid. The candidate could also have identified the amine group.

(ii) Name compound B and state the name of its homologous series. [2]

alcohol ✓✗

This question asks for two things – the homologous series and the name of compound B. The candidate has only answered one part of the question, so achieves one mark only. The name of the compound is ethanol.

★ Exam tip

If there are two marks for a question, make sure you make two points in your answer.

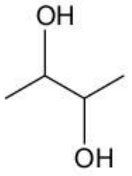
(iii) Name the type of reaction that occurs when compound A reacts with compound B to make benzocaine. [1]

condensation ✔

This is correct – the candidate has recognised that two molecules have reacted together to make one big molecule and one water molecule. An alternative correct answer is esterification.

2 This question is about the compound butane-2,3-diol.

The skeletal formula of butane-2,3-diol is given here.



(a) Name the functional group present in butane-2,3-diol. [1]

aldehyde ✘

The functional group is an alcohol.

★ Exam tip

Make sure you learn the names of functional groups very carefully.

(b) Suggest one type of reaction that butane-2,3-diol can take part in. [1]

substitution ✔

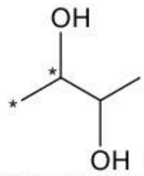
The candidate is correct. She has remembered that the alcohols react in substitution reactions. They also take part in oxidation, elimination and condensation reactions – any of these answers would have gained the mark.

(c) State and explain whether a carbon atom in butane-2,3-diol is more likely to be attacked by a nucleophile or an electrophile. [1]

nucleophile

This answer is partly correct, but the candidate did not include an explanation. She needs to add that a nucleophile is attracted to the δ+ charge on the carbon atoms that are joined to the —OH groups.

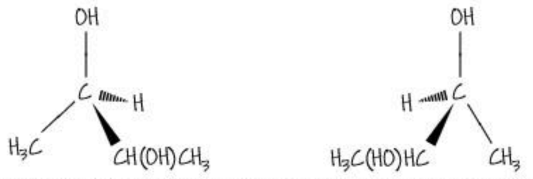
(d) On a copy of the skeletal formula, mark the two chiral centres in butane-2,3-diol. [1]



✘

This answer is wrong. The * sign on the right is correct, but that on the left is incorrect. The carbon atom on the left has three hydrogen atoms attached to it. In order to be a chiral centre, a carbon atom must have four different atoms or groups of atoms attached to it.

(e) Draw three-dimensional structures to show the two enantiomers of butane-2,3-diol. [2]



✔✔

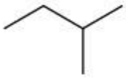
Exam-style questions

Choose your answer to questions 1 and 2 by selecting on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

1 Which skeletal formulae have the molecular formula C_5H_{12}?

1 

2 

3 

2 Which formulae show positional isomers of $CH_3CHBrCH_2CH_2CH_3$?

1 $CH_3CH_2CH_2CHBrCH_3$

2 $CH_2BrCH_2CH_2CH_2CH_3$

3 $CH_3CH_2CHBrCH_2CH_3$

3 Which equations represent addition reactions?

1 $CH_2{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_3$

2 $CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$

3 $CH_3CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2Br + H_2O$

4 This question is about the hydrocarbon hept-2-ene and its isomers.

(a) Name the homologous series of which the hydrocarbon is a member. [1]

(b) Draw the skeletal formula of hept-2-ene. [1]

(c) A structural isomer of hept-2-ene has the formula shown below:

$$CH_2{=}CHCH_2CH_2CH_2CH_2CH_3$$

What type of structural isomers are hept-2-ene and the compound shown above? [1]

(d) Hept-2-ene forms geometrical (cis–trans) isomers:

(i) Explain what causes geometrical (cis-trans) isomerism. [2]

(ii) Draw the structures of the two geometrical isomers of hept-2-ene. [2]

5 This question is about optical isomerism.

(a) Name the one property that is different between a pair of optical isomers. [1]

(b) Explain what is meant by the term **chiral centre**. [1]

(c) A compound has the molecular formula $C_6H_{13}Cl$.

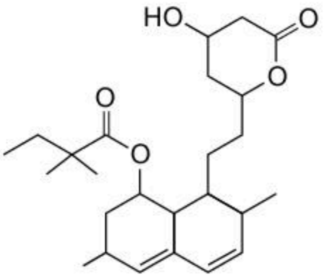
(i) Give the name of the isomer of $C_6H_{13}Cl$ that has a chiral centre. [1]

(ii) Draw the three-dimensional structures of the two optical isomers of $C_6H_{13}Cl$. [2]

(d) Simvastatin is a medicine that is used to reduce cholesterol in the blood.

It has the formula shown below.

Circle **three** chiral centres on a copy of the formula. [1]



6 The structural formula of but-2-ene-2,3-diol is given below.

$$CH_3C(OH){=}C(OH)CH_3$$

(a) Draw the two geometrical (cis–trans) isomers of but-2-ene-2,3-diol. [2]

(b) Label the isomers you drew to answer part **(a)** above to show which is the cis isomer and which is the trans isomer. [1]

(c) Deduce the molecular formula of but-2-ene-2,3-diol. [1]

(d) Draw a displayed formula of a structural isomer of but-2-ene-2,3-diol that is a carboxylic acid. [2]

(e) Draw a displayed formula of a structural isomer of but-2-ene-2,3-diol that is an ester. [2]

15 Hydrocarbons

AS 14.1–14.9 pages 280–300;
15.1–15.7 pages 303–315
A 26.1–26.11 pages 486–502

Key points

- ☐ Describe the reactions of alkanes.
- ☐ Describe the mechanism of free radical substitution.
- ☐ Explain the purposes of cracking.
- ☐ Describe the reactions of alkenes.
- ☐ Describe the mechanism of electrophilic addition.
- ☐ Explain the inductive effects of alkyl groups.
- ☐ Describe the characteristics of addition polymerisation.
- ☐ Identify monomers and repeat units in polymers.
- ☐ Recognise the difficult of disposing of poly(alkene)s.
- ☐ Explain the environmental consequences of using alkanes as fuels.
- ☐ Outline the use of infra-red spectroscopy in monitoring air pollution.
- ☐ Describe the reactions of benzene and methylbenzene.
- ☐ Describe the mechanism of electrophilic substitution in arenes.
- ☐ Predict the position of substitution in reactions of arenes.

Reactions of alkanes

Alkanes are made up of carbon and hydrogen atoms only, joined together by single bonds.

Carbon and hydrogen have similar electronegativity values, so C—H bonds are **non-polar**. This means that there are no centres of electrical charge in alkanes, so they do not react with polar substances.

Alkanes take part in **combustion reactions**, for example:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Alkanes also react with chlorine and bromine, for example:

$$\begin{aligned} CH_4 + Cl_2 &\rightarrow CH_3Cl + HCl \\ CH_3Cl + Cl_2 &\rightarrow CH_2Cl_2 + HCl \\ CH_2Cl_2 + Cl_2 &\rightarrow CHCl_3 + HCl \\ CHCl_3 + Cl_2 &\rightarrow CCl_4 + HCl \end{aligned}$$

In industry, the mixture of products made in this reaction are separated by distillation.

Reactions of alkanes with halogens occur by **free radical substitution**. There are three steps in this mechanism.

Initiation

Light provides energy for Cl—Cl bonds to break

This is an example of homolytic fission.

Key terms

Non-polar: a non-polar molecule has no centres of electrical charge.

Combustion reaction: in a combustion reaction a substance burns and energy is transferred to the surroundings.

Free radical substitution: a reaction in which an atom or group of atoms with a single unpaired electron replaces an atom or group of atoms in a molecule.

Key term

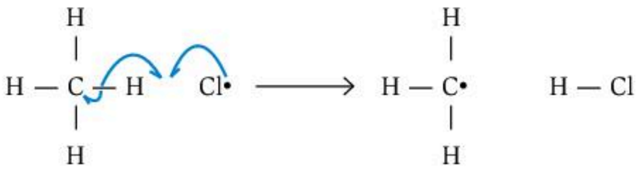
Initiation: the first step of a free radical substitution reaction, in which a molecule breaks up to make two free radicals.

Propagation

The chlorine atoms are free radicals. They are very reactive.

They collide with methane molecules and make more free radicals.

$$CH_4 + Cl\bullet \rightarrow CH_3\bullet + HCl$$



Then the $CH_3\bullet$ reacts with another chlorine molecule:

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

The propagation steps allow a chain reaction to continue.

Termination

When two free radicals combine, the chain reaction ends:

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$
$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$$
$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$

Key terms

Propagation: the steps in a free radical substitution reaction ensure that the reaction continues.

Termination: in the termination step of a free radical substitution reaction, two free radicals join together.

Remember

A curly half arrow shows the movement of one electron, but a complete curly arrow shows the movement of two electrons.

Catalytic cracking of alkanes

The alkanes, and other hydrocarbons, are obtained by the fractional distillation of crude oil. Catalytic cracking reactions may then be used to break up long-chain alkanes, for example:

$$C_{12}H_{26} \rightarrow C_{10}H_{22} + C_2H_4$$

Worked example

State two purposes of cracking reactions.

Answer

Cracking reactions make:

- alkanes of lower M_r, which are used in petroleum fuel
- alkenes of lower M_r, which are used to make polymers and other useful products.

Addition reactions of alkenes

Alkenes take part in addition reactions with hydrogen, steam, hydrogen halides and halogens, listed in Table 15.1.

Key term

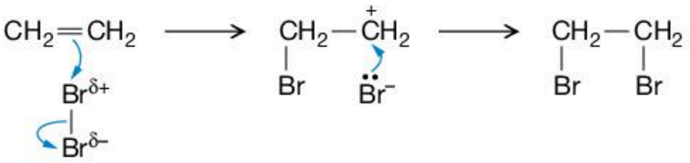
Markovnikov's rule: when a molecule HX adds to an asymmetric alkene, the major product is the one in which the hydrogen atom joins to the carbon atom already joined to the larger number of hydrogen atoms.

▼ **Table 15.1** Addition reactions of alkenes

Equation	Temperature /°C	Pressure / atm	Catalyst	Notes
$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$	140	1	Ni	
$CH_2{=}CH{-}CH_3 + H_2O \rightarrow CH_3{-}CHOH{-}CH_3$	330	60	H_3PO_4	major product predicted by **Markovnikov's rule**
$CH_2{=}CH{-}CH_3 + HCl \rightarrow CH_3{-}CHCl{-}CH_3$	room temp.	1	none	
$CH_2{=}CH{-}CH_3 + Br_2 \rightarrow CH_2Br{-}CHBr{-}CH_3$	room temp.	1	none	a useful test for C=C bonds

The mechanism of electrophilic addition reactions of alkenes

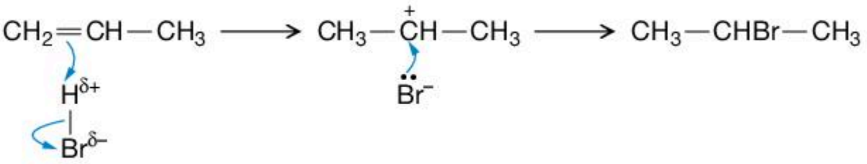
The π electrons in the double bond of an alkene form a region of high electron density. This is why alkenes are attractive to **electrophiles**. For example, in the reaction of bromine with ethene:



Worked example

Use curly arrows to show the mechanism of the reaction of HBr with propene.

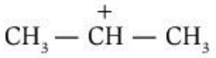
Answer



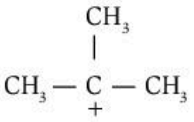
The cation formed in the reaction in the worked example has alkyl groups on both sides of the positively charged carbon atom. The alkyl groups stabilise the cation by pushing electrons towards the positively charged carbon atom. This is an example of the **positive inductive effect**.

Worked example

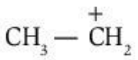
Which of the cations below is most stable? Explain your answer.


$CH_3-\overset{+}{C}H-CH_3$

A


$CH_3-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH_3$

B


$CH_3-\overset{+}{C}H_2$

C

Answer

B is the most stable cation because it has the greatest number of alkyl groups pushing electrons towards the positively charged carbon atom as a result of the positive inductive effect.

Oxidation reactions of alkenes

Alkenes react with potassium manganate(VII). The products depend on the conditions.

- With cold, dilute acidified $KMnO_4$ the product is a diol.

$$CH_2{=}CH_2 + H_2O + [O] \rightarrow CH_2OH{-}CH_2OH$$

- With hot, concentrated acidified $KMnO_4$ the double bond breaks completely. The products are aldehydes or ketones. Aldehydes made in these reactions are further oxidised to carboxylic acids. This reaction is used to find the position of a double bond in an alkene molecule.

$$CH_3{-}CH_2{-}CH{=}CH{-}CH_3 + 2[O] \rightarrow CH_3{-}CH_2{-}CHO + CH_3{-}CHO$$

Then $CH_3{-}CH_2{-}CHO + CH_3{-}CHO + 2[O] \rightarrow CH_3{-}CH_2{-}COOH + CH_3{-}COOH$

Remember

A curly arrow shows the movement of an electron pair. It always starts at a bond or a lone pair.

Key term

Electrophiles: electrophiles are attracted to groups or areas of negative charge that can donate electron pairs.

Chemical tests

If a gas decolorises bromine water when bubbled through it, molecules of the gas include a double bond.

Exam tip

You might be asked to predict products of reactions of more complicated molecules that include a C=C double bond. All you need to do is to apply what you have learnt about the reactions of ethene and propene to the bigger molecule.

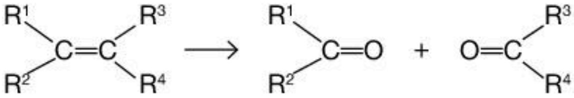
Key term

Positive inductive effect: this effect pushes electrons in a covalent bond towards a carbon atom.

Common error

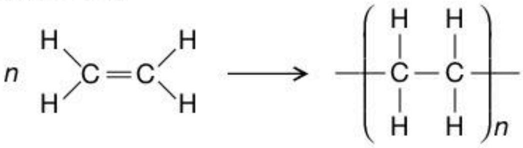
Students sometimes confuse the products of the reaction with potassium manganate(VII) under different conditions. Make sure you learn which conditions result in which products.

In general terms:



Polymerisation reactions of alkenes

Alkenes form polymers in addition polymerisation reactions. For example ethene forms poly(ethene):



In the reaction above, ethene is the monomer. The repeating unit is shown in brackets.

Link

Unit 21, Polymerisation, covers polymerisation, including condensation polymerisation, in more detail.

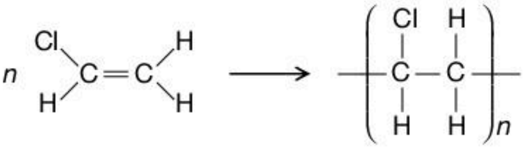
The conditions required to make poly(ethene) are:

- 200 °C and 2000 atm to make low-density poly(ethene)
- 60 °C and 3 atm and a catalyst to make high-density poly(ethene).

Worked examples

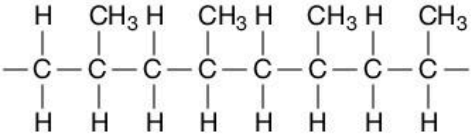
1 Write an equation to show the polymer formed from chloroethene, and give the systematic and common name of the polymer formed.

Answer



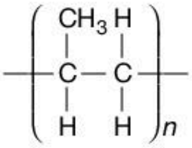
The name of the polymer is poly(chloroethene), or poly(vinylchloride), PVC.

2 Identify the repeat unit of the addition polymer below, and give the formula of the monomer. Give the systematic name of the polymer.



Answer

The repeat unit of the polymer, and the formula of the monomer, are shown below. The name of the polymer is poly(propene).



$CH_3-CH=CH_2$

Exam tip

You might be asked to deduce the repeat unit of an addition polymer, or identify the monomer it is made from.

Disposing of polymers

Poly(alkenes) are not biodegradable, and their combustion products are harmful. This means that the disposal of poly(alkenes) is difficult. For this reason chemists are developing new biodegradable polymers. People are also encouraged to use fewer products made from poly(alkenes), such as shopping bags, and to reuse and recycle poly(alkene) products.

Using hydrocarbons as fuel

The combustion reactions of alkanes are exothermic. Alkanes that are in the liquid or gas state at room temperature are easy to transport. This means that alkanes are used as fuels at home, in transport and in industry.

The combustion of alkanes produces undesirable products:

- Carbon dioxide contributes to the **enhanced greenhouse effect**.
- Carbon monoxide is a product of incomplete combustion. In the blood, it joins to haemoglobin in place of oxygen. For this reason it is poisonous, and can kill.
- At the high temperatures of diesel and petrol engines, nitrogen and oxygen from the air react to make nitrogen monoxide. In the air, this is oxidised to nitrogen dioxide. Oxides of nitrogen, NO_x, are harmful to health, and cause acid rain.
- Unburnt hydrocarbons contribute to the enhanced greenhouse effect. They are also harmful to health.

Catalytic converters remove harmful substance from vehicle exhausts. The catalysts are metals such as platinum, rhodium and palladium.

The main reaction that occurs is:

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

Infra-red spectroscopy is used to monitor air pollution.

Key term

Enhanced greenhouse effect: the increase in the mean surface temperature of Earth as a result of increased concentrations of greenhouse gases such as carbon dioxide in the atmosphere.

✗ Common error

Students often confuse the effects of different pollutants. Make sure you learn which problems are caused by which pollutants.

Link

Catalytic converters are described in Unit 13, Nitrogen and sulfur. Infra-red spectroscopy is covered in Unit 22, Analytical techniques.

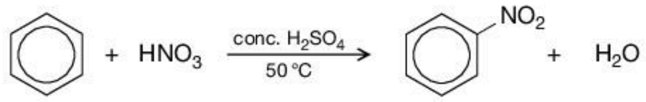
Electrophilic substitution reactions of benzene

The high negative charge density of the **delocalised electron system** of the benzene ring attracts electrophiles. For example:

- With a catalyst such as iron, $FeBr_3$, or $AlCl_3$, benzene reacts with chlorine and bromine:

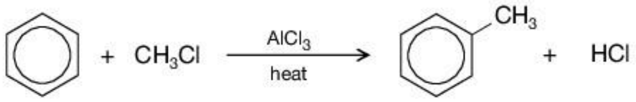
chlorobenzene

- With a mixture of concentrated nitric acid and concentrated sulfuric acid at 50 °C, benzene reacts to make nitrobenzene:



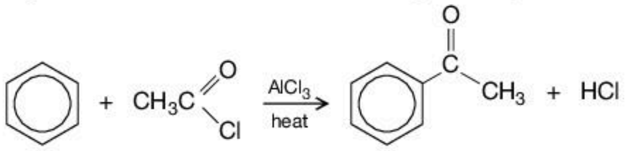
nitrobenzene
(a yellow oil)

- **Friedel–Crafts alkylation reactions** occur when benzene reacts with a halogenoalkane. The aluminium chloride catalyst polarises the halogenoalkane to give the alkyl group a δ+ charge so that it can attack the benzene ring.



methylbenzene

- Friedel–Crafts acylation is the reaction of benzene with an acyl halide. Again, an aluminium chloride catalyst is required.



phenylethanone

The mechanism of electrophilic substitution reactions of benzene

Nitration

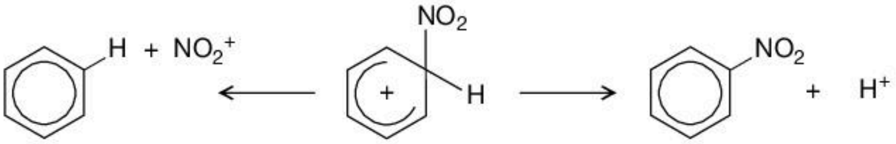
First, the two acids react to make a nitronium ion, also called a nitryl ion, NO_2^+:

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

The NO_2^+ ion is a strong electrophile, and is attracted to the π electron system in benzene. It joins loosely with the benzene ring:

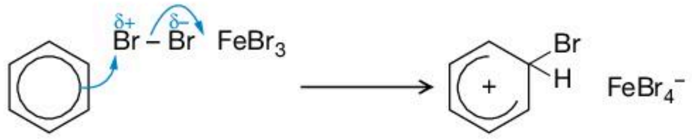
Then the NO_2^+ attacks and bonds to a carbon atom in the benzene ring. A lot of energy is needed to disrupt the π electron system. This is the reason for the high activation energy of the reaction.

Lastly, the intermediate ion breaks down. This step is exothermic because the delocalised π electron system is restored.

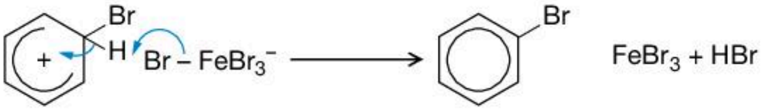


Bromination

In the presence of an $FeBr_3$ catalyst, a bromine molecule is polarised when it approaches a benzene ring:

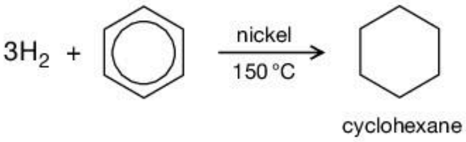


Then the $FeBr_4^-$ ion removes the hydrogen atom:



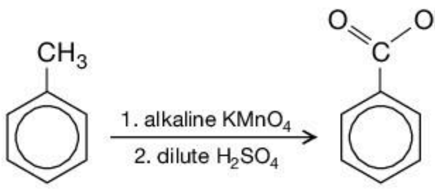
Other reactions of arenes

Benzene reacts with hydrogen in the presence of a nickel catalyst to make cyclohexane. A high temperature is required because energy is needed to break up the π electron system.



Reactions of methylbenzene

Methylbenzene is oxidised to benzoic acid when it is treated with acidified $KMnO_4$ followed by dilute sulfuric acid. The benzene ring has changed the properties of the methyl group:



The products of the reaction of methylbenzene with halogens depend on the reaction conditions:

- In the presence of sunlight, the side chain is substituted.
- In the absence of sunlight and in the presence of $AlCl_3$, the ring is substituted. There is a mixture of products.

Worked example

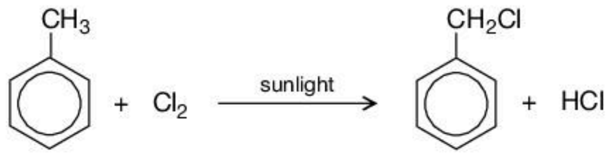
Write equations to show the reactions of methylbenzene with chlorine

a) in the presence of sunlight

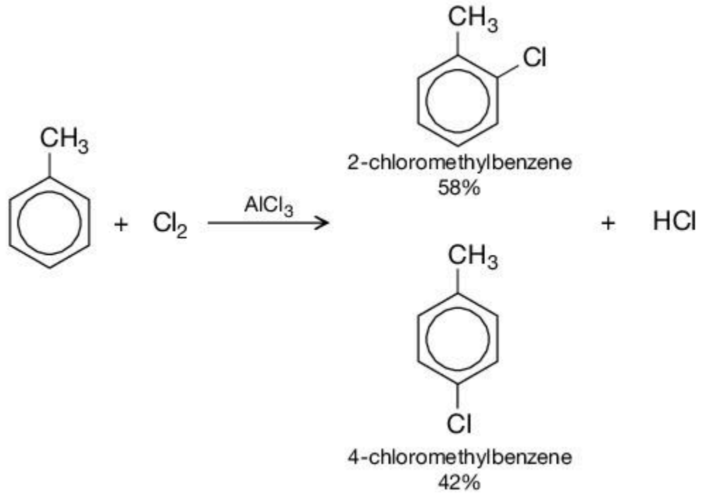
b) in the absence of sunlight but in the presence of $AlCl_3$.

Answers

a)



b)



Comparing the reactivity of benzene and chlorobenzene

Chlorobenzene reacts less vigorously than benzene with electrophiles. This is because the chlorine atom pulls electrons towards itself, resulting in a lower electron density in the benzene ring.

★ Exam tip

Table 9 of the data booklet gives the positions of incoming groups for different arenes.

The position of substitution in arenes

The position of the incoming group is determined by the nature of the group that is already bonded to the benzene ring.

Raise your grade

1 This question is about propane and propene.

(a) Propane and propene are obtained from crude oil.

(i) Name the physical process in which a fraction containing propane is obtained from crude oil. [1]

Fractional distillation. ✓

(ii) Name the type of reaction in which propene is obtained from larger hydrocarbon molecules obtained from crude oil. [1]

Cracking. ✓

(b) Suggest one use of propane. [1]

As a fuel. ✓

(c) Explain why propene is more reactive than propane, using ideas about electron density. [2]

Propene is more reactive because it has a double bond. ✓✗

This explanation is correct so far, but is incomplete. To finish the answer, the candidate needs to state that the double bond is electron-rich, and is therefore attractive to electrophiles. Propane does not have any centres of negative or positive charge.

(d) Propane and propene take part in combustion reactions.

(i) Write balanced equations for the complete combustion reactions of propane and propene. [2]

propane: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ ✓

propene: $C_3H_6 + O_2 \rightarrow 3CO_2 + 3H_2O$ ✗

The equation for propene shows the correct reactants and products, but is not balanced. The balanced equation is:

$$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$$

(ii) Describe one environmental problem caused by one of the products of the complete combustion reactions of propane and propene. [2]

Carbon dioxide is a greenhouse gas. ✓✗

This answer is correct so far, but is incomplete. The candidate could add that:

Extra amounts of greenhouse gases lead to increasing mean global temperatures. This leads to rising sea levels, which may cause flooding in low-lying coastal areas.

(iii) State one condition which leads to the formation of carbon monoxide when propane burns, and describe one problem caused by this product. [2]

Carbon monoxide is formed when propane burns in less oxygen than is required for complete combustion. ✓✗

The answer so far is very clear. The candidate just needs to add that carbon monoxide is poisonous to humans and other animals.

(e) Propane reacts with chlorine in a free radical substitution reaction. A mixture of products is formed.

(i) Use a series of equations to describe the mechanism of the reaction of propane and chlorine to make 1-chloropropane, and name each of the three steps. [3]

$Cl{-}Cl \rightarrow Cl\bullet + Cl\bullet$ Initiation

$CH_4 + Cl\bullet \rightarrow CH_3Cl + H\bullet$ propagation

$$\left.\begin{array}{l} Cl\bullet + Cl\bullet \rightarrow Cl_2 \\ CH_3\bullet + Cl\bullet \rightarrow CH_3Cl \end{array}\right] \text{termination}$$

✓ ✗ ✗

The candidate has named the three steps correctly, and the equations for initiation and for the first termination reaction are correct. However, the other two equations are incorrect, and they apply to a different reaction – that of methane with chlorine. The correct equations are given below.

$Cl{-}Cl \rightarrow Cl\bullet + Cl\bullet$ Initiation

$$\left.\begin{array}{l} CH_3CH_2CH_3 + Cl\bullet \rightarrow CH_3CH_2CH_2\bullet + HCl \\ CH_3CH_2CH_2\bullet + Cl_2 \rightarrow CH_3CH_2CH_2Cl + Cl\bullet \end{array}\right] \text{propagation}$$

$$\left.\begin{array}{l} CH_3CH_2CH_2\bullet + CH_3CH_2CH_2\bullet \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3 \\ Cl\bullet + Cl\bullet \rightarrow Cl_2 \\ CH_3CH_2CH_2\bullet + Cl\bullet \rightarrow CH_3CH_2CH_2Cl \end{array}\right] \text{termination}$$

Exam tip

Read the question properly, and – if necessary – apply your knowledge to a different reaction or another type of new situation.

(ii) Name a hydrocarbon formed in the reaction of propane with chlorine. [1]

Ethane ✗

The candidate has not applied his learning to the reaction given in this question. The termination reactions given above show that hexane is another product of the reaction.

(iii) Describe two ways in which the reaction of propane and chlorine is different from the reaction of propene and chlorine. [2]

One is a substitution reaction and the other is an addition reaction. One has a free radical mechanism and the other does not. ✗ ✗

Unfortunately the candidate has gained no marks here since he has not stated which statement applies to the propene reaction, and which applies to the propane reaction. A better answer would be:

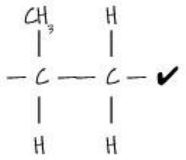
The reaction with propane is a substitution reaction, but the reaction with propene is an addition reaction. The mechanism of the propane reaction involves free radicals, but the mechanism of the propene reaction involves an electrophile.

(f) When warmed in the presence of a catalyst, propene forms a polymer.

(i) Give the name of the polymer formed. [1]

poly(propene) ✓

(ii) Draw the repeat unit of the polymer. [1]



(iii) Describe one difference in the properties of propene and its polymer. [1]

Propene is a gas but poly(propene) is solid. ✘

Unfortunately this answer gains no credit, since the candidate did not point out that the states are given at room temperature.

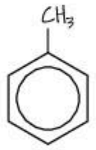
(iv) Give two reasons to explain why the polymer is difficult to dispose of. [2]

It is not easily biodegradable, and on burning it produces harmful products. ✔✔

There are two marks for this question, and the candidate made two – correct – points, so gaining two marks.

2 Benzene reacts with chloromethane when heated with an aluminium chloride catalyst to make compound **A**. Compound **A** then reacts with dilute alkaline $KMnO_4(aq)$ followed by dilute sulfuric acid to make compound **B**. Finally, compound **B** is treated with a mixture of concentrated nitric and sulfuric acids to make a mixture of compounds, **C** and **D**.

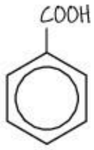
(a) Give the structural formula of compound **A**, and name the type of reaction that has occurred. [2]



The reaction is a Friedel–Crafts alkylation reaction. ✔✔

Both parts of this answer are correct, so the candidate gains full marks.

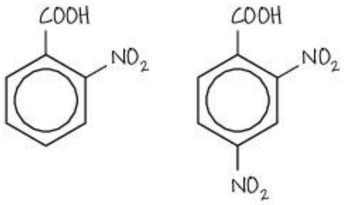
(b) Give the name and structural formula of compound **B**. [2]



The compound is an acid. ✔✘

The name of the acid is benzoic acid.

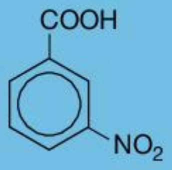
(c) Give the names and structural formulae of compounds **C** and **D**. Compound **C** has a smaller M_r than compound **D**. [2]



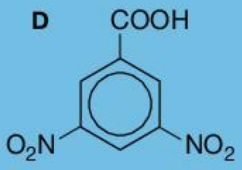
✘✘

The candidate has given incorrect formulae – the data booklet shows that a carboxylic acid group on a benzene ring directs the incoming group to the 3-position. The correct formulae, and the names of the compounds, are given below.

C



D



Compound C is 3-nitrobenzoic acid and compound D is 3,5-dinitrobenzoic acid.

Exam-style questions

1 What is the major product of the reaction when but-1-ene reacts with steam at 330 °C and 60 atm pressure with a phosphoric acid catalyst?

A butan-2-ol

B butan-1-ol

C butan-1,2-diol

D butane

2 In the reaction of ethane with chlorine in the presence of light, which equation shows a termination step?

A $Cl_2 \rightarrow Cl\bullet + Cl\bullet$

B $CH_4 + Cl\bullet \rightarrow CH_3\bullet + HCl$

C $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

D $CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$

3 This question is about the reactions of alkenes with potassium manganate(VII) and bromine.

(a) Propene reacts with cold, dilute potassium manganate(VII).

Give the structural and skeletal formulae of the products formed. [2]

(b) Alkene **X** reacts with hot, concentrated potassium manganate(VII).

There is a mixture of organic products, **Y** and **Z**. Their relative molecular mass values are given in the table.

Compound	M_r
Y	74
Z	60

(i) Name the homologous series of which **Y** and **Z** are members. [1]

(ii) Give the structural formulae of compounds **Y** and **Z**. [2]

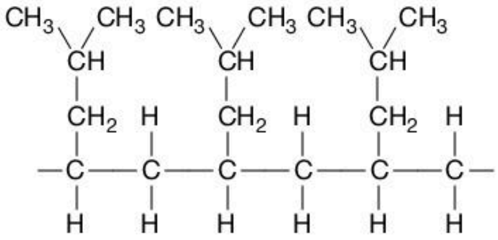
(iii) Deduce the skeletal formula of alkene **X**, and state its name. [2]

(c) (i) Use curly arrows to describe the mechanism of the reaction of hydrogen bromide with but-1-ene. [3]

(ii) Name the main product formed in the reaction in part **(i)**. [1]

4 The polymer polymethylpentene, PMP, is used to make gas-permeable packaging, as well as medical and laboratory equipment.

A section of the polymer molecule is shown below.



(a) Draw the structural formula of the monomer used to make PMP. [1]

(b) Give the systematic name of the monomer you identified in part **(a)**. [1]

(c) Draw the skeletal formula of the monomer you identified in part **(a)**. [1]

(d) PMP is not biodegradable.

Suggest how this property of PMP makes its disposal difficult. [1]

(e) PMP can be disposed of by combustion.

(i) Name the products of the complete combustion of PMP. [1]

(ii) Describe one problem caused by one of the products of the combustion reaction. [1]

5 This question is about the reactions of arenes.

(a) Alkaline potassium manganate(VII) is added to methylbenzene, followed by dilute sulfuric acid. Name the product formed. [1]

(b) Chlorine is bubbled through methylbenzene in the absence of sunlight and in the presence of $AlCl_3$. A mixture of two products is formed.

Draw the formulae of the two products. [1]

(c) Benzene and hydrogen are heated together in the presence of a nickel catalyst.

(i) Name the product of the reaction. [1]

(ii) Explain why the reactants must be heated together in order for the reaction to occur. [1]

16 Halogen derivatives

Key points

- ☐ Describe nucleophilic substitution and elimination reactions of halogenoalkanes.
- ☐ Describe S_N1 and S_N2 mechanisms.
- ☐ Explain the inductive effect of alkyl groups and use this to predict reaction mechanisms.
- ☐ Interpret reactivities of halogenoalkanes.
- ☐ Explain the uses of halogenoalkanes and their effects on the ozone layer.

Nucleophilic substitution reactions

Table 16.1 shows some reactions of bromoethane. Other halogenoalkanes have similar reactions.

▼ **Table 16.1** Reactions of bromoethane

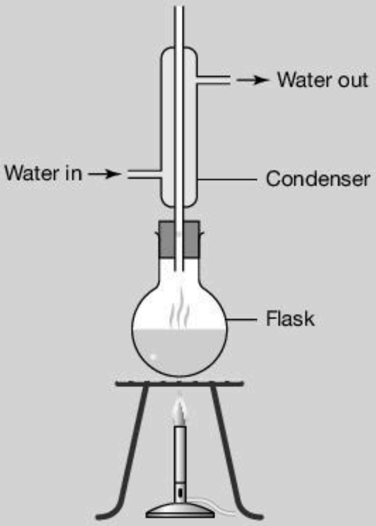
Equation	Conditions	Notes
$CH_3CH_2Br + H_2O \rightarrow CH_3CH_2OH + HBr$	heat under reflux with water	very slow
$CH_3CH_2Br + {}^{-}OH \rightarrow CH_3CH_2OH + Br^{-}$	heat under reflux with NaOH (aq)	faster than the reaction with water
$CH_3CH_2Br + CN^{-} \rightarrow CH_3CH_2CN + Br^{-}$	heat under reflux with KCN in ethanol	increases the carbon chain length
$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$	heat in a sealed tube with concentrated NH_3(aq)	makes a mixture of products

Practical skills

Heating under reflux

Many organic reactions are slow at room temperature. If reacting mixtures are heated in an ordinary flask, the reactants, products or solvent might escape to the surroundings as vapours.

This is why organic reaction mixtures are often heated under reflux. The reacting mixture boils continuously in the flask When vapour forms, it rises into the condenser. Here, it cools and condenses, before running back into the flask, as shown in Figure 16.1.



▲ **Figure 16.1** Heating under reflux

Worked example

Write equations for the reaction of 1-iodopropane with

a) potassium cyanide

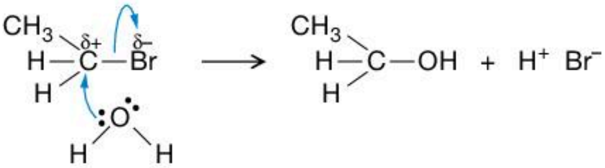
b) ammonia.

Answer

a) $CH_3CH_2CH_2I + KCN \rightarrow CH_3CH_2CH_2CN + KI$

b) $CH_3CH_2CH_2I + NH_3 \rightarrow CH_3CH_2CH_2NH_2 + HI$

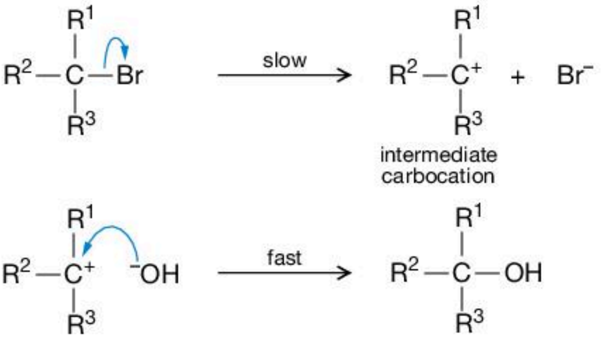
The reactions in Table 16.1 are **nucleophilic substitution reactions**. They occur because the C—Br bond is polar. A lone pair of electrons on a nucleophile attacks the δ+ carbon atom:



There are two mechanisms for nucleophilic substitution reactions: S_N1 and S_N2.

The S_N1 reaction mechanism

The S_N1 has two steps, shown below. R^1, R^2 and R^3 are alkyl groups or hydrogen atoms.

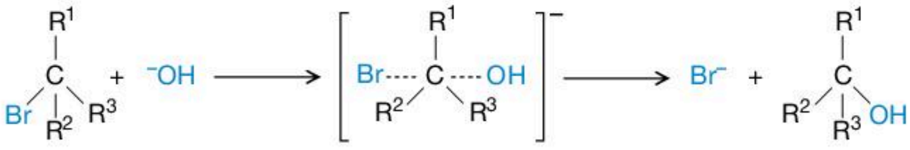


The first step is slow. The second step is fast because the intermediate carbocation is unstable. The mechanism is called S_N1 because one molecule forms the intermediate.

Tertiary halogenoalkanes tend to react by the **S_N1 mechanism**. In these compounds, R^1, R^2 and R^3 are alkyl groups. They stabilise the C^+ in the carbocation by the positive inductive effect.

The S_N2 reaction mechanism

This has one step:



The mechanism is called S_N2 because two particles collide to start the reaction.

Exam tip

Make sure you balance organic equations, and include all products.

Key term

Nucleophilic substitution reaction: in a nucleophilic substitution reaction the C—X bond breaks (X represents a halogen atom), and the X is replaced by another atom or group of atoms.

Remember

A bond is polar if the atoms it joins have different electronegativities.

Exam tip

Show the start and end points of curly arrows clearly.

Key terms

Tertiary halogenoalkane: in a tertiary halogenoalkane the halogen atom is joined to a carbon atom that is joined to three carbon atoms.

S_N1 mechanism: the mechanism of a nucleophilic substitution reaction in which one molecule breaks up to form an intermediate carbocation.

Link

There is more about the inductive effect in Unit 15, Hydrocarbons.

Primary halogenoalkanes tend to react by the **S_N2 mechanism**. In these compounds, two or three of R^1, R^2 and R^3 are hydrogen atoms, so there is enough space for incoming nucleophiles.

Secondary halogenoalkanes react by a mixture of S_N1 and S_N2 mechanisms.

Key terms

Primary halogenoalkane: in a primary halogenoalkane the halogen atom is joined to a carbon atom that is joined to one carbon atom, or no carbon atoms at all.

S_N2 mechanism: the mechanism of a nucleophilic substitution reaction that starts when two particles collide to form a transition state.

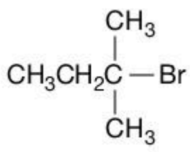
Secondary halogenoalkane: in a secondary halogenoalkane the halogen atom is joined to a carbon atom that is joined to two carbon atoms.

Worked example

State whether each compound below reacts mainly by S_N1, mainly by S_N2, or by a mixture of the two. Give reasons for your decisions.

a) $CH_3CH_2CH_2Br$

b)



$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}-Br$

Answer

a) S_N2 because the compound is a primary halogenoalkane. There is space around the carbon atom in C—Br for a fifth atom to approach.

b) S_N1 because the compound is a tertiary halogenoalkane. The alkyl groups stabilise the C^+ atom in the carbocation by the positive inductive effect.

✗ Common error

Many candidates get S_N1 and S_N2 mechanisms confused. One molecule forms the intermediate in the S_N1 mechanism. Two particles collide to start the reaction in the S_N2 mechanism.

Elimination reactions

When a halogenoalkane is heated with sodium hydroxide in ethanol, there is an elimination reaction.

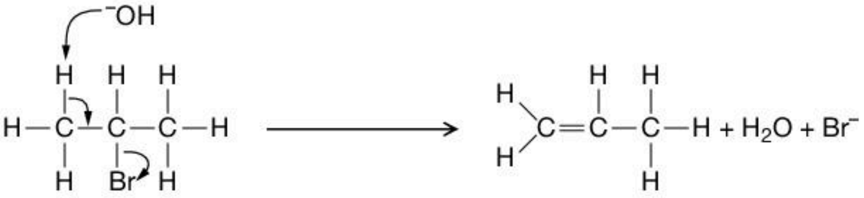
$$CH_3CH_2Br + {}^-OH \longrightarrow CH_2{=}CH_2 + H_2O + Br^-$$

In elimination reactions, the ^-OH ion acts as a base:

Worked example

Draw the reaction mechanism to show how a hydroxide dissolved in ethanol reacts with 2-bromopropane.

Answer



Common error

Some candidates show the ⁻OH ion approaching the halogenoalkane from the wrong side of the molecule. The ⁻OH ion is repelled by the halogen atom, so it approaches from the opposite side of the molecule, as shown above.

Relative strength of the C–X bond

Different halogenoalkanes have different reactivities. For a given alkyl group, the iodo compound reacts most readily and the fluoro compound reacts least readily. The C—X **bond energies**, listed in Table 16.2, explain this trend (X represents a halogen atom).

▼ **Table 16.2** C–X bond strengths

Bond	Bond energy / kJ mol^{-1}
C—F	484
C—Cl	338
C—Br	276
C—I	238

Key term

Bond energy: the bond energy of a bond in a given compound is the energy required to break one mole of those bonds under standard conditions in the gas state. Bond energy values are endothermic.

Link

There is more about bond energies in Unit 5, Chemical energetics.

Using halogenoalkanes

Fluoroalkanes are **inert** (unreactive). They are non-toxic and do not catch fire easily. They are used in refrigerants and to propel aerosols.

Chlorofluorocarbons have similar properties to fluoroalkanes. In the past, they were also used as refrigerants and to propel aerosols. However, high in the atmosphere ultraviolet radiation makes C—Cl bonds break. The resulting Cl• free radicals initiate a series of reactions that destroy ozone, O_3, molecules. The **ozone layer** is important because it protects us from harmful ultraviolet radiation from the Sun.

Key terms

Inert: chemically unreactive.

Ozone layer: a region high in the Earth's atmosphere that has a high concentration of ozone, O_3. The ozone layer absorbs harmful ultraviolet radiation from the Sun.

Practical skills

Using a water bath

In some chemical reactions, solutions need to reach, or be kept at, a certain temperature. Test tubes containing the solutions can be placed in a thermostatically controlled water bath. After a while, the solutions reach the same temperature as the water bath.

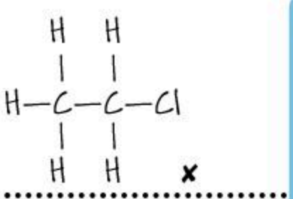
Link

The Raise your grade question refers to a water bath.

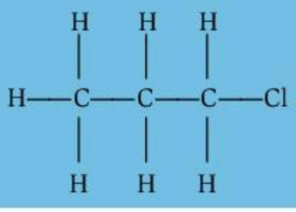
Raise your grade

1 Primary halogenolakanes undergo hydrolysis reactions when heated with water or solutions containing water.

(a) Draw the structural formula of 1-chloropropane. [1]


✗

This formula is incorrect, since 1-chloropropane has three carbon atoms, not two. The correct formula is shown below.



(b) Write an equation for the reaction of 1-chloropropane with water. [1]

$CH_3CH_2CH_2Cl + H_2O \rightarrow CH_3CH_2CH_2OH$ ✗

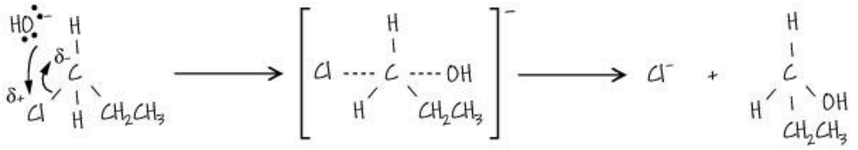
The formula of the organic product is correct, but the candidate did not give the other product, HCl (or H^+ and Cl^-).

Exam tip

When writing equations for organic reactions, always check that you have included all products, not just the organic one.

(c) The reaction proceeds by the S_N2 reaction mechanism.

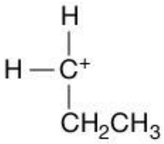
(i) Use curly arrows to show the reaction mechanism, including the transition state. [4]


✓✗✗✗

The candidate achieves one of the four marks for this question. The first part of the mechanism has three mistakes – the δ+ sign should be on the carbon atom and the δ- sign on the chlorine atom, since chlorine is more electronegative than carbon. Also, the OH^- ion attacks the δ+ carbon atom from the opposite side of the molecule to the chlorine atom, so as to reduce the repulsive forces between the nucleophile and the δ- charge on the chlorine atom. Finally, the left-hand curly arrow should start at the negative charge on the OH^- ion.

(ii) Explain why the reaction does not proceed by the S_N1 mechanism. [2]

The intermediate carbocation would have the structure below.



This is not stable since there is only one alkyl group to donate charge towards the positively charged carbon atom by the positive inductive effect. ✓✓

(d) A student does an investigation to compare the rates of reaction of 1-chloropropane, 1-bromopropane and 1-iodopropane.

He places two drops of each halogenoalkane in separate test tubes, and adds 1 cm^3 of ethanol. He measures out 1 cm^3 of silver nitrate solution into three separate test tubes.

He places all six test tubes in a water bath at 60 °C, and waits until their contents reach 60 °C.

He then quickly adds aqueous silver nitrate to each of the halogenoalkane solutions at the same time.

The table shows the student's observations.

Compound	Observations
1-chloropropane	white precipitate forms slowly
1-bromopropane	cream precipitate forms, quicker than for 1-chloropropane but slower than for 1-iodopropane
1-iodopropane	yellow precipitate forms immediately

(i) Suggest the purpose of the ethanol. [1]

as a solvent ✗

This answer is partly correct, but the student needs to mention that halogenoalkanes are not soluble in water.

(ii) Explain why the test tubes and their contents are placed in a water bath at 60°C. [1]

so that they are the correct temperature ✗

Again, this answer is incomplete. The students needs to mention that all the reactions happen too slowly to conveniently compare at room temperature.

(iii) Name the nucleophile in the reaction, and state which reagent it comes from. [1]

water, from the silver nitrate solution ✓

(iv) Give the name of the substance that forms as a white precipitate. [1]

silver chloride ✓

This answer is correct – the student has correctly applied knowledge from Unit 11.

(v) Write an ionic equation, with state symbols, to show how the white precipitate forms. [1]

$Ag^+ + Cl^- \rightarrow AgCl$ ✗

The student does not gain the mark for this question since she has not included the state symbols, which the question asks for.

★ Exam tip

Read exam questions carefully, and make sure you do everything that is asked of you.

(vi) Explain why the student adds silver nitrate solution to each halogenoalkane solution at the same time. [1]

To make it fair. ✗

This answer is partly correct, but needs more detail. The candidate should amend her answer to:

The student adds silver nitrate solution to each halogenoalkane at the same time so that he can compare the time for the precipitates to form.

(vii) Explain the relative relative rates of formation of the three precipitates. [2]

Bond energies of C–Cl, C–Br and C–I are different. ✓✗

The answer is partly correct, but incomplete. The candidate needs to add that bond energy decreases from C—Cl to C—Br and C—I. This means that least energy is required to break the C—I bond, so the reaction of 1-iodopropane is quickest.

Exam-style questions

Choose your answer to questions 1, 2 and 3 by selecting on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

1 Which products can be made in a single step by a nucleophilic substitution reaction of 1-bromobutane? [1]

1 $CH_3CH_2CH_2CN$

2 $CH_3CH_2CH_2CH_2OH$

3 $CH_3CH_2CH_2CH_2NH_2$

2 Which statements describe part of the S_N2 reaction mechanism? [1]

1 A nucleophile approaches the carbon attached to the halogen atom on the same side of the molecule as the halogen atom.

2 A lone pair of electrons on the nucleophile is donated to a $\delta+$ carbon atom.

3 As a bond forms between the nucleophile and the $\delta+$ carbon atom, the carbon–halogen bond breaks.

3 Which statements about chlorofluoroalkanes are correct? [1]

1 Their C—Cl bonds can break in the presence of ultraviolet radiation to make Cl• radicals.

2 They are non-flammable and non-toxic.

3 In the past, they were used as aerosol propellants.

4 Which substances below always, or sometimes, react with OH^- via the S_N1 reaction mechanism?

1 1-bromobutane

2 2-bromobutane

3 2-bromo-2-methylbutane

5 This question is about 2-bromobutane.

(a) Draw the displayed and skeletal formulae of 2-bromobutane. [2]

(b) **(i)** On your displayed formula, circle the polar bond. [1]

(ii) Explain why this bond is polar. [1]

(c) 2-bromobutane reacts with sodium hydroxide dissolved in ethanol.

(i) Draw the structural formulae of the two organic products of the reaction. [2]

(ii) Give the names of the organic products. [2]

(iii) Name the mechanism of the reaction. [1]

(iv) Use curly arrows to show the mechanism of the reaction that makes one of the products you named in part **(ii)**. [2]

(d) 2-bromobutane reacts with aqueous sodium hydroxide by a nucleophilic substitution reaction.

(i) Explain what is meant by the term *nucleophile*. [1]

(ii) Give the formula of the nucleophile in the reaction. [1]

(iii) The reaction proceeds via a mixture of the S_N1 and S_N2 mechanisms. Draw the intermediate formed in the S_N1 reaction. [1]

(e) 2-iodobutane also reacts with aqueous sodium hydroxide.

(i) Predict whether the reaction occurs slower or faster than the reaction of 2-bromobutane with aqueous sodium hydroxide. [1]

(ii) Explain your prediction. [1]

17 Hydroxy compounds

AS 17.1–17.5 pages 330–339
A 19.3 pages 360–363;
19.5 pages 365–367; 26.10–26.11
pages 499–502

Key points

☐ Describe the chemistry of alcohols, including these reactions:
  - combustion
  - substitution to give halogenoalkanes
  - reaction with sodium
  - oxidation to carbonyls and carboxylic acids
  - dehydration to alkenes
  - reactions with carboxylic acids to form esters
  - reaction with acyl chlorides to form esters

☐ Classify alcohols as primary, secondary or tertiary and suggest how to distinguish them.

☐ Describe reactions of phenol, including these reactions:
  - with bases
  - with sodium
  - with diazonium salts
  - nitration and bromination of the benzene ring.

☐ Explain the relative acidities of water, ethanol and phenol.

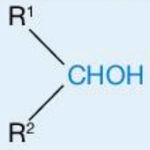
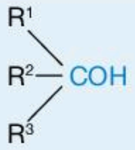
Primary, secondary and tertiary alcohols

Alcohols are **aliphatic compounds** that contain the hydroxy functional group, —OH. Table 17.1 gives examples of primary, secondary and tertiary alcohols.

Key term

Aliphatic compound: a compound in which carbon atoms are joined to each other in straight or branched chains.

▼ **Table 17.1** Primary, secondary and tertiary alcohols

Type of alcohol	General formula (R^1, R^2 and R^3 are alkyl groups and R is an H atom or an alkyl group)	Example
Primary	RCH_2OH	propan-1-ol
Secondary		propan-2-ol
Tertiary		2-methylpropan-2-ol

Worked example

Classify the alcohols below as primary, secondary or tertiary, and give their names.

a) $CH_3CH_2CH(OH)CH_2CH_3$

b) $(CH_3CH_2)_3COH$

Answer

a) secondary alcohol, pentan-3-ol

b) tertiary alcohol, 3-ethylpentan-3-ol

★ Exam tip

When given formulae in the format shown in the worked example, it helps to draw displayed formulae first, to help you to work out the answer.

Combustion reactions

Alcohols react with oxygen in combustion reactions. The reactions are exothermic, so alcohols are useful as fuels.

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Worked example

Write a balanced equation for the complete combustion of propan-1-ol.

Answer

$2CH_3CH_2CH_2OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$

Common error

Candidates often balance alcohol combustion equations incorrectly. Remember to include the oxygen atom in the alcohol molecule, as well as those in the O_2 molecules.

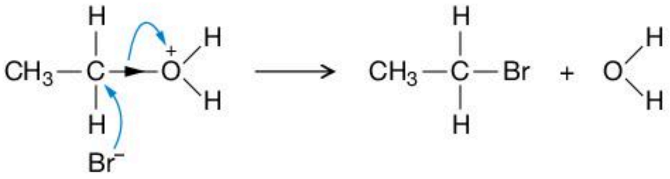
Substitution reactions

In substitution reactions, a halogen atom replaces the hydroxy group. The products are halogenoalkanes. There are several ways of doing these reactions, including:

- Heating with a mixture of the sodium halide (e.g. NaBr) and concentrated sulfuric acid. This makes the hydrogen halide, which reacts with the alcohol. For example:

$$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$$

First, H^+ joins to the oxygen atom. Then the second part of the reaction, shown below, takes place:



- Reacting with liquid phosphorus trichloride, PCl_3, or with a mixture of phosphorus and bromine or iodine. The phosphorus and halogen react together before reacting with the alcohol. For example:

$$3CH_3CH_2OH + PBr_3 \rightarrow 3CH_3CH_2Br + H_3PO_3$$

- Reacting with $SOCl_2$, for example:

$$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$$

Worked example

Write an equation for the reaction of propan-2-ol with a mixture of phosphorus and bromine.

Answer

$3CH_3CHOHCH_3 + PBr_3 \rightarrow 3CH_3CHBrCH_3 + H_3PO_3$

Reactions with sodium

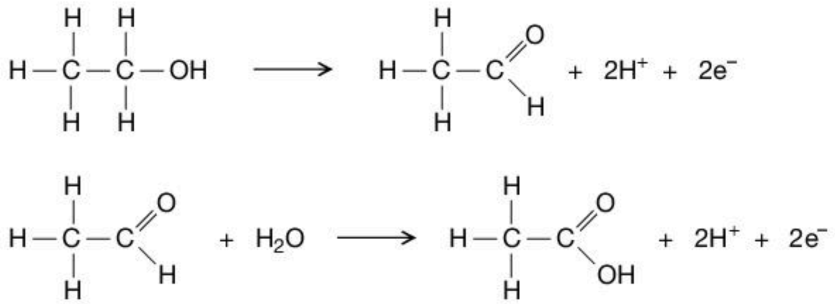
Ethanol reacts steadily with sodium to make a salt, sodium ethoxide, and hydrogen gas.

$$2Na + 2CH_3CH_2OH \rightarrow 2CH_3CH_2ONa + H_2$$

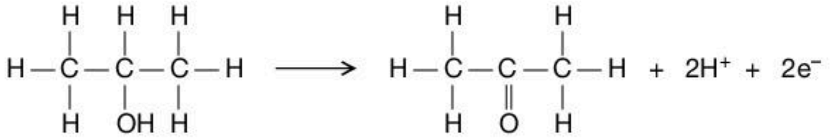
Oxidation reactions

Primary and secondary alcohols are oxidised by heating with acidified potassium dichromate(VI), $Cr_2O_7^{2-}$:

- A primary alcohol forms an aldehyde, which is further oxidised to a carboxylic acid:



- A secondary alcohol forms a ketone:



In all the half-equations shown above, the electrons are accepted by the oxidising agent.

Chemical tests

Potassium dichromate(vi) is orange. It makes green Cr^{3+} when it is reduced in reactions with alcohols.

Practical skills

To obtain an aldehyde from the oxidation of an alcohol, the aldehyde is removed from the mixture by distillation as it is formed. To obtain the carboxylic acid, the reacting mixture is heated under reflux.

Worked example

Alcohol X is heated under reflux with acidified potassium dichromate. There is a colour change from orange to green. Alcohol Y is heated under reflux with acidified potassium dichromate. No colour change is observed. State what the observations tell you about the nature of alcohols X and Y.

Answer

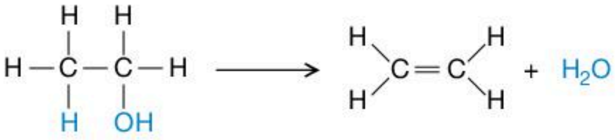
Alcohol Y is not oxidised, so it must be a tertiary alcohol. Alcohol X is oxidised, so it must be a primary or secondary alcohol.

Remember

Oxidation reactions can be used to distinguish between primary, secondary and tertiary alcohols.

Dehydration reactions

Alcohols are **dehydrated** in elimination reactions. The products are alkenes. The reactions occur when an alcohol is heated at 170 °C with excess concentrated sulfuric acid:

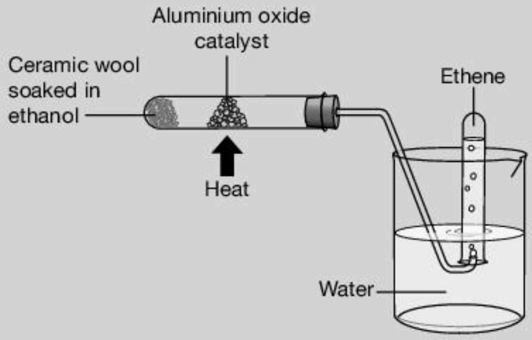


Key term

Dehydration: in a dehydration reaction, a water molecule is lost from the reacting molecule.

Practical skills

You can also dehydrate an alcohol by passing the alcohol vapour over a catalyst. The alkene is collected over water.



▲ **Figure 17.1** Dehydration of an alcohol

Worked example

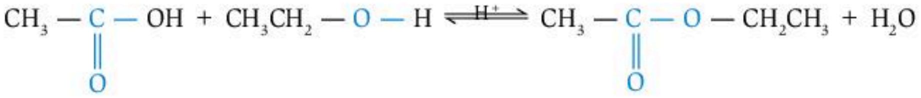
Explain why you must remove the delivery tube from the water (Figure 17.1) before you stop heating the catalyst.

Answer

As the hot test tube cools, the pressure inside it decreases. Cold water from the beaker would quickly enter the hot test tube, which would cool very quickly and break.

Esterification reactions

In the presence of concentrated sulfuric acid, alcohols react with carboxylic acids to make esters. It is the O—H bond in the alcohol that breaks.



$$CH_3-\underset{\underset{O}{\|}}{C}-OH + CH_3CH_2-O-H \xrightleftharpoons{H^+} CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2CH_3 + H_2O$$

ethanoic acid ethanol ethyl ethanoate (an ester)

Remember

When naming an ester, the alcohol gives the ester the first part of its name, and the carboxylic acid gives the ester the second part of its name.

Worked example

Write an equation for the reaction of methanol with propanoic acid. Give the name and structural formula of the ester formed.

Answer

$$CH_3CH_2-\underset{\underset{O}{\|}}{C}-OH + CH_3-O-H \rightleftharpoons CH_3CH_2-\underset{\underset{O}{\|}}{C}-O-CH_3 + H_2O$$

The name of the ester is methyl propanoate.

An ester is also made when an alcohol reacts with an acyl chloride. For example:

$$CH_3-\underset{\underset{O}{\|}}{C}-Cl + CH_3CH_2-O-H \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2CH_3 + HCl$$

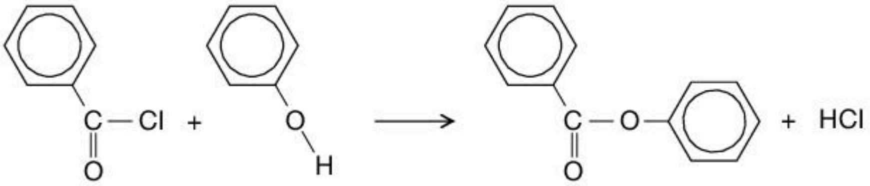
Link

Unit 19, Carboxylic acids and derivatives, describes how to make a small amount of an ester in the laboratory.

Worked example

Write an equation to show how phenyl benzoate is formed from benzoyl chloride in an esterification reaction. Include structural formulae.

Answer



★ **Exam tip**

Remember to include both products in **esterification reactions**, and to check that the equation is balanced.

Key term

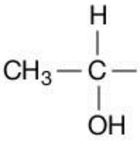
Esterification reaction: in an esterification reaction an ester is formed from an alcohol and a carboxylic acid or acyl chloride.

Distinguishing alcohols

Oxidation reactions

Primary and secondary alcohols are oxidised by acidified dichromate(VI) solution. Tertiary alcohols are not.

The tri-iodomethane reaction



If an alcohol has the $CH_3CH(OH)$— group in it (as shown on the right), it reacts with aqueous alkaline iodine to form tri-iodomethane, CHI_3. The compound forms as a yellow crystalline precipitate. The other organic product is a salt, such as sodium ethoxide, $CH_3CH_2O^-Na^+$.

Link

In Unit 18, Carbonyl compounds, you will learn that ethanal, and some ketones, also react with aqueous alkaline iodine to form tri-iodomethane.

Chemical tests

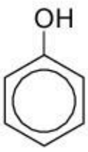
The tri-iodomethane reaction is a useful test for compounds containing the $CH_3CH(OH)$— group and the CH_3CO— group.

Phenol

Phenol has a hydroxy group attached to an aromatic ring. It is a stronger acid than ethanol and water (Table 17.2).

▼ **Table 17.2** Acid dissociation constants

Compound	K_a /mol dm^{-3}
Phenol	1.3×10^{-10}
Water	3.2×10^{-16}
Ethanol	1.3×10^{-16}

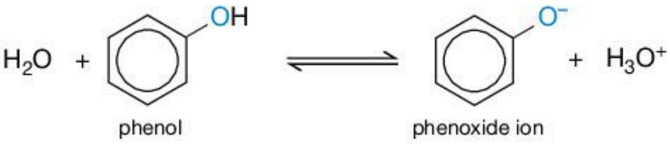


Worked example

Explain why phenol is a stronger acid than ethanol.

Answer

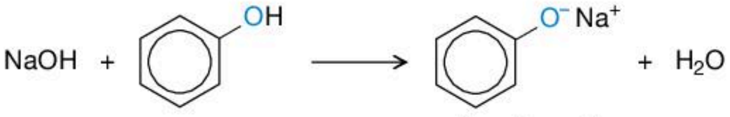
When phenol dissolves in water, some of its molecules ionise. The phenoxide ion is stabilised because the negative charge is delocalised around the π electron system in the ring. This shifts the equilibrium to the right compared to the equivalent equilibrium for ethanol.



Reactions of phenol

Reactions with bases

Phenol reacts with sodium hydroxide:

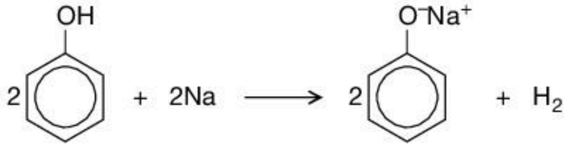


sodium phenoxide

However, phenol does not react with sodium carbonate, as it is too weak an acid.

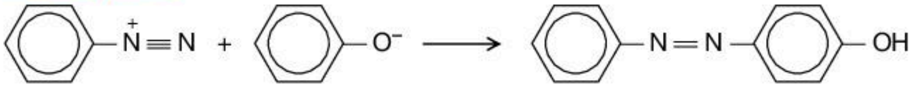
Reaction with sodium

Phenol reacts slowly with sodium to give hydrogen and sodium phenoxide.



Reactions with diazonium salts

A cold solution of phenol in sodium hydroxide reacts with a solution containing benzenediazonium ions to make an orange precipitate called an **azo compound**.



Key term

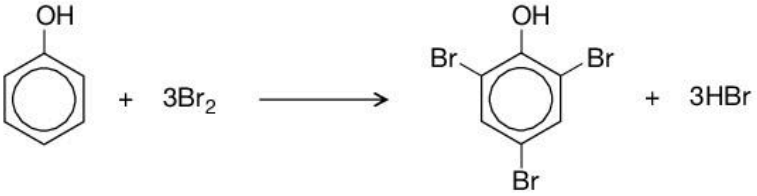
Azo compound: an azo compound has the functional group R—N=N—R′. R and R′ can be alkyl or aryl groups.

Exam tip

Make sure you can draw the structure of azo compounds. The coupling always occurs at the 4-position, opposite the —OH group.

Nitration and bromination of the aromatic ring

Bromine water reacts with an aqueous solution of phenol to make 2,4,6-tribromophenol.



2,4,6-tribromophenol

Worked example

Describe what you would observe when bromine water is added to aqueous phenol.

Answer

The brown bromine water is decolorised, and a white precipitate forms.

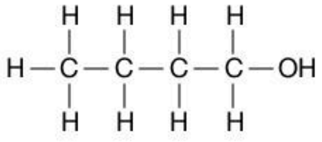
Nitration also occurs at the 2, 4 and 6 positions:

- Dilute nitric acid makes a mixture of 2- and 4-nitrophenol.
- A mixture of concentrated HNO_3 and H_2SO_4 makes 2,4,6-trinitrophenol.

Raise your grade

1 This question is about alcohols with the molecular formula $C_4H_{10}O$.

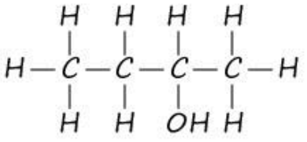
(a) Draw a different displayed formula in each box for alcohols with the molecular formula $C_4H_{10}O$. Box A is already completed. [3]



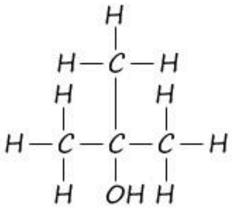
A a primary alcohol

$(CH_3)_2CHCH_2OH$

B a primary alcohol ✘



C a secondary alcohol ✔



D a tertiary alcohol ✔

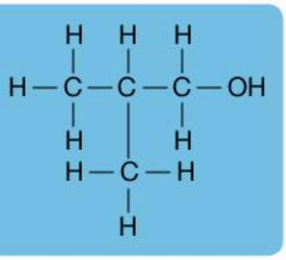
The candidate has drawn two of the displayed formulae correctly. The formula in box B is correct, but it is not a displayed formula, so does not achieve the mark.

(b) Give the names of alcohols A and B. [2]

Name of alcohol A butan-1-ol ✔

Name of alcohol B 2-methylbutan-1-ol ✘

The correct name is 2-methylpropan-1-ol. This is easier to work out from the displayed formula.



(c) Give the letter of an alcohol which is **not** oxidised by acidified potassium dichromate(VI). [1]

B ✘

Since B is a primary alcohol, it is oxidised to an aldehyde by acidified potassium dichromate(VI). The correct answer is D, since tertiary alcohols are not oxidised under these conditions.

★ Exam tip

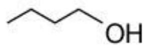
When a word in a question is written in bold, the word is important.

(d) Give the letter of an alcohol which is oxidised to form a ketone, and give the name of the ketone formed. [2]

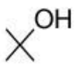
C ✔✘

This answer is correct. Secondary alcohols are oxidised to form ketones. The name of the ketone, butanone, is also needed.

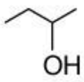
(e) Draw skeletal formulae for alcohols **A**, **B** and **C**. [3]



Skeletal formula of **A** ✔

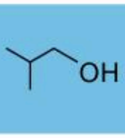


Skeletal formula of **B** ✘



Skeletal formula of **C** ✔

The skeletal formula for **B** is incorrect – it shows the skeletal formula for alcohol **D**. The correct answer is given on the right. There is a carbon atom at the end of each line and where the lines meet or bend.



Exam-style questions

1 Compound **X** produces a ketone when heated under reflux with acidified potassium dichromate(VI). Compound **X** does not react with aqueous alkaline iodine.

What could be the identity of compound **X**?

A methanol

B ethanol

C propan-2-ol

D pentan-3-ol

Exam tip

If you cannot spot the correct answer straight away, start by crossing out the answers that are definitely wrong.

2 An alcohol reacts with a carboxylic acid to make an ester with the formula $C_3H_7COOC_3H_7$.

What could be the identities of the alcohol and carboxylic acid?

A propan-1-ol and propanoic acid

B butan-1-ol and butanoic acid

C butan-1-ol and propanoic acid

D propan-1-ol and butanoic acid

3 Butyl pentanoate is used to flavour foods.

It is formed when compounds X and Y are heated together with concentrated sulfuric acid.

What could be the identities of X and Y?

A pentan-1-ol and butanoic acid

B pentan-2-ol and butanoic acid

C butan-1-ol and pentanoic acid

D butan-2-ol and pentanoic acid

4 An alcohol, C_3H_7OH, reacted with excess oxygen in a combustion reaction.

The reaction produced 130 dm^3 of carbon dioxide gas under room conditions.

(a) Write an equation for the reaction. [1]

(b) Calculate the mass of alcohol that reacted. [4]

Exam tip

The molar volume of gas is given in the data booklet.

5 This question is about the reactions of butan-1-ol.

(a) Write an equation for the reaction of sodium with butan-1-ol, and name the salt formed. [2]

(b) Ethanoic acid reacts with butan-1-ol.

(i) Write an equation for the reaction. [1]

(ii) Name the organic product of the reaction. [1]

(iii) State the conditions required for the reaction. [1]

6 This question is about the reactions of pentan-2-ol.

(a) **(i)** Draw the displayed formulae of the two structural isomers that are formed when pentan-2-ol is heated to 170 °C with excess concentrated sulfuric acid. [2]

(ii) Give the names of the isomers formed in part **(i)**. [2]

(b) **(i)** Name the reagents required to make 2-bromopentane from pentan-2-ol. [1]

(ii) Draw the skeletal formula of 2-bromopentane. [1]

(c) **(i)** Name the product formed when pentan-2-ol is warmed with acidified potassium dichromate(VI) solution. [1]

(ii) Describe an observation that would be made in the reaction in part **(i)**. [1]

7 This question is about phenol and its reactions.

(a) Explain why phenol is more acidic than ethanol. [2]

(b) Write equations for the reactions of phenol with:

(i) sodium [1]

(ii) sodium hydroxide. [1]

(c) Draw the structural formulae and give the names of the products formed in the nitration reactions of phenol with:

(i) dilute nitric acid [2]

(ii) a mixture of concentrated nitric acid and concentrated sulfuric acid. [1]

18 Carbonyl compounds

AS 18.1–18.7 pages 342–353

Key points

- ☐ Describe the formation of aldehydes and ketones.
- ☐ Describe reactions of aldehydes and ketones, including
  - reduction reactions
  - reactions with HCN and NaCN.
- ☐ Describe the mechanism of nucleophilic addition reactions.
- ☐ Describe tests for carbonyl compounds, including
  - 2,4-dinitrophenylhydrazine
  - reactions with Fehling's and Tollens' reagents
  - ease of oxidation
  - reactions with aqueous iodine.

Making aldehydes and ketones

Aldehydes are made by oxidising primary alcohols. Ketones are made by oxidising secondary alcohols. The oxidising agent is acidified potassium dichromate(VI), $Cr_2O_7^{2-}$ solution. Aldehydes and ketones both contain a **carbonyl group, C═O**.

Key term

Carbonyl group, C═O: in an aldehyde the carbonyl group is at the end of the carbon chain, and in a ketone the carbonyl group is not at the end of the chain.

Link

The equations for the oxidation of alcohols to make aldehydes and ketones are shown in Unit 17, Hydroxy compounds.

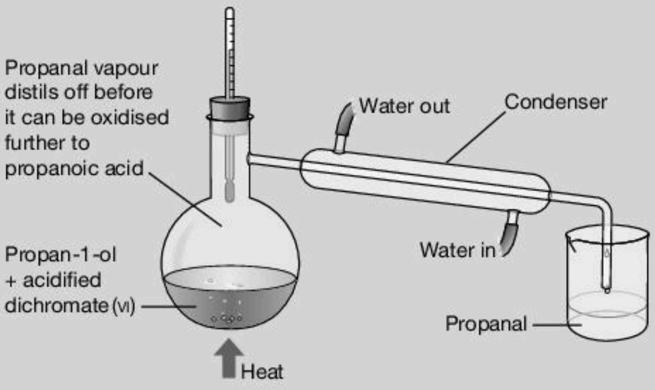
★ Exam tip

You can simplify equations involving oxidising agents in organic reactions by representing the oxidising agent as [O]. For example:

$$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$$

Practical skills

The apparatus shown in Figure 18.1 is used to prepare propanal from propan-1-ol.



▲ **Figure 18.1** Preparation of propanal

Worked example

Describe and explain the colour change in the flask in Figure 18.1 as a carbonyl compound is formed from an alcohol.

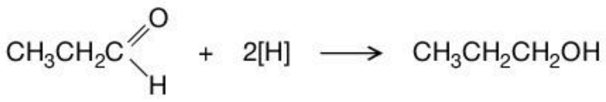
Answer

Dichromate(VI) ions are orange. They are reduced to green Cr^{3+} ions when they oxidise the alcohol.

Reduction reactions of aldehydes and ketones

$LiAlH_4$ and $NaBH_4$ reduce carbonyl compounds to alcohols.

$LiAlH_4$ is the more powerful of the two reducing agents – it also reduces carboxylic acids, esters and amides. In equations, you can show the hydrogen atoms in square brackets:



$$CH_3CH_2CHO + 2[H] \longrightarrow CH_3CH_2CH_2OH$$

Remember

The conditions for the two reducing agents are different:

- $LiAlH_4$ is dissolved in dry ethoxyethane.
- $NaBH_4$ is dissolved in a mixture of water and methanol.

Worked example

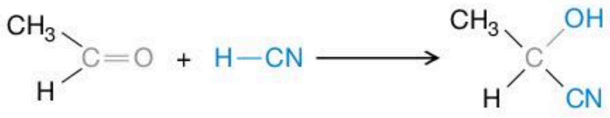
Name the product formed when butanone is reduced by $LiAlH_4$, and state whether the product is a primary, secondary or tertiary alcohol.

Answer

The product is butan-2-ol, which is a secondary alcohol.

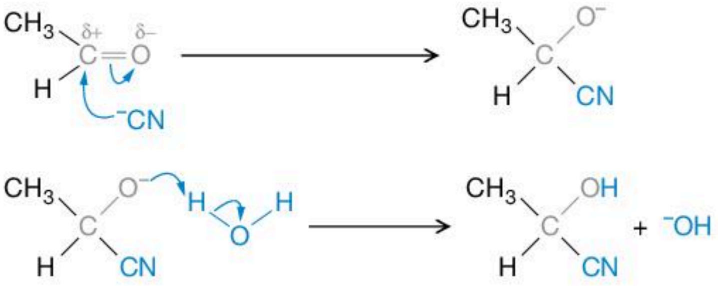
Addition reactions of aldehydes and ketones

Aldehydes and ketones take part in nucleophilic addition reactions. For example:



The reaction with hydrogen cyanide to make a nitrile is useful because it increases the length of the carbon chain.

There are two steps in the reaction mechanism for nucleophilic addition reactions:



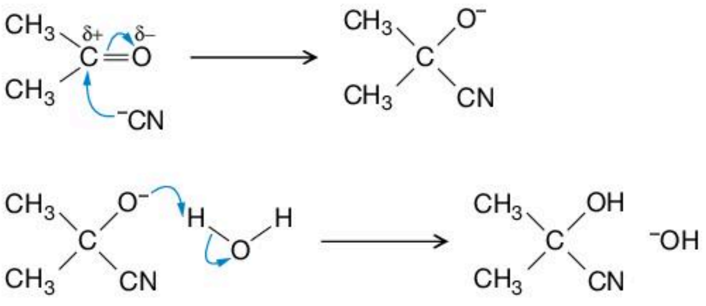
Common error

Candidates sometimes show curly arrows incorrectly. The arrow head shows where electrons are moving to. The other end of the arrow shows where the electrons are coming from.

Worked example

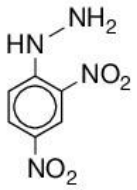
Draw the reaction mechanism for the nucleophilic addition reaction of propanone with HCN in the presence of NaCN and H_2O.

Answer



Detecting carbonyl compounds

The addition of 2,4-dinitrophenylhydrazine (2,4-DNPH) to a carbonyl compound results in the formation of an orange or yellow precipitate. This is a useful test for carbonyl compounds.



▲ **Figure 18.2** The formula of 2,4-dinitrophenylhydrazine

Exam tip

Learn the formulae of organic reagents, and make sure you write them correctly.

Distinguishing aldehydes and ketones

Aldehydes are oxidised to carboxylic acids by acidified dichromate(VI), as well as by Fehling's reagent and Tollens' reagent (Table 18.1). Ketones do not react with these reagents.

Chemical tests

Fehling's and Tollens' reagents, and acidified dichromate(VI), distinguish between aldehydes and ketones.

▼ **Table 18.1** Testing for aldehydes and ketones

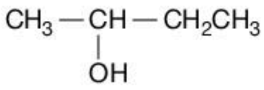
Reagent	Products with aldehyde	Observations
Acidified dichromate(VI)	carboxylic acid and Cr^{3+}	Orange solution to green solution
Tollens' (complex of Ag^{+})	carboxylic acid and Ag	Colourless solution to silver mirror
Fehling's (complex of Cu^{2+})	carboxylic acid and Cu_2O	Blue solution to red precipitate

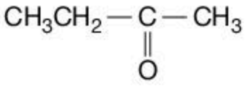
Reaction with tri-iodomethane

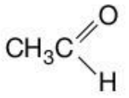
Ethanal and propanone, and other methyl ketones, contain the CH_3CO— group. This means that they react with aqueous alkaline iodine to form tri-iodomethane, which is a yellow crystalline precipitate.

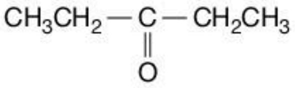
Worked example

Which of the following substances react with aqueous alkaline iodine to form tri-iodomethane?

A

$CH_3-CH(OH)-CH_2CH_3$

B

$CH_3CH_2-C(=O)-CH_3$

C

CH_3CHO

D

$CH_3CH_2-C(=O)-CH_2CH_3$

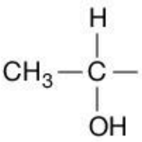
E CH_3CH_2OH

Answer

A, B, C and E react with aqueous alkaline iodine to form tri-iodomethane.

Link

Unit 17, Hydroxy compounds, describes how alcohols with the group shown below also form tri-iodomethane with aqueous alkaline iodine.

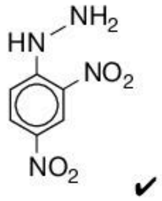

$CH_3-CH(OH)-$

Raise your grade

1 Compound **X** is made up of atoms of carbon, hydrogen and oxygen.

On reacting **X** with 2,4-DNPH an orange precipitate was formed. A separate sample of **X** reacted with Fehling's solution to form a red precipitate. A third sample of **X** reacted with aqueous alkaline iodine to form a yellow precipitate.

(a) Draw the structural formula of 2,4-DNPH and give its full name. [2]



2,4-dinitrophenylhydrogen ✘

The candidate has correctly drawn the formula of the reagent. However, the name given is incorrect – it should be 2,4-dinitrophenylhydrazine.

★ **Exam tip**

It is vital to learn names and formulae of reagents correctly.

(b) Name and give the formula of

(i) the red precipitate [2]

Copper oxide ✘

Cu_2O ✔

The formula is correct.
The name does not include the oxidation number of copper, so is incorrect. The correct name is copper(I) oxide.

(ii) the yellow precipitate. [2]

CHI_3 ✔

Iodomethane ✘

The formula is correct, but the name is incorrect. Since there are three iodine atoms joined to the central carbon atom, the name is tri-iodomethane.

★ **Exam tip**

Remember to apply naming rules to all formulae.

(c) Give the name and structural formula of compound **X** and explain in detail how you worked it out. [5]

X reacts with 2,4-DNPH so it must be an aldehyde or ketone. ✔

X reacts with Fehling's solution so it must be a ketone. ✘

The candidate has got confused here. Aldehydes react with Fehling's solution. Ketones do not.

X has a positive test with aqueous alkaline iodine, so it must include the CH_3CO— group or the CH_3CHOH— group. ✔

The candidate has correctly learned this fact.

The compound is a ketone with the CH_3CO— group, so it must be propanone. ✘

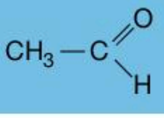
There are many ketones that include the CH_3O— group, not just propanone. For this reason, the candidate did not achieve the mark, even though the first part of the answer follows logically from their earlier reasoning.

Compound X must be ethanal, the only aldehyde that reacts with aqueous alkaline iodine.

The formula of propanone is C_3H_6O. ✘

This is a molecular formula. Since the question asked for a structural formula, no mark is awarded here.

The structural formula of ethanal is



CH_3-CHO

Exam tip

Read questions carefully to avoid losing marks unnecessarily.

(d) Calculate the relative molecular mass of compound **X**. [1]

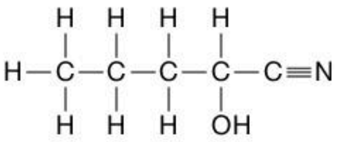
$(3 \times 12) + (6 \times 1) + 16 = 58$ ✔ ecf

The candidate has achieved the mark here, since they correctly calculated the relative molecular mass of the compound they identified as X. The initials ecf stand for ‘error carried forward’.

The relative molecular mass of ethanal (the correct identity of compound X) is:

$$(2 \times 12.0) + (4 \times 1.0) + 16.0 = 46.0$$

(e) Compound **Y** is also made up of atoms of carbon, hydrogen and oxygen.
On reacting **Y** with HCN the product with the formula shown below was formed.



$CH_3CH_2CH_2CH(OH)C\equiv N$

(i) Give the conditions required for the reaction to occur. [1]

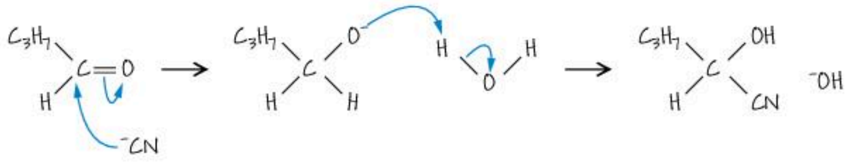
a mixture of HCN and NaCN dissolved in water ✔

(ii) Give the name and structural formula of compound Y. [2]

Y is pentan-2-one. ✘

Y is actually butanal. Of the five carbon atoms in the product, one has come from a CN$^-$ ion and the other four from the starting material, butanone.

(iii) Show the mechanism for the reaction of Y with HCN. [4]



✔✔ ✔✔

The candidate has correctly written the mechanism for the reaction, and achieved full marks.

Exam-style questions

Choose your answer to questions 1 and 2 by selecting on the basis of:

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

Exam tip

As you read each answer, decide whether it is true or false. Put a tick by those which are true. When you have made decisions for each statement, choose the correct answer by using the table above.

1 Which substance or substances give a positive result with Tollens' reagent? [1]

1 $CH_3CH_2CH_2CHO$
2 $CH_3CH_2COCH_2CH_3$
3 $CH_3COCH_3CH_3$

2 Which substance or substances reduce carbonyl compounds to alcohols? [1]

1 $Cr_2O_7^{2-}/H^+$
2 $LiAlH_4$
3 $NaBH_4$

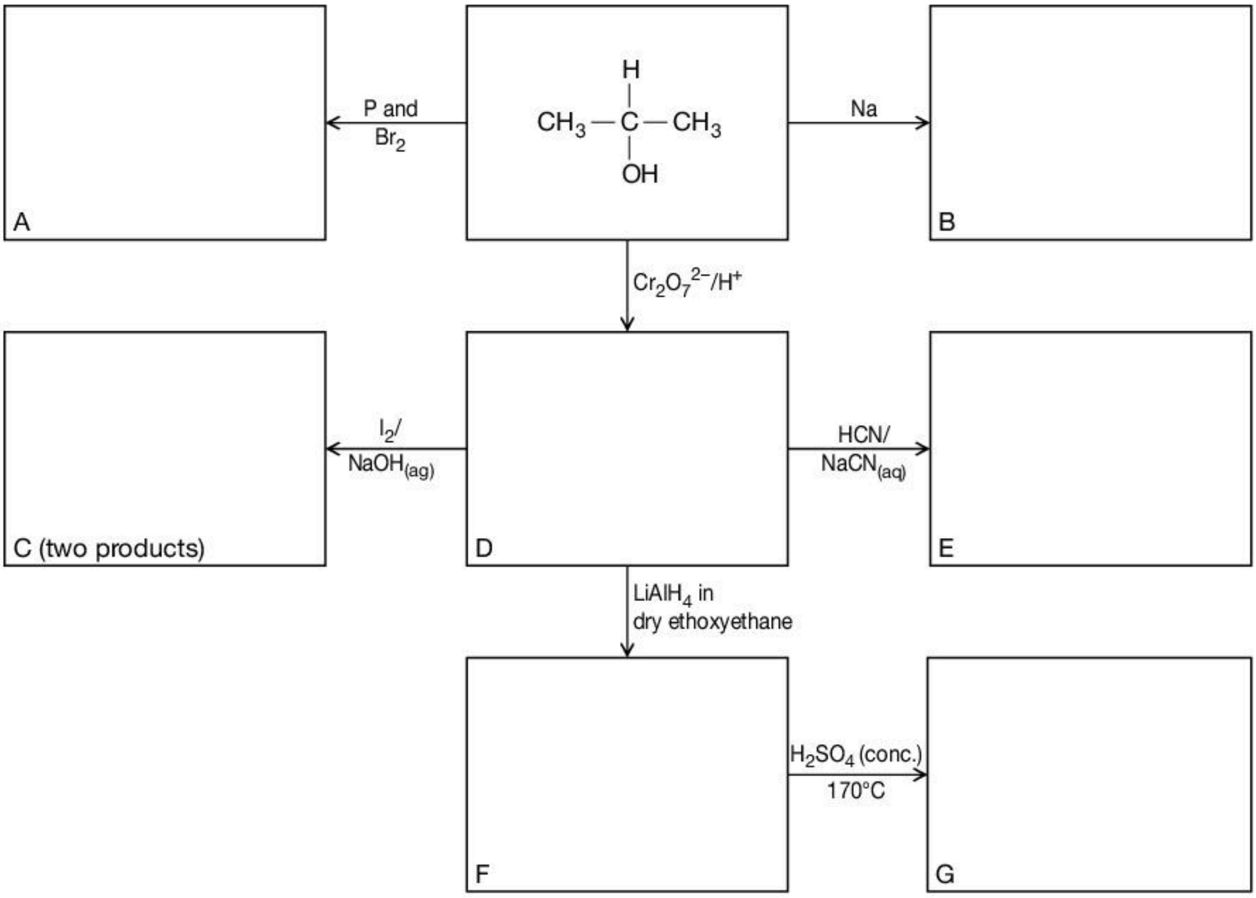
3 **(a)** Complete the reaction scheme below. In each empty box, write the **structural formula** of the organic compound that is formed. [8]

Exam tip

This question is testing knowledge from two topics: 17, Hydroxy compounds, and 18, Carbonyl compounds.

(b) State the names of the compounds listed below. [5]

Compound A
Compound B
Compound C (name of salt only)
Compound D
Compound G



19 Carboxylic acids and derivatives

AS 19.1–19.3 pages 356–363
A 19.2 page 360; 19.4–19.5 pages 364–367

Key points

- ☐ Describe how to make carboxylic acids.
- ☐ Describe the reactions of carboxylic acids to make
  - salts
  - esters
  - alcohols
  - acyl chlorides.
- ☐ Know how to oxidise methanoic acid and ethanedioic acid.
- ☐ Explain relative acidities.
- ☐ Describe some reactions of acyl chlorides:
  - hydrolysis
  - with alcohols, phenols, ammonia and amines.
- ☐ Esters
  - describe hydrolysis
  - state some uses.

Making carboxylic acids

Carboxylic acids are made

- by oxidising alcohols and aldehydes
- in hydrolysis reactions, by heating nitriles with strong acids:

$$CH_3CN + 2H_2O + H^+ \rightarrow CH_3COOH + NH_4^+$$

Link

The oxidation reactions of alcohols are given in Unit 17, Hydroxy compounds, and the oxidation reactions of aldehydes are given in Unit 18, Carbonyl compounds.

Worked example

Write equations for the two steps needed to make propanoic acid from bromoethane. Give the conditions needed for both reactions.

Answer

- Step 1: $CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$
  Conditions – heat under reflux with a solution of potassium cyanide in ethanol.
- Step 2: $CH_3CH_2CN + 2H_2O + H^+ \rightarrow CH_3CH_2COOH + NH_4^+$
  Conditions – heat with strong acid.

Remember

Reactions with nitriles increase the length of the carbon chain.

Reactions of carboxylic acids

Carboxylic acids form salts with reactive metals, alkalis and carbonates. For example:

$$2CH_3COOH + Mg \rightarrow (CH_3COO^-)_2Mg^{2+} + H_2$$

The salts are ionic, and most are solid at room temperature.

Remember

An acid reacts with a metal to make a salt and hydrogen, and with an alkali to make a salt and water.

Worked example

Write equations to show the following reactions:

a) methanoic acid with sodium hydroxide

b) butanoic acid with calcium carbonate.

Answer

a) $HCOOH + NaOH \rightarrow HCOO^-Na^+ + H_2O$

b) $2C_3H_7COOH + CaCO_3 \rightarrow (C_3H_7COO^-)_2Ca + H_2O + CO_2$

Common error

Candidates sometimes write incorrect formulae for carboxylate salts. Remember that carboxylate ions have a charge of −1. The negative ion is written first in the formula, and then the positive ion.

Chemical tests

If you add a carbonate to an acid, you will notice bubbles of carbon dioxide gas.

Carboxylic acids react with alcohols to make esters. The reactions take place in the presence of concentrated sulfuric acid. The mixture must be heated.

Link

Esterification reactions are described in Unit 17, Hydroxy compounds.

Practical skills

You can carry out an esterification reaction by warming 2 cm^3 of ethanol, 1 cm^3 of glacial ethanoic acid and three drops of concentrated sulfuric acid in a test tube. Then pour the mixture into aqueous sodium carbonate and note the sweet smell of the ester.

Carboxylic acids are reduced to alcohols by $LiAlH_4$. The reactions are carried out in dry ethoxyethane at room temperature. Dilute sulfuric acid must then be added.

Common error

$NaBH_4$ is not a strong enough reducing agent to reduce carboxylic acids.

Exam tip

You can use a simplified equation to show the reduction reaction:

$$CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$$

Carboxylic acids make acyl chlorides in reactions with PCl_3, PCl_5 and $SOCl_2$. The equations for the reactions are:

1 $3CH_3COOH(aq) + PCl_3(s) \rightarrow 3CH_3COCl(l) + H_3PO_3(l)$

2 $CH_3COOH(aq) + PCl_5(l) \rightarrow CH_3COCl(l) + POCl_3(l) + HCl(g)$

3 $CH_3COOH(aq) + SOCl_2(l) \rightarrow CH_3COCl(l) + SO_2(g) + HCl(g)$

Link

Unit 17, Hydroxy compounds, describes how PCl_3 and $SOCl_2$ react with alcohols. The products of these reactions are chloroalkanes.

Worked example

Suggest one advantage of Reaction 3 for the preparation of ethanoyl chloride, compared with Reactions 1 and 2.

Answer

The by-products of Reaction 3 (sulfur dioxide and hydrogen chloride) form as gases, so can easily be separated from the desired product. In Reactions 1 and 2, the products must be separated by fractional distillation.

Exam tip

The question in the worked example asks you to **compare** the reactions. This means that you need to give an advantage of Reaction 3, and state why Reactions 1 and 2 do not have this same advantage.

Oxidising carboxylic acids

Methanoic acid is oxidised by Tollens' and Fehling's reagents:

$$HCOOH + [O] \rightarrow H_2O + CO_2$$

Link

Tollens' and Fehling's reagents also oxidise aldehydes. See Unit 18, Carbonyl compounds.

Worked example

Describe what you would observe on warming separate samples of methanoic acid with

a) Tollens' reagent

b) Fehling's reagent.

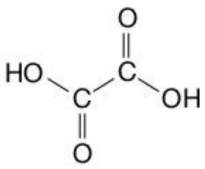
Answer

a) The colourless solution forms a silver mirror on the walls of the test tube.

b) The blue solution forms a red precipitate of copper(I) oxide, Cu_2O.

Ethanedioic acid is oxidised to carbon dioxide and water on heating with acidified $KMnO_4$:

$$(COOH)_2 + [O] \rightarrow H_2O + 2CO_2$$



▲ **Figure 19.1** The structure of ethanedioic acid

Practical skills

The reaction of ethanedioic acid with acidified potassium manganate(VII) is used to standardise potassium manganate(VII) solution.

Worked example

Write half-equations for the oxidation of ethanedioic acid and the reduction of manganate(VII) ions. Then combine the two half-equations to write a full equation for the reaction.

Answer

$$(COOH)_2 \rightarrow 2CO_2 + 2H^+ + 2e^-$$

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

$$2MnO_4^- + 5(COOH)_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Remember

When combining half-equations, multiply the balancing numbers of each equation so that the number of electrons is the same on both sides. In this case, the balancing numbers of the first half-equation are multiplied by 5 and the balancing numbers of the second half-equation are multiplied by 2.

Comparing acidities

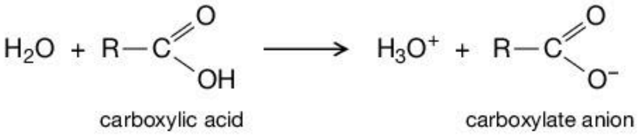
Relative acidities of carboxylic acids, phenols and alcohols

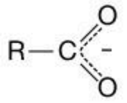
Carboxylic acids are stronger acids than phenols and alcohols (see Table 19.1).

▼ **Table 19.1** Acid dissociation constants

Compound	K_a/mol dm^{-3}
ethanoic acid	1.7×10^{-5}
phenol	1.3×10^{-10}
ethanol	1.3×10^{-16}

On dissociation in water, carboxylic acids make carboxylate ions:





The negative charge and double bond character are distributed over the whole carboxylate group. This delocalises the negative charge and stabilises the ion.

This means that the equilibrium below lies further to the right than the similar equilibria for phenols and alcohols:

$$RCOOH(aq) + H_2O(l) \rightleftharpoons RCOO^-(aq) + H_3O^+(aq)$$

Relative acidities of chlorine-substituted ethanoic acids

Chlorine-substituted ethanoic acids are stronger acids than ethanoic acid (Table 19.2). This is because chlorine atoms have an electron-withdrawing effect, so they reduce the negative charge density on the COO^- group of the carboxylate ion. This stabilises it and shifts the equilibrium to the right.

▼ **Table 19.2** Acid dissociation constants

Acid	Formula	K_a/mol dm^{-3}
ethanoic acid	CH_3COOH	1.7×10^{-5}
chloroethanoic acid	$CH_2ClCOOH$	1.3×10^{-3}
trichloroethanoic acid	Cl_3COOH	2.3×10^{-1}

Worked example

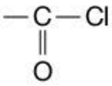
Which K_a value below is most likely to be the K_a value of dichloroethanoic acid? Use the values from Table 19.2 to explain your prediction.

5.0×10^{-4} mol dm^{-3} 5.0×10^{-2} mol dm^{-3} 5.0×10^{1} mol dm^{-3}

Answer

The K_a value is likely to be 5.0×10^{-2} mol dm^{-3} since this value is between those for chloroethanoic acid and trichloroethanoic acid. The magnitude of the electron-withdrawing inductive effect of two chlorine atoms is between that of one and three chlorine atoms.

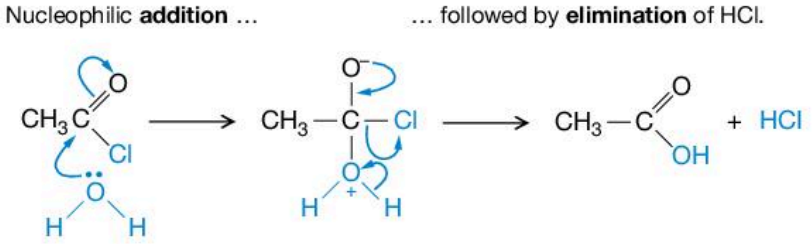
Reactions of acyl chlorides

Acyl chlorides include the group  $-\underset{\substack{\|\\O}}{C}-Cl$

There is a violent reaction when water is added to ethanoyl chloride:

$$CH_3COCl(l) + H_2O(l) \rightarrow CH_3COOH(aq) + HCl(g)$$

The mechanism of the reaction is nucleophilic addition–elimination.



The reaction is very vigorous because the carbon atom in the COCl group is very attractive to nucleophiles. For comparison, alkyl chlorides react very slowly with cold water, and aryl chlorides do not react with cold water.

Worked example

Explain why the C atom in a COCl group is more attractive to nucleophiles than the C atom in a C—Cl group.

Answer

O and Cl atoms are electronegative. In a COCl, both O and Cl atoms pull electrons in the bonds away from the carbon atom. In a C—Cl group, there is just one electronegative atom pulling electrons in the bond away from the carbon atom. This means that the C in the COCl has a greater δ+ charge than the C in the C—Cl group, so the C in COCl is more attractive to nucleophiles.

Ethanoyl chloride also reacts vigorously with concentrated aqueous solutions of ammonia and amines. The products are amides, for example:

$$CH_3COCl(l) + NH_3(aq) \rightarrow CH_3CONH_2\ (aq) + HCl(aq)$$

ethanamide

$$CH_3COCl(l) + CH_3CH_2NH_2(aq) \rightarrow CH_3CONHCH_2CH_3\ (aq) + HCl(aq)$$

N-ethylethanamide

Link

Unit 20, Nitrogen compounds, describes the chemistry of amines and amides.

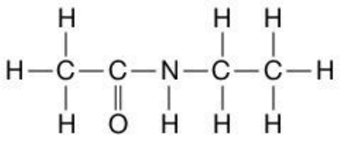
Worked example

a) Draw a displayed formula for *N*-ethylethanamide.

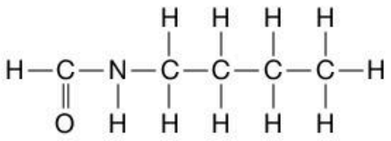
b) Give the structural formula of the product of methanoyl chloride with butylamine.

Answer

a)



b)



Acyl chlorides react with alcohols to make esters. The reactions are more vigorous than the reactions of carboxylic acids with alcohols.

$$CH_3COCl(l) + CH_3CH_2CH_2OH(l) \rightarrow CH_3COOCH_2CH_2CH_3(l) + HCl(g)$$

Acyl chlorides also react with phenol. These reactions are useful because carboxylic acids do not react directly with phenol.

Link

Unit 17, Hydroxy compounds, describes the reactions of acyl chlorides with alcohols and phenol.

Worked example

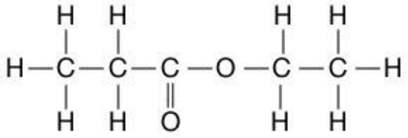
Give the names and displayed formulae of the organic products of the reactions of:

a) propanoyl chloride and ethanol

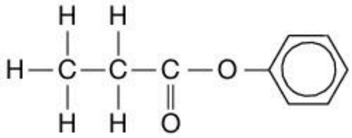
b) propanoyl chloride and phenol.

Answers

a) ethyl propanoate



b) phenyl propanoate



Esters

Esters are used as solvents, perfumes and fruit flavourings.

Esters are hydrolysed by water in the presence of an acid catalyst. The mixture must be heated under reflux. For example, methyl propanoate makes methanol and propanoic acid:

$$CH_3CH_2COOCH_3 + H_2O \xrightleftharpoons{H^+} CH_3CH_2COOH + CH_3OH$$

Link

The reactions that form esters are described in Unit 17, Hydroxy compounds, and earlier in this unit.

Exam tip

Practise working out the products of hydrolysis reactions:

- the ***yl*** part of the name gives the alcohol that is formed
- the ***oate*** part of the name gives the acid that is formed.

Esters are also hydrolysed by bases. The reaction mixture is heated under reflux. The product is a carboxylate salt. For example:

$$CH_3CH_2COOCH_3 + NaOH \rightleftharpoons CH_3CH_2COO^-Na^+ + CH_3OH$$

The alcohol is removed by distillation. Adding HCl to the remaining solution of the carboxylate salt results in the formation of the carboxylic acid.

Raise your grade

1 This question is about a carboxylic acid, **X**.

(a) $LiAlH_4$ dissolved in dry ethoxyethane is added to a sample of **X**, followed by dilute sulfuric acid. The organic product of the reaction has a relative molecular mass of 74.

(i) Name the homologous series of the organic product of this reaction. [1]

The organic product is an alcohol. ✔

(ii) Give the name, molecular formula and skeletal formula of the organic product. [3]

M_r of alcohol is 74, so its formula is C_4H_9OH. ✔✘

Its name is butanol. ✘

The candidate has given the correct molecular formula for the product, but a skeletal formula was asked for, so the second mark could not be awarded. The skeletal formula is  OH.

The name is almost correct, but the candidate needs to indicate that the alcohol is a primary alcohol by giving its full name, butan-1-ol.

The candidate could show how they worked out that the alcohol has four carbon atoms. For example, by trial and error:

M_r of ethanol, $C_2H_5OH = (2 \times 12) + (6 \times 1) + 16 = 46$

M_r of propanol, $C_3H_7OH = (3 \times 12) + (8 \times 1) + 16 = 60$

M_r of butanol, $C_4H_9OH = (4 \times 12) + (10 \times 1) + 16 = 74$

(b) A small piece of magnesium is added to a separate sample of carboxylic acid **X**, and fizzing is observed.

(i) Name the gas made in the reaction. [1]

carbon dioxide. ✘

The reaction of a reactive metal with an acid produces hydrogen gas.

(ii) Deduce the salt made in this reaction, and give its name and formula. [2]

The salt is magnesium butanoate. ✔

Its formula is MgC_3H_7COOH ✘

The candidate has correctly deduced the name of the salt, having deduced from part **a** that acid **X** is butanoic acid.

The charge on any carboxylate ion is –1, and the formula of a magnesium ion is Mg^{2+}. This means that magnesium butanoate has two butanoate ions for every one magnesium ion. In salts of carboxylic acids, the formula of the negative ion is given first. This means that the correct formula is $(C_3H_7COO)_2Mg$.

(c) A student wants to make a small amount of ester of M_r 102 from a separate sample of **X**.

(i) Name the ester and describe what the student should do. Include the names of the reagent(s) required. [4]

$C_3H_7COOCH_3$

The ester is methyl butanoate as its $M_r = 102$. ✓

This part of the answer is correct, but it would have been better to have included working, as credit might then be given even if a mistake is made.

The student needs to heat 2 cm^3 of butanoic acid with 2 cm^3 of methanoic acid ✗
and few drops of concentrated sulfuric acid. ✓

The candidate made a mistake here – the second reagent is an alcohol, methanol, not methanoic acid.

Exam tip

Check your answers very carefully and correct mistakes like this one.

Then the student needs to pour the products into a small beaker of $Na_2CO_3(aq)$. ✓

(ii) Write an equation for the reaction. [1]

$C_3H_7COOH + CH_3OH \rightarrow C_3H_7COOCH_3$ ✗

The candidate has forgotten to include the other product of the reaction, water.

Exam tip

Check that all equations are balanced, and that all products are included.

2 A student had samples of two carboxylic acids. Acid **A** reacted with a complex of Ag^+ ions to produce a silver mirror on the side of the test tube. Acid **B** was heated with acidified potassium manganate(VII), and bubbles of gas were observed.

(a) Give the name of acid **A**. [1]

methanoic acid ✓

(b) **(i)** Give the name of acid **B**. [1]

ethanedioate acid ✗

The correct name of the acid is ethanedioic acid.

Exam tip

Learn the names of organic compounds carefully. You will lose marks if you make mistakes like this one.

(ii) Write a balanced equation for the reaction that occurs when B reacts with acidified potassium manganate(VII). [3]

The half-equations are:

$(COOH)_2 \rightarrow 2CO_2 + 2H^+ + 2e^-$ ✓ $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ ✓

So the overall equation is

$$2MnO_4^- + 5(COOH)_2 + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 4H_2O$$ ✗

The candidate achieved two of the three available marks by giving the half-equations correctly. The candidate made just one error in the overall equation – there should be 8 moles of water in the products, not just four.

Exam-style questions

Choose your answer to questions 1, 2 and 3 by selecting on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

1 Which of these substances reacts with ethanoic acid to make calcium ethanoate? [1]

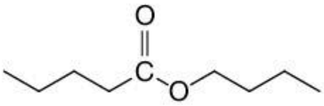
- **1** Ca
- **2** $CaCO_3$
- **3** $Ca(OH)_2$

2 Which of the following are commercial uses of esters? [1]

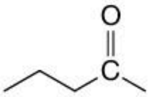
- **1** to add fruit flavourings to food
- **2** as solvents
- **3** as perfumes.

3 Which of these esters can be made from butanoic acid and another reagent? [1]

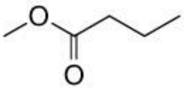
1



2



3



4 A student has a sample of a carboxylic acid, **C**. Acid **C** reacts with $SOCl_2$ to make ethanoyl chloride and a mixture of gases.

(a) Name the two gaseous products of the reaction of acid **C** with $SOCl_2$. [1]

(b) Explain why acid **C** is

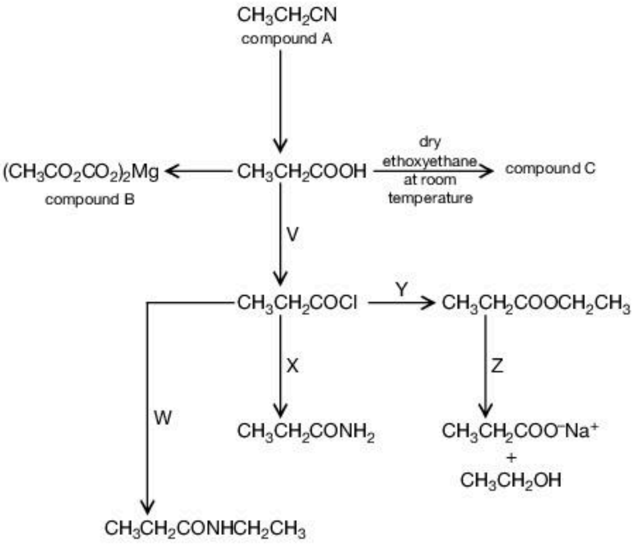
(i) more acidic than ethanol [2]

(ii) less acidic than trichloroethanoic acid. [2]

Exam tip

If you are asked to compare two things, write about the situation in both of them, and say how they are similar and how they are different.

5 The following chart shows some reactions of ethanoic acid and compounds produced from it.



(a) Draw the structure of compound **C**. [1]

(b) Give the name of

(i) compound **A** [1]

(ii) compound **B**. [1]

(c) Suggest reagents and conditions for reactions V, W, X, Y and Z

Reaction V [1]

Reaction W [1]

Reaction X [1]

Reaction Y [1]

Reaction Z [1]

20 Nitrogen compounds

A 27.2–27.8
pages 506–516;
29.2 pages 532–535

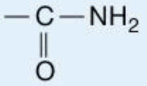
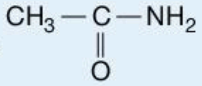
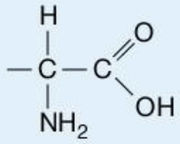
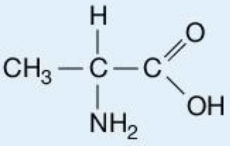
Key points

- ☐ Describe how to make primary amines.
- ☐ Describe and explain the relative basicity of different amines.
- ☐ Describe some reactions of phenylamines.
- ☐ Describe coupling reactions that make dyes.
- ☐ Describe how to make amides.
- ☐ Recognise that amides are neutral.
- ☐ Describe some reactions of amides.
- ☐ Describe the acid/base properties of amino acids.
- ☐ Describe the formation of di- and tri-peptides.
- ☐ Describe the process of electrophoresis and the effect of pH.

Organic nitrogen compounds

Some organic nitrogen compounds are listed in Table 20.1.

▼ **Table 20.1** Amines, amides and amino acids

Type of compound	Functional group	Example
Amine	$-NH_2$	ethylamine $CH_3CH_2NH_2$
Amide	 $-C(=O)-NH_2$	ethanamide  $CH_3-C(=O)-NH_2$
Amino acid		alanine 

Making primary amines

There are several ways of making primary aliphatic amines:

- Heat a halogenoalkane with concentrated aqueous ammonia in a sealed tube:

$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$$

- Reduce an amide with $LiAlH_4$ in dry ethoxyethane at room temperature, then add dilute acid:

$$CH_3CONH_2 + 4[H] \rightarrow CH_3CH_2NH_2 + H_2O$$

- Reduce a nitrile with $LiAlH_4$ in dry ethoxyethane, then add dilute acid:

$$CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$$

- Reduce a nitrile by heating with hydrogen and a nickel catalyst:

$$CH_3CN + 2H_2 \rightarrow CH_3CH_2NH_2$$

Remember

A mixture of products is formed in this reaction – this equation is simplified.

Link

The first reaction is a nucleophilic substitution reaction. These are discussed in Unit 16, Halogen derivatives.

Worked example

Describe two methods for making propylamine from a nitrile. Give the names and formulae of the reagents and state reaction conditions for both methods.

Answer

Method 1: Add $LiAlH_4$ in dry ethoxyethane to propanenitrile, CH_3CH_2CN, then add dilute acid.

Method 2: Heat propanenitrile, CH_3CH_2CN, with hydrogen, H_2, and a nickel catalyst.

Exam tip

You need to learn all four methods for making primary amines. Make sure you remember the reaction conditions and reagents.

Making phenylamine

Phenylamine is made in a reduction reaction. In the reaction, nitrobenzene is heated with tin and concentrated hydrochloric acid:

The basicity of amines

An amine is a base because its nitrogen atom has a lone pair of electrons. This means that it can bond to a hydrogen atom. For example:

Remember

A base accepts H^+ ions.

Worked example

Write an equation for the reaction of ethylamine with hydrochloric acid to form a salt. Explain how the ethylamine is acting as a base in this reaction.

Answer

$$CH_3CH_2NH_2(aq) + HCl\,(aq) \rightleftharpoons CH_3CH_2NH_3{}^+Cl^-(aq)$$

The ethylamine is acting as a base because it joins to a hydrogen ion, H^+.

In the equilibria below, the stronger the base, the further the equilibrium is to the right:

$$NH_3\,(aq) + H^+\,(aq) \rightleftharpoons NH_4{}^+(aq)$$

$$CH_3CH_2NH_2\,(aq) + H^+\,(aq) \rightleftharpoons CH_3CH_2NH_3{}^+(aq)$$

The stability of the positive ion determines the position of the equilibrium. An alkyl group pushes electrons towards the $NH_3{}^+$ group, so stabilising the ion. This explains why the equilibrium for ethylamine is further to the right than the equilibrium for ammonia. Ethylamine is a stronger base than ammonia.

Phenylamine is a weaker base than ammonia. This is because the lone pair of electrons on its nitrogen atom becomes delocalised with the ring electrons. It is less available to join to hydrogen ions than the nitrogen atoms in ethylamine or ammonia.

Worked example

Suggest an explanation for the data in the table.

Substance	K_b at 25 °C /mol dm^{-3}
Diethylamine, $(CH_3CH_2)_2NH$	5.4×10^{-3}
Ethylamine, $CH_3CH_2NH_2$	5.4×10^{-4}

Answer

Equilibrium 1: $(CH_3CH_2)_2NH + H^+ \rightleftharpoons (CH_3CH_2)_2NH_2^+$

Equilibrium 2: $CH_3CH_2NH_2 + H^+ \rightleftharpoons CH_3CH_2NH_3^+$

Equilibrium 1 lies further to the right than Equilibrium 2. This is because the diethylammonium ion is more stable than the ethylammonium ion. The diethylammonium ion has two ethyl groups pushing electrons towards the NH_2^+ group to stabilise it, but the ethylammonium ion has only one ethyl group pushing electrons towards the NH_3^+ group to stabilise it. This means that diethylamine is more basic than ethylamine.

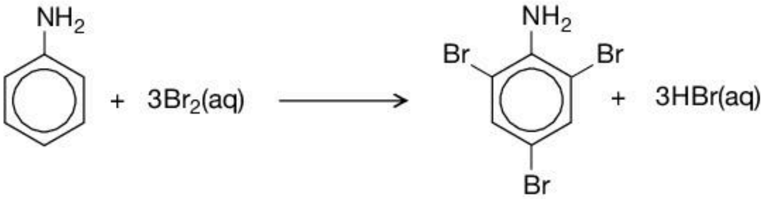
Exam tip

In exam questions, it can be helpful to include equations or equilibrium expressions to help you to explain something.

Reactions of phenylamine

Reaction with bromine

Phenylamine reacts with aqueous bromine at room temperature. A catalyst is not needed. The organic product forms as a white precipitate.



2,4,6-tribromophenylamine

The reaction occurs readily because delocalised electrons from the nitrogen atom increase the electron density of the benzene ring. This makes the benzene ring more attractive to electrophiles.

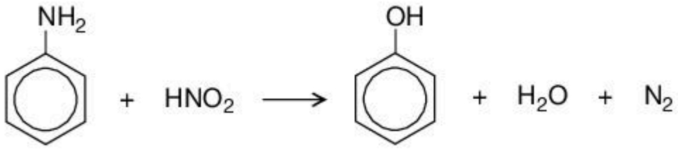
Remember

The 2, 4, 6 positions of phenylamine are substituted.

Reaction with nitrous acid

Phenylamine also reacts with nitrous acid, HNO_2 (formed in the reaction vessel from HCl and $NaNO_2$, as it is unstable). The products depend on the temperature:

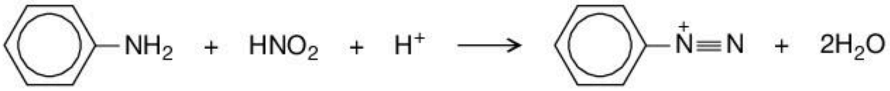
- On warming, one of the products is phenol:



Common error

Students sometimes get confused between the reactions that occur at different temperatures. Make sure you know that the reaction in the cold makes benzenediazonium ions.

- Below 10 °C, when phenylamine is dissolved in cold nitrous acid, benzenediazonium ions are formed:



Practical skills

To carry out this reaction, dissolve phenylamine in hydrochloric acid, HCl, cooled in an ice bath. Then slowly add sodium nitrite solution, $NaNO_2$. Make sure the temperature remains at about 5 °C.

Worked example

Phenylamine is dissolved in cold hydrochloric acid. Cold sodium nitrite solution is slowly added. Name the products of the reaction.

Answer

The products are a salt, benzenediazonium chloride, and water.

Link

Coupling reactions are described in Unit 17, Hydroxy compounds.

Coupling reactions

Benzenediazonium salts react with phenol in coupling reactions to give azo compounds. For example, mixing cold solutions of benzene diazonium chloride and phenol makes a bright orange precipitate. There are many azo compounds. They are used as dyes.

Exam tip

Make sure you can draw the structure of a benzenediazonium ion.

Making amides

Amides are formed in the reactions of ammonia or primary amines with acyl chlorides. The reactions are very vigorous.

Link

See Unit 19, Carboxylic acids and derivatives, for more about acyl chlorides.

Worked example

Write an equation for the reaction of ammonia with propanoyl chloride. Name the products formed.

Answer

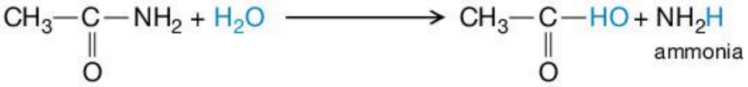
$$CH_3CH_2COCl(l) + NH_3(aq) \rightarrow CH_3CH_2CONH_2(aq) + HCl(aq)$$

The products are propanamide and hydrogen chloride.

The reactions of amides

Amides are neither acidic nor basic; they are neutral. This is because the lone pair of electrons on the nitrogen atom is delocalised onto the C=O group. The lone pair of electrons is no longer available for bonding to hydrogen ions.

An amide hydrolyses when it is heated with aqueous acid or alkali.



$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-HO + \underset{\text{ammonia}}{NH_2H}$$

- In the presence of an alkali, the carboxylic acid reacts to form a salt.
- In the presence of excess acid, the ammonia and the acid form a salt.

Worked example

Name and give the formulae of the salt formed in the hydrolysis of propanamide:

a) in the presence of sodium hydroxide

b) in the presence of excess hydrochloric acid.

Answer

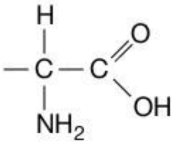
a) sodium propanoate, $CH_3CH_2COO^-Na^+$

b) ammonium chloride, NH_4Cl

Amides are reduced to amines by $LiAlH_4$ in dry ethoxyethane solution. This is one of the methods for the preparation of amines described earlier.

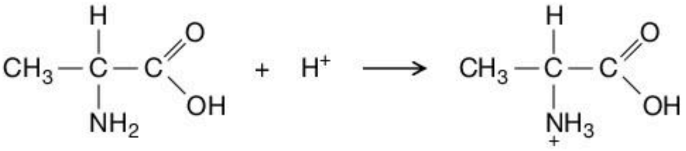
Amino acids

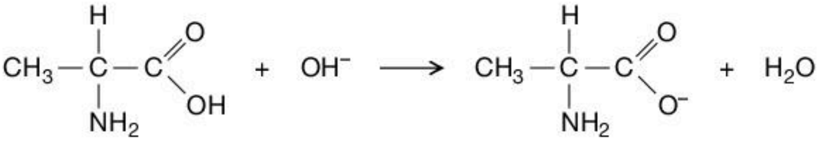
There are 20 naturally occurring amino acids. Most include the group shown in Figure 20.1.



▲ **Figure 20.1** All amino acids contain this group.

Since an amino acid includes both the $—NH_2$ and $—COOH$ functional groups, it can act as an acid and a base. For example:





Worked example

In which reaction above is the amino acid acting as an acid? Explain your answer.

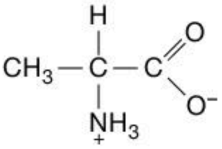
Answer

The amino acid is acting as an acid in the second reaction because it donates a hydrogen ion, H^+, to a base, OH^-.

Key term

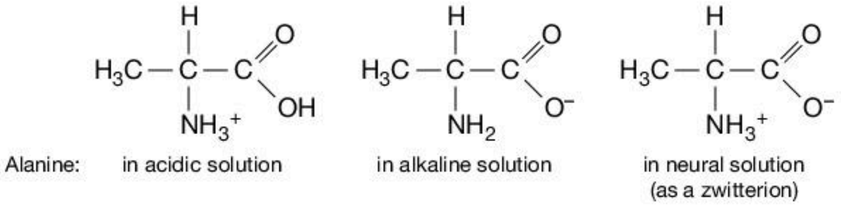
Zwitterion: an ion or molecule that has separate positively and negatively charged atoms or groups.

An amino acid can also form **zwitterions**. In a zwitterion, a proton from the carboxylic acid group has been donated to the nitrogen atom of the amine group. The zwitterion of alanine has this structure:



Because amino acids exist as ions, they have high melting points and are soluble in water.

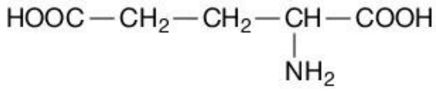
A zwitterion shows the behaviour of both an acid and a base, depending on the conditions. The form of a zwitterion depends on the pH.



Worked example

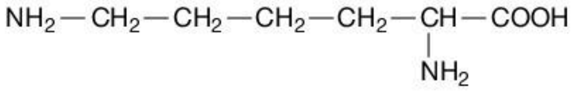
Look at amino acids **A**, **B** and **C**. State and explain which is basic, which is acidic and which is neutral in aqueous solution.

A glutamic acid



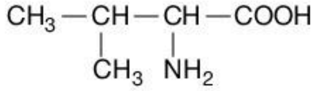
$HOOC-CH_2-CH_2-CH(NH_2)-COOH$

B lysine



$NH_2-CH_2-CH_2-CH_2-CH_2-CH(NH_2)-COOH$

C valine



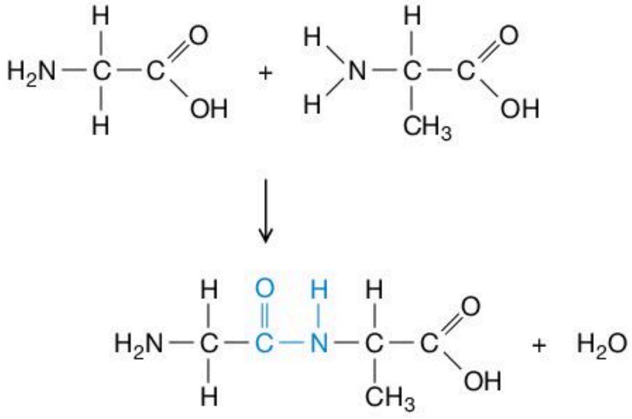
$CH_3-CH(CH_3)-CH(NH_2)-COOH$

Answer

A is acidic as it has two —COOH groups. **B** is basic, as it has two —NH_2 groups. **C** is neutral as it has one —COOH group and one —NH_2 group.

The formation of peptide bonds

Amino acids join together in condensation reactions. The —COOH group of one acid joins to the —NH_2 group of another. This makes peptide bonds. Peptide bonds form easily in living organisms, but do not form easily in the laboratory.



▲ **Figure 20.2** Forming a peptide bond, shown in blue

- A di-peptide is made up of two amino acids.
- A tri-peptide is made up of three amino acids.
- A polypeptide is made up of many amino acids.

Link

Proteins are polypeptides. They are covered in Unit 21, Polymerisation.

Electrophoresis

In **electrophoresis**, a drop containing a mixture of amino acids is placed on the centre of some gel or a strip of paper which has been soaked in buffer solution. An electric circuit is set up. When the circuit is switched on:

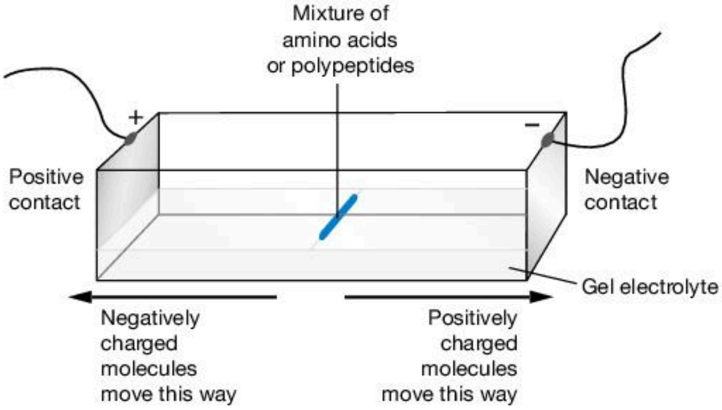
- Positive ions move towards the negative electrode.
- Negative ions move towards the positive electrode.
- Molecules with no overall charge do not move.

Bigger ions move more slowly than smaller ones.

Amino acids are colourless, so ninhydrin spray is used to convert them to purple substances which show up on the paper or gel.

Key term

Electrophoresis: the movement of ions in an electric field. It can be used to separate and identify amino acids.



▲ **Figure 20.3** Electrophoresis

Worked example

In which directions will the amino acids below move when placed in an electrophoresis cell at pH 7? Explain your answer.

a) lysine

b) glutamic acid

c) valine.

Answer

a) Lysine moves towards the negative electrode. This is because it has two —NH_2 groups, which each gain an extra H^+, and one —COOH group, which loses an H^+ ion.

b) Glutamic acid moves towards the positive electrode. This is because it has two —COOH groups, which each lose an H^+ ion, and one —NH_2 group.

c) Valine does not move at all since it has one —COOH group and one —NH_2 group. This means that it has no overall charge.

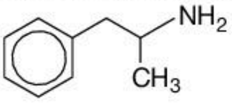
★ Exam tip

The formulae of ten amino acids are given in Table 10 of the data booklet.

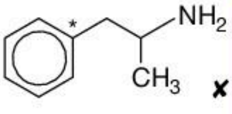
Raise your grade

1 Amphetamine is a medicine. It is used to treat several medical conditions.

The formula of amphetamine is:

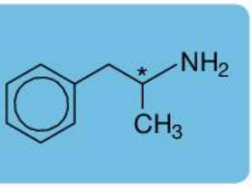


(a) Amphetamine shows optical isomerism.
Mark the chiral centre on the structural formula. [1]



✘

The candidate has marked the chiral centre incorrectly. The chiral centre is as marked here – there are four different groups attached to this carbon atom: an H atom, $-CH_3$, $-NH_2$ and $-CH_2C_6H_5$.



Exam tip

This question tests several sections of the syllabus – not just nitrogen compounds. This is typical of questions in the A level question paper.

(b) Deduce the molecular formula of amphetamine. [1]

$C_9H_{11}N$ ✘

The candidate has not counted two of the hydrogen atoms – the correct molecular formula is $C_9H_{13}N$.

(c) Name the functional group in an amphetamine molecule. [1]

Amide ✘

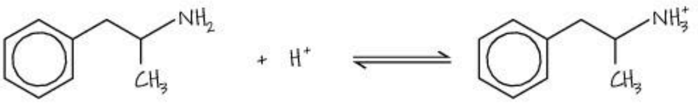
Amides have the functional group $CONH_2$. Since there is no oxygen in the molecule, it cannot be an amide. In fact, it is an amine.

(d) Predict, with reasons, whether amphetamine is a stronger or weaker base than

(i) ammonia [2]

The equilibria below show ammonia and amphetamine acting as bases.

$NH_3 + H^+ \rightleftharpoons NH_4^+$



Amphetamine is a stronger base than ammonia because the position of equilibrium for the amphetamine reaction is further to the right than for the ammonia reaction. This is because the ion formed in the amphetamine reaction is stabilised by the electron-donating effect of the alkyl groups next to it. ✔✔

This is an excellent answer, enhanced by the inclusion of the equilibrium expressions.

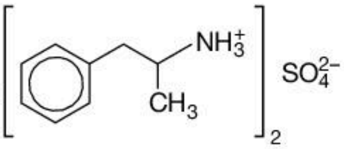
(ii) phenylamine [2]

Phenylamine is a stronger base because of the benzene ring. ✗✗

This answer is inadequate. Phenylamine is a weaker base because the lone pair of electrons in its nitrogen atom become delocalised within the benzene ring system. This means that its nitrogen atom is less available to join to hydrogen ions than the nitrogen atoms in amphetamine.

(e) One manufacturer supplies amphetamine in tablets that contain 2.5 mg of a salt, amphetamine sulfate.

The formula of amphetamine sulfate is:



Calculate the amount in moles of amphetamine sulfate in one tablet. [4]

Molecular formula = $(C_9H_{14}N)_2SO_4$ ✔

Mass of one mole = (18 × 12.0) + (28 × 1.0) + (2 × 14.0) + 32.1 + (4 × 16.0) = 368.1 g ✔

2.5 mg is 0.0025 g

$$\text{So amount in mol} = \frac{\text{mass in g}}{\text{mass of 1 mol in g/mol}}$$

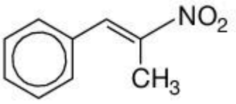
= 0.0025 g ÷ 368.1 g/mol ✔

= 6.79×10^{-5} mol ✗

The candidate has shown his working very clearly, and achieved 3 of the 4 marks. The final answer is out by a factor of 10. The correct answer is 6.79×10^{-6} mol.

(f) There are several methods of synthesis of amphetamine.
One synthesis involves the conversion of the compound with the formula below to amphetamine.

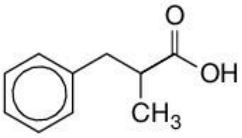
Name the type of reaction that occurs. [1]



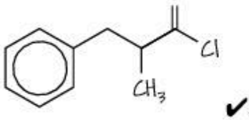
In fact the reaction is a reduction, since oxygen is removed and replaced by hydrogen.

The reaction is an oxidation. ✗

(g) Another synthesis involves reacting the compound below with $SOCl_2$ followed by ammonia, NH_3.



(i) Predict the formulae of the one organic and two other products of the first reaction, with $SOCl_2$. [3]



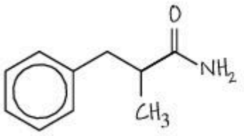
✓✗✗

The candidate has shown that $SOCl_2$ reacts with a carboxylic acid to form an acyl chloride. However, he has not included the formulae of the other two products of the reaction, which are SO_2 and HCl.

Exam tip

Read exam questions very carefully, and make sure you answer all parts of each question.

(ii) Predict the organic product of the second reaction, with NH_3. [1]



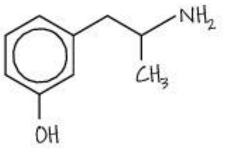
✓

This answer is correct. The candidate has remembered that acyl chlorides react with ammonia to form amides.

(h) In the body, amphetamine takes part in chemical reactions.

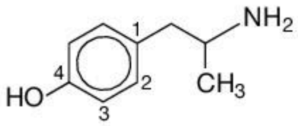
(i) The product of one of these reactions is 4-hydroxyamphetamine.

Give the structural formula of 4-hydroxyamphetamine. [1]



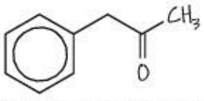
✗

The candidate has drawn the —OH group in the wrong position. The formula below shows how to choose the correct position for this benzene ring substituent.



(ii) The product of another reaction of amphetamine that occurs in the body is phenylpropanone.

Give the structural formula of phenylpropanone. [1]

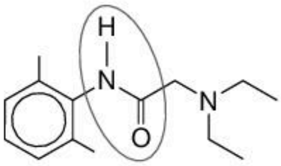


✓

Exam-style questions

1 Lidocaine is a local anaesthetic.

(a) Give the name of the functional group circled in the formula of lidocaine below. [1]



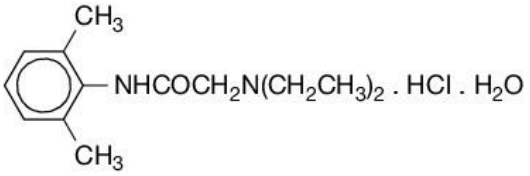
(b) **(i)** Suggest which part of the lidocaine molecule might act as a base. [1]

(ii) Explain your answer to part **(i)**. [2]

(c) The systematic name of lidocaine is 2-diethylamino-*N*-(*x*,*y*–dimethylphenyl)-ethanamide, where *x* and *y* are numbers.

Give the numerical values of *x* and *y*. [1]

(d) Lidocaine is usually supplied as the monohydrochloride monohydrate, which has the formula below.



Calculate the relative formula mass of the monohydrochloride monohydrate. [2]

(e) Lidocaine monohydrochloride monohydrate can be supplied as a solution containing 20 mg/cm^3 of the compound.

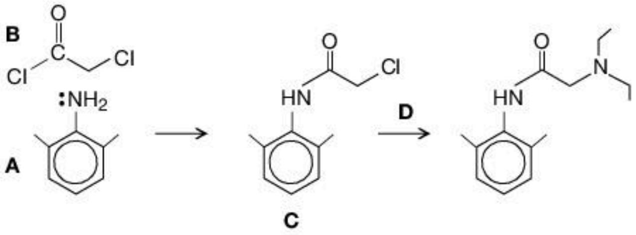
(i) A typical single dose of the anaesthetic is 10 cm^3.

Give the mass in grams of lidocaine monohydrochloride monohydrate in this dose. [1]

(ii) Calculate the concentration of lidocaine monohydrochloride monohydrate in mol/dm^3. [3]

(f) The first step of one method of synthesising lidocaine involves treating compound **A** with compound **B** to form compound **C**.

An outline of the synthesis is shown below.



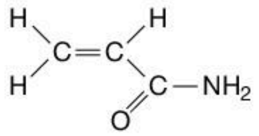
(i) Give the name of compound **A**. [1]

(ii) Add one curly arrow to show how electrons from one atom in compound **A** attack one atom in compound **B**. [2]

(iii) In the second step of the synthesis of lidocaine, compound **C** is heated under reflux with another compound, compound **D**.

Suggest the functional group present in compound **D**. [1]

2 Acrylamide is a compound that is formed when starchy foods are cooked at high temperatures.



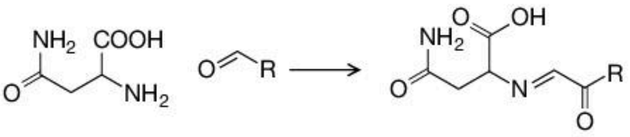
(a) A sample of acrylamide is added to $LiAlH_4$ in dry ethoxyethane at room temperature. Predict the formula of the organic product of the reaction. [1]

(b) Acrylamide reacts with sodium hydroxide in a hydrolysis reaction.

(i) Predict the formula of the organic product of the reaction. [1]

(ii) Name the gas produced in the reaction, and suggest how to identify it. [2]

(c) During cooking, acrylamide is synthesised from sugars and from an amino acid in a series of chemical reactions. The equation for one of the reactions involved is given below.



(i) Name the three functional groups in the amino acid in the reaction above. [3]

(ii) Copy the equation, and draw a curly arrow to show how the lone pair on the nitrogen atom attacks the aldehyde. [1]

21 Polymerisation

A 28.3–28.5 pages 523–529;
29.2–29.5 pages 532–544

Key points

- ☐ Describe the formation of polyesters and polyamides.
- ☐ Deduce the repeat unit of a condensation polymer and identify monomers in a polymer.
- ☐ Predict the type of polymerisation for a given monomer or pair of monomers.
- ☐ Deduce the type of polymerisation reaction that produces a given polymer.
- ☐ Discuss and explain properties of polymers including:
  - the effect of their method of formation
  - the effect of side-chains and intermolecular forces
  - the significance of hydrogen bonding in DNA base pairs
  - primary, secondary and tertiary structures of proteins
  - how they are designed to act as adhesives and electrical conductors.
- ☐ Recognise and describe how polymers can be degraded.
- ☐ Describe the hydrolysis of proteins.

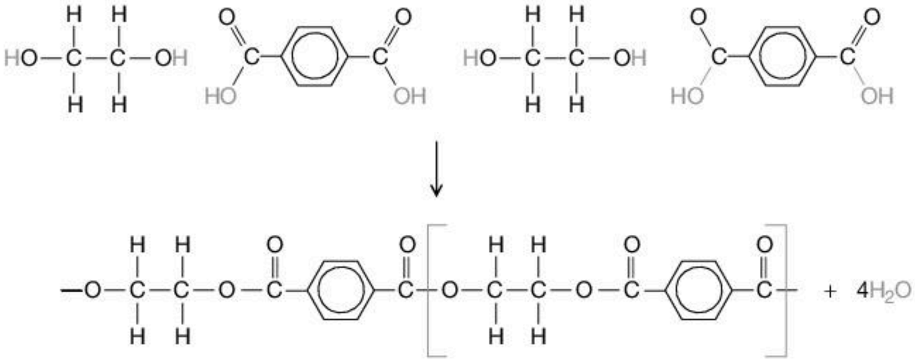
Condensation polymerisation

Condensation polymers include **polyesters** and **polyamides**. They are formed in condensation reactions between two types of **monomer** (or one monomer with two functional groups). When a condensation polymer is formed, a small molecule such as H_2O or HCl is also produced.

A common polyester is Terylene. It is formed from two monomers:

- ethane-1,2-diol
- benzene-1,4-dicarboxylic acid.

The **repeating unit** is shown in square brackets in Figure 21.1.



▲ Figure 21.1 Formation of Terylene

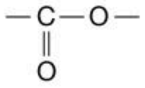
A common polyamide is nylon 6,6 (see Figure 21.2). It is formed from two monomers:

- 1,6-diaminohexane
- hexanedioic acid.

Key terms

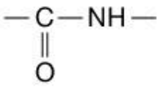
Condensation polymer: a polymer formed in a condensation reaction between two monomers.

Polyester: a polymer with ester linkages, as shown below.



$$-\underset{\underset{O}{\|}}{C}-O-$$

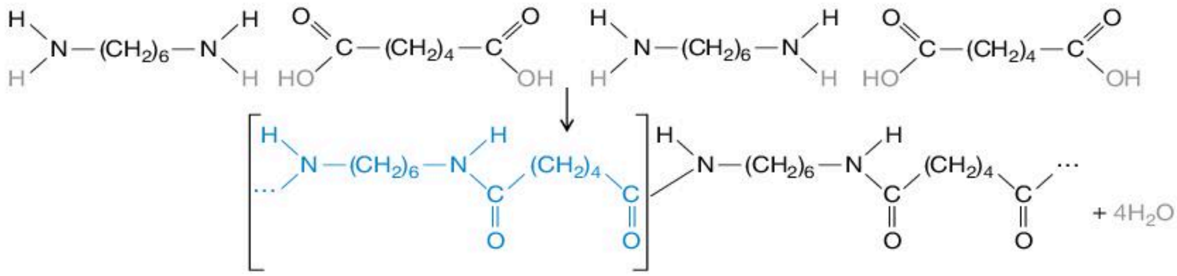
Polyamide: a polymer with amide linkages, as shown below.



$$-\underset{\underset{O}{\|}}{C}-NH-$$

Monomer: a small molecule that joins with many other molecules to make a polymer molecule.

Repeating unit: an arrangement of atoms that occurs many times in the structure of a polymer.



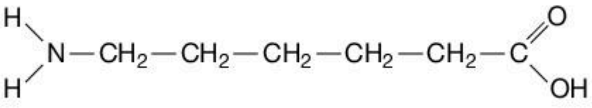
▲ **Figure 21.2** Formation of nylon 6,6, with one repeating unit shown in blue

Worked example

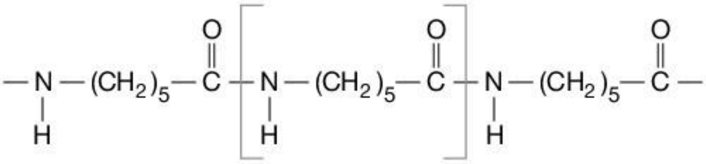
Nylon 6 is made from the monomer 6-aminohexanoic acid. Give the structural formula of the monomer, and draw a section of polymer chain made from three monomer units. Then draw square brackets around the repeating unit.

Answer

Monomer:



Section of polymer chain:

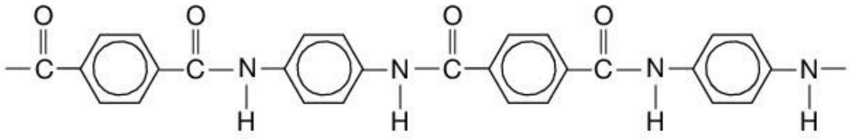


Link

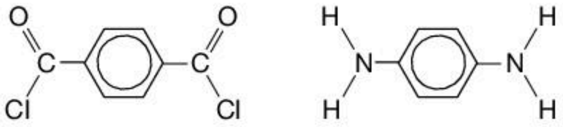
Polypeptides and proteins are also polyamides. They are discussed in Unit 20, Nitrogen compounds.

Worked example

A section of the polymer Kevlar is shown below. Suggest the formulae of its two monomers.



Answer



Predicting polymerisation

You can predict the type of polymerisation that will occur for a given monomer or pair of monomers. You can also predict the type of polymerisation reaction that produces a given section of a polymer molecule.

Link

Addition polymers are discussed in Unit 15, Hydrocarbons.

Worked example

A polymer is made from the monomer propene. Give the formula of the monomer, and predict the type of polymerisation that will occur. Explain your prediction.

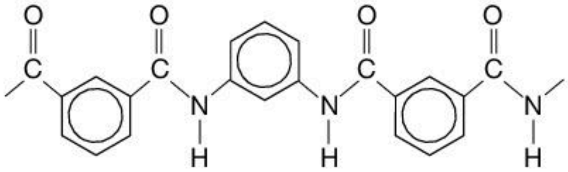
Answer

The formula of propene is $CH_2{=}CH{-}CH_3$.

It undergoes addition polymerisation because it is an alkene.

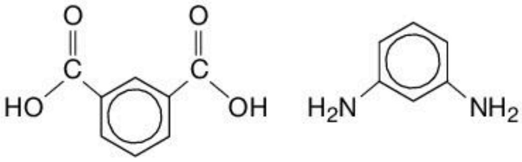
Worked example

The repeating unit of a polymer is given below. Predict whether the polymer was formed as a result of addition or condensation polymerisation. Then predict the formula of the monomer or formulae of the monomers from which it was made.



Answer

The polymer was made in a condensation reaction. The formulae of its monomers are given below.



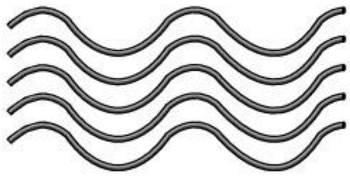
An acyl chloride may be used in place of the carboxylic acid monomer.

Polymer properties

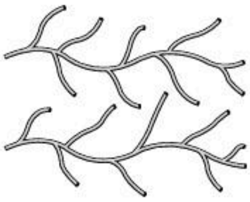
The presence of side-chains and intermolecular forces affects the properties of polymeric materials. The two forms of poly(ethene) illustrate this point, as shown in Table 21.1.

▼ **Table 21.1** A comparison of the properties of HDPE and LDPE

High-density poly(ethene), HDPE	Low-density poly(ethene), LDPE
non-branched chains	branched chains
molecules pack together closely	molecules pack together less closely
higher density	lower density
stronger intermolecular forces	weaker intermolecular forces
higher melting temperatures	lower melting temperatures
more rigid	more flexible



▲ **Figure 21.3** A simple representation of HDPE



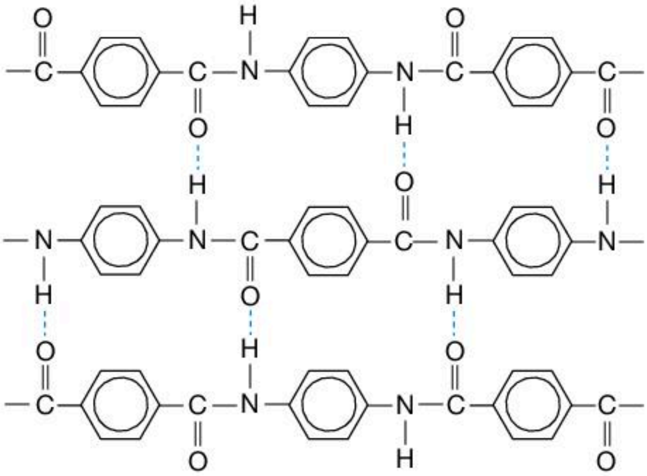
▲ **Figure 21.4** A simple representation of LDPE

Kevlar is very strong. It is used to make body armour to protect from knives and bullets. Its strength results from the strong hydrogen bonds between its C═O and N—H groups. The polymer chains in Kevlar are also rigid. This contributes to the rigidity of the material.

Worked example

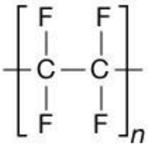
Draw three strands of Kevlar to show how they are held together by hydrogen bonds.

Answer



Teflon

Poly(tetrafluoroethene), Teflon, has a non-stick surface, because fluorocarbons are hydrophobic. Its strong C—F bonds make it unreactive. It has a high melting point as its rod-like molecules are closely packed.



▲ **Figure 21.5** The repeating unit of Teflon

The polymers of life

DNA

Deoxyribonucleic acid (DNA) carries the genetic code for making proteins. DNA has a double helix structure, which is held together by hydrogen bonds. This means that a single DNA strand can create a copy of itself by replication.

DNA replication depends on the four bases in DNA being present in the correct order. The four bases are adenine A, thymine T, cytosine C and guanine G.

In DNA:

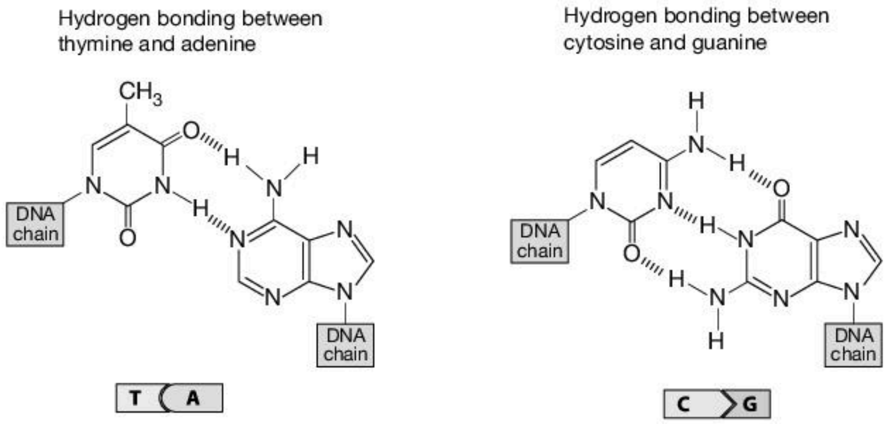
- A pairs with T by making two hydrogen bonds.
- C pairs with G by making three hydrogen bonds.

Key term

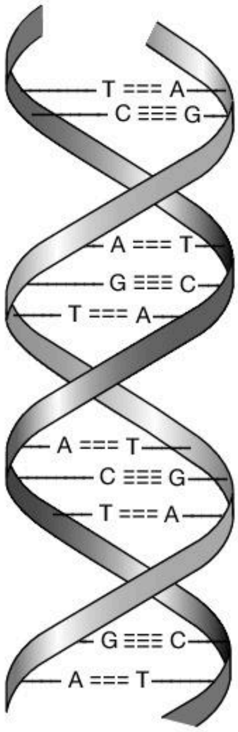
DNA replication: the making of two identical copies of DNA from one original DNA molecule.

★ Exam tip

You do not need to learn the structures of the four bases, but you do need to remember the positions of the hydrogen bonds that hold them together.



▲ **Figure 21.6** Complementary base-pairings in DNA



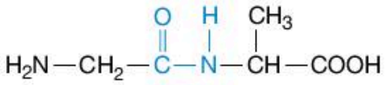
▲ **Figure 21.7** The dotted lines show hydrogen bonds between the bases in DNA

Proteins

Polypeptides are formed in condensation reactions from amino acid monomers. There are peptide links between the —NH_2 group of one amino acid and the —COOH group of the next.

Key term

Polypeptide: a chain of amino acids.



$$H_2N-CH_2-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-\overset{\overset{CH_3}{|}}{CH}-COOH$$

▲ **Figure 21.8** The peptide link in a dipeptide, made by joining together two amino acid molecules

Worked example

Deduce the names and formulae of the amino acids from which the dipeptide in Figure 21.8 was formed.

Answer

The formulae of the amino acids are H_2NCH_2COOH (glycine) and $H_2NCH(CH_3)COOH$ (alanine).

★ Exam tip

There are 20 naturally occurring amino acids. The formulae of ten of these are given in the data booklet.

Proteins have a primary structure, a secondary structure and a tertiary structure:

Key term

Protein: a polypeptide with a particular biological function.

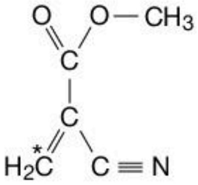
- The primary structure is the order of amino acids in the polypeptide chain.
- The secondary structure is the coiling or folding of the primary structure, normally into an α-helix or β-pleated sheet. It is stabilised through hydrogen bonding between the C=O and N—H bonds of peptide groups.
- The tertiary structure is the folding of the secondary structure into its final shape. It results from interactions between the side-chains of the amino acids that make up the polypeptide chain. These interactions include hydrogen bonds, dipole interactions and ionic attractions. The tertiary structure of a protein enables it to perform its function.

Polymers fit for purpose

Chemists design polymers with perfect properties for particular purposes:

- Epoxy resin glues are sold in two tubes. Each tube contains a different monomer. When mixed together, a cross-linked polymer forms. This hard, rigid substance acts as a glue and is not changed by heating.

- A tube of superglue contains the monomer with the formula on the right. Water vapour, a nucleophile, attacks the carbon atom with the * symbol. This initiates the formation of long polymer chains, making the glue set.
- Most polymers do not conduct electricity. But poly(ethyne), also called polyacetylene, has delocalised π electrons, so it is able to conduct electricity.



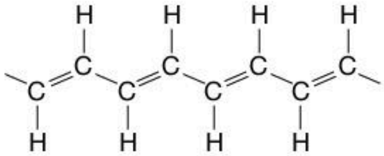
Worked example

Draw the monomer that makes poly(ethyne), and a section of the polymer chain. Then explain how the polymer conducts electricity.

Answer

The monomer is ethyne, with the formula H—C≡C—H

This is a section of the polymer chain:



The polymer has alternating single and double bonds. This results in delocalised π electrons which are free to move, carrying electric charge along the chain.

Degradable polymers

Poly(alkenes) do not take part in chemical reactions; they are chemically inert. This means that they are not easily **biodegradable**.

Key term

Biodegradable: a substance is biodegradable if it can be decomposed by bacteria or fungi.

Some polymers, for example poly(ethene) and poly(propene), are degraded over time by the action of ultraviolet light. UV light has enough energy to break C—C bonds in the polymer, forming free radicals. These free radicals react with oxygen free radicals in the air to make carbonyl compounds.

Polyesters and polyamides biodegrade in hydrolysis reactions:

- In polyesters, ester links are attacked by alkalis. The products of the hydrolysis reaction are an alcohol and a carboxylate salt.
- In polyamides, amide links are attacked by strong acids. The products of the reaction are the original monomers.

Worked example

Predict the products of the hydrolysis of:

a) Terylene

b) nylon 6,6.

Answer

a) The products are ethane-1,2-diol and the sodium salt of benzene-1,4-dicarboxylic acid.

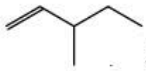
b) The products are 1,6-diaminohexane and hexanedioic acid.

Proteins too can be hydrolysed. The products are the amino acids from which the protein was made. In living organisms, digestive enzymes (such as pepsin and trypsin) carry out this hydrolysis. In the laboratory, proteins are hydrolysed by boiling with aqueous hydrochloric acid.

Raise your grade

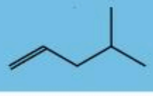
1 Poly(4-methylpent-1-ene) is a polymer. It is used to make medical and laboratory equipment.

(a) Draw the skeletal formula of the monomer of poly(4-methylpent-1-ene). [1]



✘

This is the formula of 3-methylpent-1-ene. The correct formula is:



Exam tip

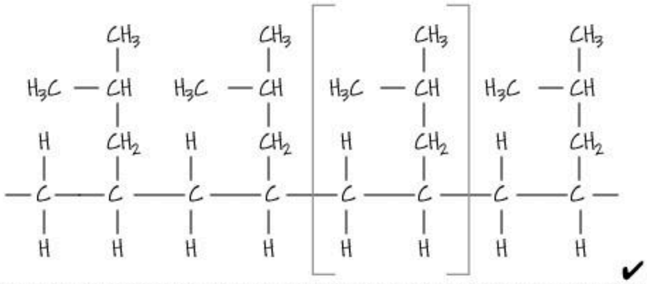
Count carefully when drawing skeletal formulae.

(b) Predict whether poly(4-methylpent-1-ene) is formed by condensation or addition polymerisation. Justify your prediction. [2]

Addition polymerisation. ✔✘

The candidate has chosen the correct type of polymerisation, but has not justified her answer. She needs to add that, since the monomer is an alkene, it takes part in addition polymerisation.

(c) **(i)** Draw the structural formula of a section of poly(4-methylpent-1-ene) made from four monomer molecules. [1]



✔

The candidate has answered this question correctly and achieved the mark.

(ii) Draw square brackets around the repeating unit of the section of the polymer you drew in part **(i)**. [1]

✔

The candidate has correctly drawn square brackets around the repeating unit.

(d) Poly(4-methylpent-1-ene) does not biodegrade easily. Suggest why. [1]

It has strong bonds.

The candidate has stated correctly that the polymer has strong bonds. However, this is not enough to gain the mark. She also needs to state that there are no centres of negative or positive charge that are attractive to nucleophiles or electrophiles.

(e) Poly(4-methylpent-1-ene) is degraded by light.

Suggest the type of reaction mechanism by which this degradation occurs. [1]

Free radical. ✔

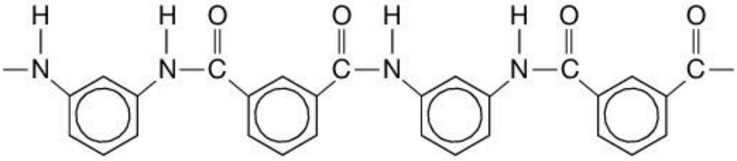
(f) Poly(4-methylpent-1-ene) has a low density. Suggest why. [1]

Carbon and hydrogen atoms are light. ✘

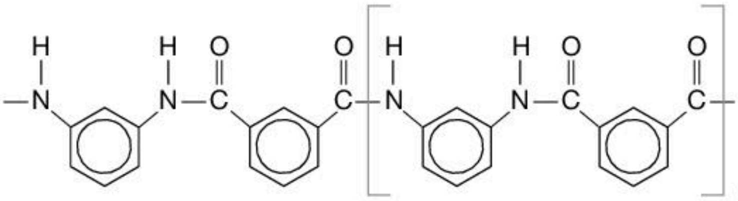
This does not fully explain the low density of the polymer. To achieve the mark here, the candidate needs to add that the side-chains result in an open structure, so reducing the number of atoms – and hence mass – per volume.

2 The polymer Nomex is used to make protective clothing for firefighters.

The formula below shows part of the Nomex polymer chain.



(a) Draw square brackets around the repeating unit of Nomex. [1]



✔

The candidate has drawn the square brackets correctly, around one repeating unit.

(b) **(i)** State whether Nomex is a polyalkene, a polyester or a polyamide. [1]

Polyester. ✘

The polymer is a polyamide, since it includes NH—CO groups.

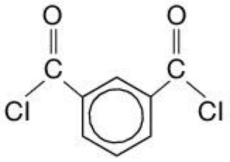
(ii) Justify your answer to part **(i)**. [1]

???

Exam tip

Write an answer to every question part, even if it is a guess. If you write nothing, you are guaranteed to achieve no marks.

(c) In large-scale production processes, Nomex is made from two monomers. One of them has the formula below.



Exam tip

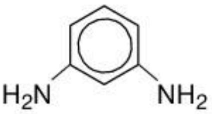
Remember to learn the names of functional groups.

(i) Name the functional group present in the monomer above. [1]

halogen ✘

The functional group is an acyl chloride.

(ii) Predict the formula of the other monomer used to make nomex. [1]

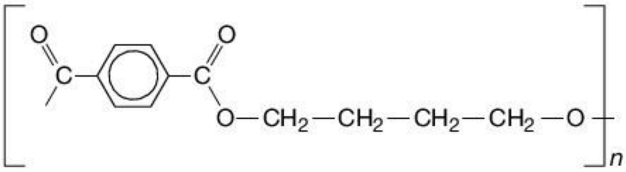


✔

Exam-style questions

1 The polymer PBT is used as an insulator in the electronic industry. It is also made into stretchy threads which are used in sports clothes.

The repeating unit of PBT is shown below.



(a) Give the molecular formula of the repeating unit of PBT. [1]

(b) State whether PBT is a polyamide, a polyalkene or a polyester. [1]

(c) Give the structural formulae of two monomers that can be used to make PBT. [2]

(d) Give the names of the monomers in part **(c)**. [2]

(e) State the type of polymerisation that occurs when PBT is made from its monomers. [1]

(f) Until recently, both PBT monomers were made from substances obtained from crude oil.

In 2016, a factory in Italy started to make one PBT monomer from plant sugars.

Suggest one advantage of making a PBT monomer from plants instead of fossil fuels. [1]

(g) This question part is about the properties of PBT.

(i) A company has recently developed a hydrolysis-resistant type of PBT.

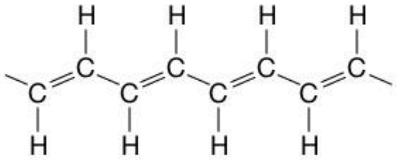
Suggest one advantage and one disadvantage of this polymer compared with PBT that is not hydrolysis-resistant. [2]

(ii) If used outside, PBT requires UV protection. Suggest why. [1]

(iii) PBT is flammable. Predict three products made when it burns. [3]

(h) PBT is an electrical insulator.

Another polymer, polyacetylene, is an electrical conductor. A section of polyacetylene is shown below.



Suggest why polyacetylene conducts electricity but PBT does not. [2]

2 This question is about compounds made from amino acids.

(a) Use the data book to draw the skeletal formulae of tyrosine and cysteine. [2]

(b) **(i)** Draw a displayed formula of a dipeptide formed from tyrosine and cysteine. [2]

(ii) Name the other product of the reaction between tyrosine and cysteine. [1]

(c) Proteins are formed when many amino acids join together.

(i) Explain what is meant by the primary structure of a protein. [1]

(ii) Describe how the secondary structure of a protein is stabilised. [1]

(iii) Name two types of bond that hold a protein in its tertiary structure. [2]

Exam tip

When drawing the formulae of dipeptides, start by drawing a general dipeptide, with side groups shown as R. Then replace each R with the correct side-chains.

22 Analytical techniques

AS 13.8 pages 263–266
A 13.7–13.9 pages 260–277

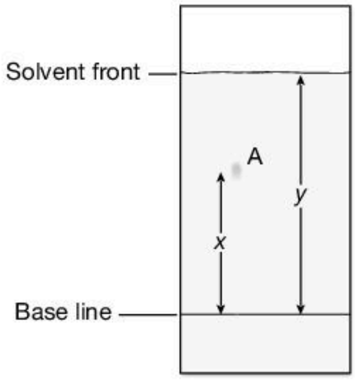
Key points

- ☐ In chromatography, calculate and use R_f values and retention times.
- ☐ Analyse infra-red spectra to identify functional groups.
- ☐ Interpret mass spectrograms.
- ☐ Interpret carbon-13 NMR spectra, and predict peaks in spectra for given molecules.
- ☐ Interpret proton NMR spectra, and predict shifts and splitting patterns for given molecules.
- ☐ Explain the use of different solvents in proton NMR spectroscopy.

Chromatography

Chromatography separates the substances in mixtures. The substances can then be identified.

Thin layer chromatography (TLC) separates substances in solution. You can use **R_f values** to identify substances on a chromatogram. On the chromatogram in Figure 22.1, the R_f value of spot A is $\frac{x}{y}$.



▲ **Figure 22.1** Calculating an R_f value

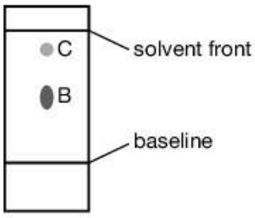
Key terms

Thin layer chromatography (TLC): a technique for separating and identifying non-volatile components in a mixture.

R_f values: these values measure how far a component in a mixture has travelled relative to the solvent front in TLC.

Worked example

Calculate R_f values for spots B and C in the chromatogram below.



Answer

R_f value for B = $\frac{0.9}{1.8}$ = 0.50

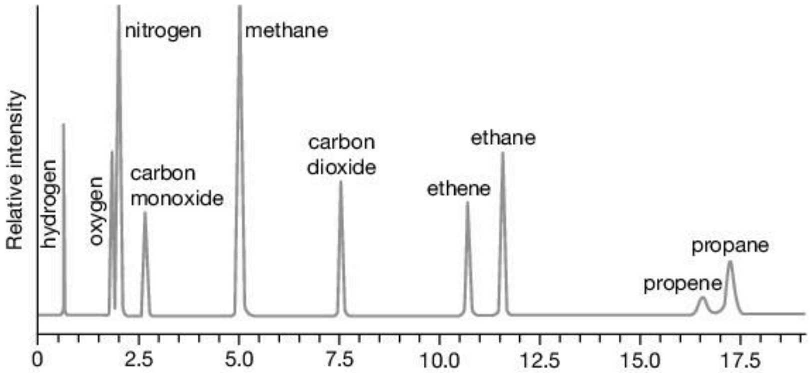
R_f value for C = $\frac{1.5}{1.8}$ = 0.83

★ Exam tip

Measure from the base line to the middle of each spot.

Gas–liquid chromatography (GLC) separates mixtures of gases or volatile liquids. You can use **retention times** to identify substances on a chromatogram. The heights of the peaks show the relative amounts of the substances in the mixture.

Worked example



The gas chromatogram shows the gases produced when a lithium ion battery decays after use.

a) Which gas has the longest retention time?

b) Which of the gases shown is produced in the smallest quantity?

c) Which two gases are produced in the largest quantities?

d) Which gas is in the column for the shortest time?

Answer

a) propane

b) propene

c) nitrogen and methane

d) hydrogen

Key terms

Gas–liquid chromatography (GLC): chromatography that separates and analyses mixtures of gases and volatile liquids, using an inert gas as the carrier.

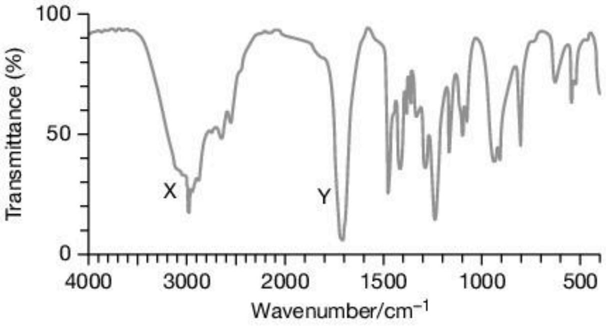
Retention time: the time that a substance spends in the detector, from when it is injected until it is detected.

Infra-red spectroscopy

Infra-red spectroscopy is used to identify bonds and functional groups in organic substances. An **infra-red spectrum** shows the wavenumbers that are absorbed by a compound.

Worked example

The infra-red spectrum of a compound is shown below. Identify the bonds that result in absorptions X and Y, and suggest the one functional group present in the molecule.



Key term

Infra-red spectrum: a readout showing the wavenumbers (related to the energy) absorbed from the infra-red region by the sample.

Link

The structures of functional groups are shown in Unit 14, An introduction to organic chemistry.

Exam tip

The absorption ranges of selected bonds in their functional groups are given in the data booklet.

Answer

The data booklet shows that absorption X (3000 cm^{-1}) is at the wavenumber characteristic of the OH bond in carboxylic acids. Absorption Y (1700 cm^{-1}) is at the wavenumber characteristic of the C═O bond. The functional group present in the molecule is the carboxylic acid group, COOH.

Mass spectrometry

Every compound has a unique **mass spectrum**. In a mass spectrum, the **molecular ion peak** gives the relative molecular mass of the compound.

Key terms

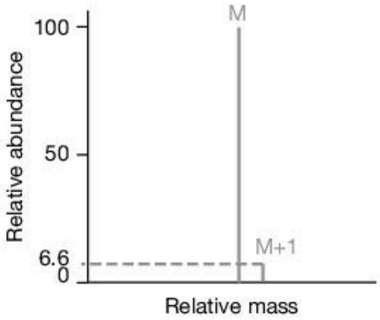
Mass spectrum: the pattern of peaks showing the mass to charge ratio of the ions formed when a sample undergoes mass spectrometry.

Molecular ion peak: the peak in a mass spectrum that is due to the positive ion formed when the parent molecule loses an electron.

On the right of the molecular ion peak is the M + 1 peak. The M + 1 peak is present because carbon exists naturally as two isotopes: C-12 (98.9%) and C-13 (1.1%). The height of the M + 1 peak can be used to calculate the number of carbon atoms.

Number of carbon atoms in molecule =

$$\frac{\text{percentage height of M + 1 peak compared to M peak}}{1.1\%}$$



▲ **Figure 22.2** The height of the M + 1 peak is 6.6% of the height of the molecular ion peak, so the number of carbon atoms is $\frac{6.6\%}{1.1\%} = 6$.

An M + 2 peak shows that a molecule includes chlorine or bromine atoms, with isotopes that differ in mass number by two:

- If the heights are the same, the molecule contains a bromine atom.
- If the ratio of the M : M + 1 peaks is 3 : 1, the molecule contains a chlorine atom.

Fragments in a mass spectrum suggest the structure of a compound. Table 22.1 shows some common fragments.

Key term

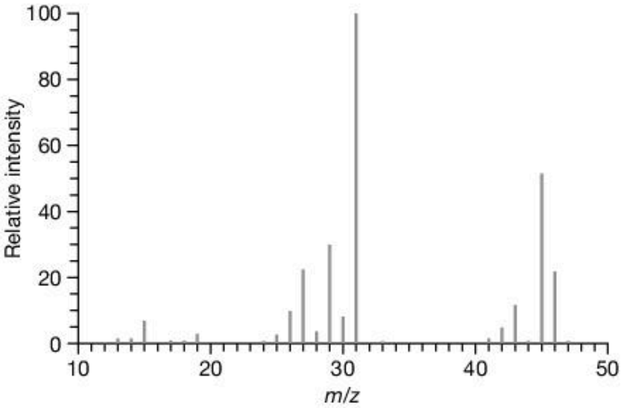
Fragments: the ions formed in mass spectrometry when the parent molecule breaks up.

▼ **Table 22.1** Fragments in a mass spectrum

Mass	Fragment
15	CH_3^+
28	CO^+
43	$CH_3CH_2CH_2^+$
77	$C_6H_5^+$ from a benzene ring

Worked example

The mass spectrum of a compound is shown below.



a) Give the relative molecular mass of the compound.

b) Suggest the formula of the fragment that the results in the peak at $m/z = 29$.

c) Suggest the formula of the fragment lost by the original molecule that results in the peak at $m/z = 31$.

d) Suggest the formula of the fragment lost by the original molecule that results in the peak at $m/z = 29$.

e) Suggest the formula of the molecule.

Answer

a) The molecular ion peak has $m/z = 46$, so this is the relative molecular mass of the compound.

b) $CH_3CH_2^+ = (2 \times 12) + (5 \times 1) = 29$

c) Mass of fragment lost = relative molecular mass – mass of fragment with m/z of 31

$$= 46 - 31$$

$$= 15$$

The formula of the fragment is likely to be CH_3^+, since this has a relative mass of $12 + (3 \times 1) = 15$.

d) Mass of fragment lost $= 46 - 29 = 17$
The formula of the fragment is likely to be OH^+, since this has a relative mass of $16 + 1 = 17$.

e) The compound breaks up to form CH_3^+, $CH_3CH_2^+$ and OH^+. This means its formula could be CH_3CH_2OH.

Proton (^{1}H) NMR spectroscopy

Proton NMR helps to identify the number of hydrogen atoms in a molecule, and their environments within the molecule.

In a **proton NMR spectrum**, the environment of a proton in a molecule determines the position of its peak in the NMR spectrum. This means that each peak represents protons in a different molecular environment. The position of a peak is measured as the chemical shift of the proton, δ, relative to TMS. Values for typical proton chemical shift values are given in the data booklet.

Remember

TMS, tetramethylsilane, is the standard for chemical shift measurements. It is unreactive and non-toxic. Its protons give one peak that is not close to the peaks of protons in other compounds.

The relative area under a peak gives the relative number of protons in that environment.

High-resolution NMR spectra show that some peaks are split into several smaller peaks:

- A group of two peaks is a doublet.
- A group of three peaks is a triplet.
- A group of four peaks is a quartet.

Splitting happens when protons joined to neighbouring carbon atoms interact. A group with n protons results in the protons in a neighbouring group splitting to make $n + 1$ peaks. This is the $n + 1$ rule.

Chemists use proton exchange to identify protons in —OH and —NH:

- First, a normal proton NMR is obtained.
- D_2O is added to the sample, with shaking.
- A second proton NMR is recorded.

Protons from —OH and —NH are exchanged with deuterium from the D_2O. Deuterium does not show up on NMR spectra, so any peaks from —OH or —NH disappear.

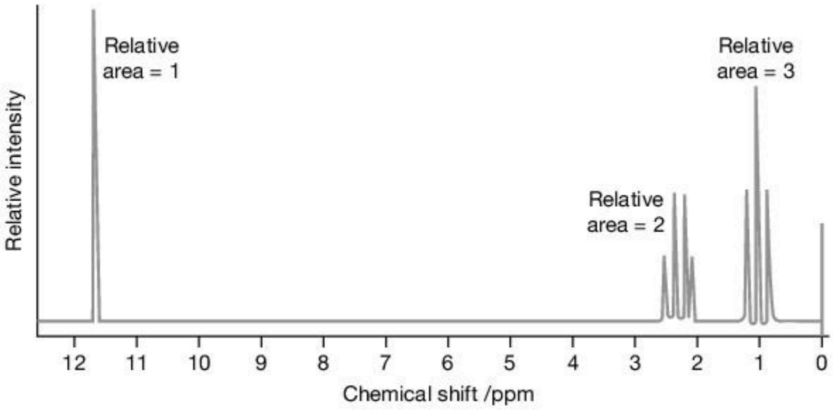
Remember

Proton NMR must be carried out in a solvent in which hydrogen has been replaced by deuterium, ^2H. Useful solvents include $CDCl_3$ and D_2O.

Worked example

The NMR spectrum is for compound **X**, which has the molecular formula $C_3H_6O_2$.

Deduce the structural formula of **X**, explaining your reasoning.



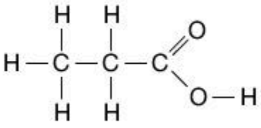
Answer

From the data booklet, the peak at $\delta = 11.7$ is from a proton joined to an oxygen atom in a carboxylic acid or from a proton joined to a nitrogen atom in an amide. Since the molecular formula shows that the compound does not have a nitrogen atom, this peak must result from a proton joined to an oxygen atom in a carboxylic acid.

The peak at δ 2.2–3.0 is caused by an alkyl group next to C=O. It is split into four, so is next to an alkyl group with three protons.

The peak at 0.9–1.7 is caused by an alkyl group. It is split into three, so is next to an alkyl group with two protons.

The structural formula is:



Carbon-13 NMR spectroscopy

Carbon-13 NMR spectroscopy uses signals from ^{13}C nuclei to identify carbon atoms in different environments in a molecule. In this type of spectroscopy, **chemical shift** values give the environments of the different carbon atoms in the molecule.

Key term

Chemical shift: the difference between the resonant frequency of a nucleus in a magnetic field and that of a named standard.

Remember

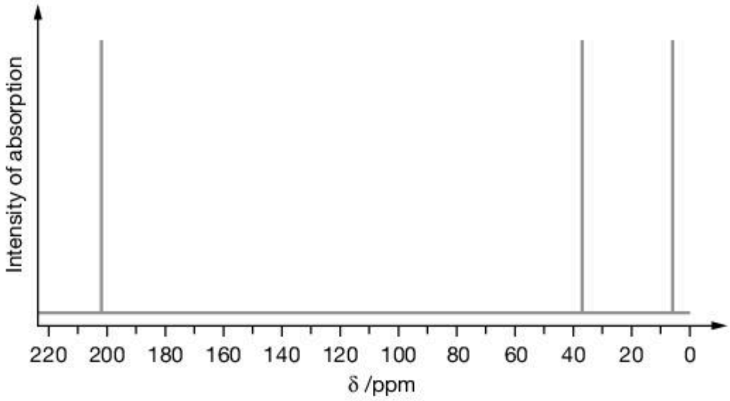
In carbon-13 spectroscopy there is no splitting.

Worked example

Substance **Y** has the carbon-13 NMR spectrum below. The molecular formula of **Y** is C_3H_6O.

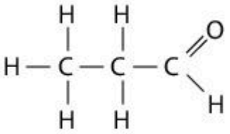
a) Draw two possible isomers for **Y**.

b) Use the spectrum to predict which of the two isomers you have drawn shows compound **Y**.



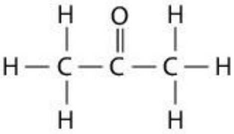
Answer

a)



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-C\overset{O}{\underset{H}{}}$

and



$H-\overset{H}{\underset{H}{C}}-\overset{O}{C}-\overset{H}{\underset{H}{C}}-H$

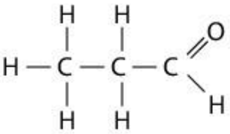
b) There are three peaks, showing that each carbon atom has a different environment.

The peak at $\delta \approx 207$ ppm shows that **Y** includes a carbonyl group, C=O.

The peak at $\delta \approx 38$ ppm shows that **Y** includes a carbon atom next to a carbonyl group.

The peak at $\delta \approx 7$ ppm shows that **Y** includes an alkyl group that is not next to an electronegative atom.

The evidence shows that **Y** is propanal:



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-C\overset{O}{\underset{H}{}}$

Worked example

Predict the number of peaks in the carbon-13 NMR spectrum of propanone. Explain your prediction.

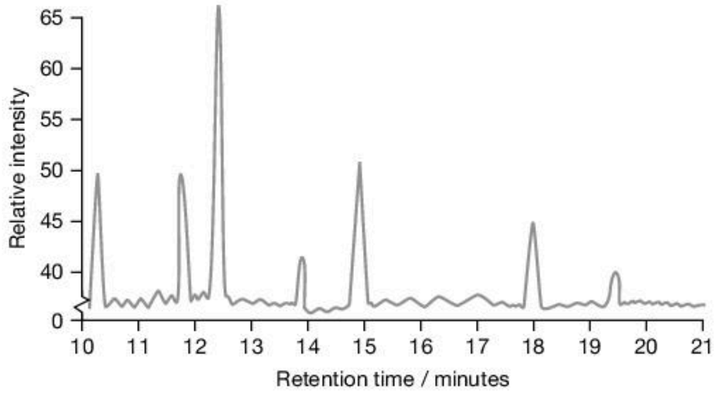
Answer

There will be two peaks. One for the two equivalent CH_3 groups, and one for the C=O carbon atom.

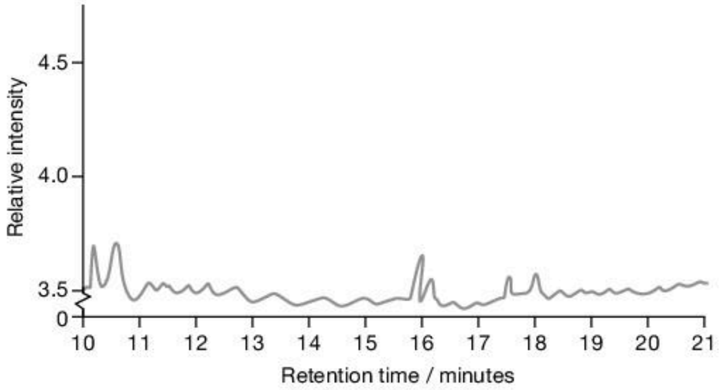
Raise your grade

1 Chromatogram **A** was obtained from the urine of a person who smokes cigarettes. Chromatogram **B** was obtained from the urine of a person who does not smoke.

A



B



The table shows the retention time of some substances under the conditions at which the chromatograms were obtained.

Substance	Retention time/min
2-methylphenol	13.9
3-methylphenol	12.5
4-chlorophenol	19.5
Phenol	10.2

(a) Name the one substance that was present in the urine of the smoker and the non-smoker. Explain your answer. [2]

Phenol. ✓✗

The candidate got the correct answer, but did not explain it. She needs to add that there is a peak at 10.2 minutes for both the smoker and non-smoker. This retention time corresponds to phenol in the table. This shows that phenol is present in the urine of both people.

(b) Estimate the relative concentration of 3-methylphenol compared to the amount of phenol in the urine of the smoker. [1]

Half the amount. ✗

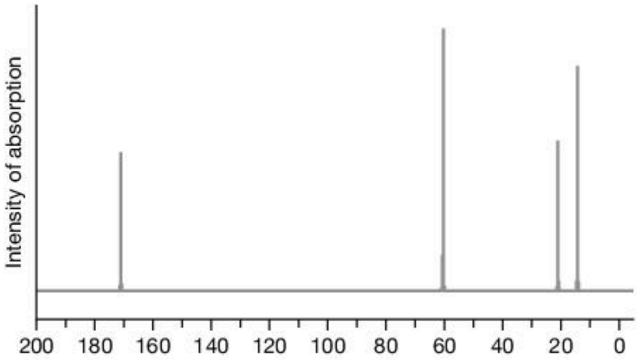
The area under the peak for 3-methylphenol is about twice the area under the peak for phenol. This shows that the concentration of 3-methylphenol is about twice the concentration of phenol.

(c) State which of the substances detected in the urine of the smoker moved through the column most quickly. [1]

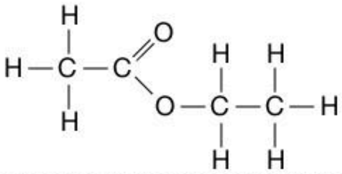
4-chlorophenol ✘

The substance with the shortest retention time moves through the column fastest. The data in the table show that phenol has the shortest retention time.

2 The C-13 NMR spectrum of ethyl ethanoate is given below.



(a) Draw the displayed formula of ethyl ethanoate. [1]



✔

(b) Explain why the C-13 NMR spectrum has four peaks. [1]

Each of the four carbon atoms is in a different environment. ✔

(c) State which carbon atoms in ethyl ethanoate caused each of the two peaks on the left of the spectrum. [2]

Left peak – carbon atom in COO group. ✔

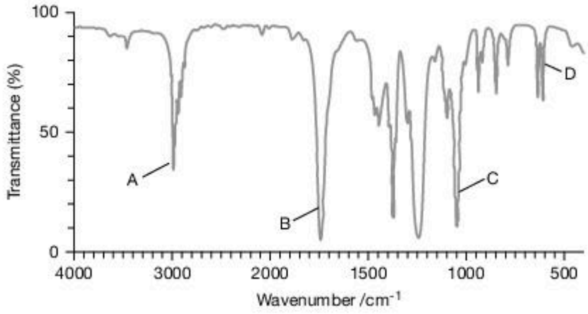
Second from left peak – carbon atom O–CH_2–CH_3 ✔ ✘

The candidate needs to make clear which of the two carbon atoms in this formula he means.

Exam-style questions

1 The image below is the infra-red spectrum for propanone.

Which labelled peak results from absorption of the C═O group? [1]



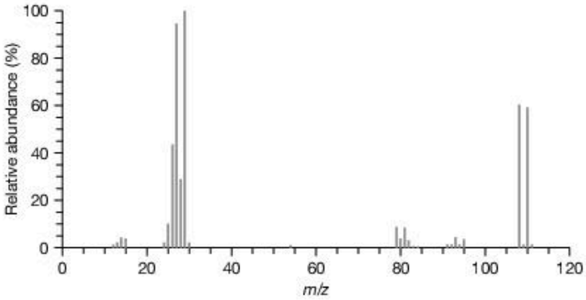
2 An infra-red spectrum shows an absorption at 1200 cm^{-1}.

Which bond might this absorption correspond to? [2]

A C—O **B** C═C

C C═O **D** C—H

3 The mass spectrum of compound **Y** is shown below.



(a) Describe and explain two deductions that can be made from the peaks at $m/z = 108$ and $m/z = 110$. [2]

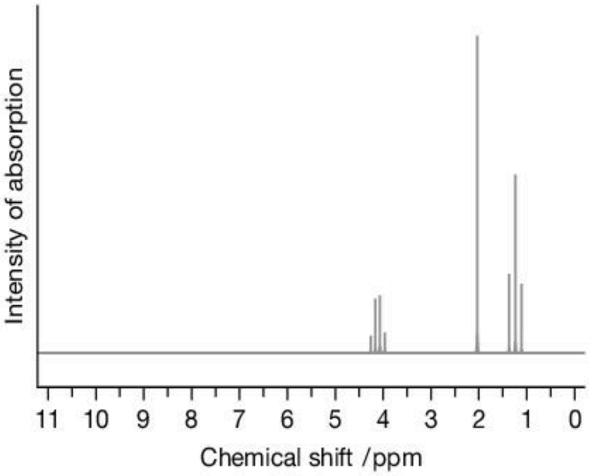
(b) Deduce the formula of the fragment at $m/z = 81$. [1]

(c) Explain how the mass spectrum suggests that compound **Y** might include an ethyl group. [2]

(d) Explain the presence of the peak at $m/z = 111$. [1]

4 The ^{1}H NMR spectrum of compound **Z** is shown below.

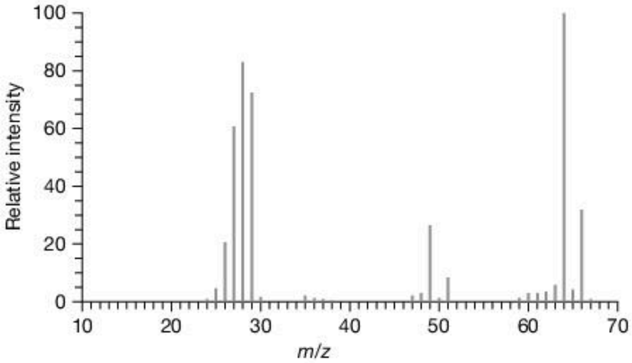
The molecular formula of **Z** is $C_4H_8O_2$.



Deduce whether compound **Z** is ethyl ethanoate or butanoic acid. Explain your deduction in detail.

Include formulae for the two compounds in your answer. [4]

5 The mass spectrum of compound **B** is shown below.



(a) Describe and explain two deductions that can be made from the peaks at $m/z = 64$ and $m/z = 66$. [2]

(b) Suggest the fragment that resulted in the peaks at 49 and 51, and explain their relative heights. [2]

23 Organic synthesis

A 30.1–30.5 pages 549–557

Key points

☐ Explain why single optical isomers of chiral drugs are often required.

☐ For organic molecules containing several functional groups
  - identify functional groups
  - predict properties

☐ Devise multi-step synthetic routes to prepare organic molecules.

☐ Analyse synthetic routes in terms of
  - type of reaction
  - reagents
  - by-products.

Chiral drugs

Some medical drugs are extracted from natural sources. Most of these drugs contain one or more chiral carbon atoms, and exist as a single optical isomer.

Most reactions in plants and animals involve enzymes, and most enzymes are able to undergo reactions with only one of the **enantiomers** of a chiral substance.

When chemists make drugs synthetically, often only a single optical isomer is required. This is for two reasons:

- Only one of the isomers may be effective in treatment.
- One of the isomers may cause harmful side effects. This was the case with thalidomide, which was used to treat pregnancy sickness in the 1960s.

If the synthetic preparation of a drug produces a mixture of isomers, chemists may need to separate the isomers so that the correct one can be used as the drug.

Key term

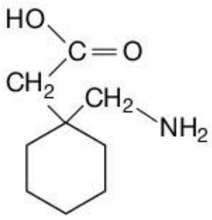
Enantiomer: one of the two optical isomers of a chiral substance.

Identifying functional groups and predicting properties

Most naturally occurring organic compounds have more than one functional group. You can predict some of the properties of a compound if you identify its functional groups. However, it is not possible to predict properties with certainty, because the properties of a functional group can change those of a nearby functional group.

Worked example

The drug gabapentin treats nerve pain. Here is its formula:



a) Name and label two functional groups in gabapentin.

b) Predict the formulae of all the products of the reaction of gabapentin in the following reactions:

i) with sodium hydroxide solution

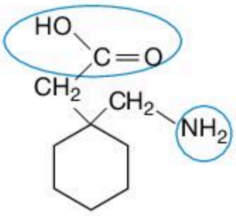
ii) with $SOCl_2$

iii) with ethanoyl chloride

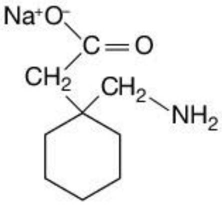
iv) with ethanol.

Answer

a) The functional groups are circled in the structure on the right: the functional group at the top is a carboxylic acid group, and the functional group on the right is an amine group.



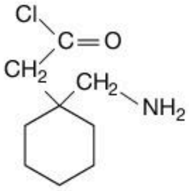
b) **i)** The carboxylic acid group reacts. The products are a salt with the formula below and water.



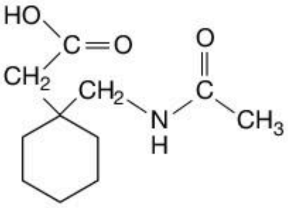
Exam tip

Take care when identifying functional groups. If you see an $-NH_2$ group, look for a C=O group on the neighbouring carbon atoms. This would mean that the compound had an amide group, not an amine group.

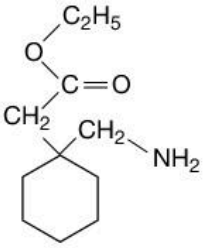
ii) The carboxylic acid group reacts. The products are HCl, SO_2, and the compound with the formula below.



iii) The amine group reacts with ethanoyl chloride to make HCl and the amide with the formula below.



iv) The carboxylic acid group reacts to make H_2O and the ester with the formula below.



Devising synthetic routes

Chemists make organic compounds for particular purposes, for example as drugs. When devising a **synthetic route**, they might follow the steps below:

- Decide the structure of the target molecule. This might be similar to, or the same as, a natural product that has been shown to treat a certain disease, for example.
- Choose starting materials. These are molecules that are simpler than the target molecule, and readily available.
- Devise possible synthetic routes with as few steps as possible, and choose the most promising to try out.
- Choose reaction conditions to maximise yield and rate, and to minimise wasteful **by-products**.

The synthetic routes you devise will be simpler than those devised by chemists working at universities or in pharmaceutical companies. You will be told the starting materials, and what you need to make.

Key terms

Synthetic route: the series of steps required to make a product.

By-product: an unwanted product made during the synthesis of something else.

Worked example

Devise a three-step synthesis to make propylamine from ethene.

Give the reactants and conditions required for each step, as well as equations.

Answer

Step 1	Bubble ethene gas through concentrated aqueous HBr.	$CH_2CH_2 + HBr \rightarrow CH_3CH_2Br$
Step 2	Heat the bromoethane under reflux with sodium cyanide dissolved in ethanol.	$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$
Step 3	Reduce the propanenitrile made in Step 2 by reacting with $LiAlH_4$ in dry ethoxyethane and then adding a small amount of dilute HCl.	$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$

Remember

If you need to increase the chain length, use the reaction with sodium cyanide.

Exam tip

Start by drawing the formulae of the starting material and target molecule. Then work out intermediate compounds for the synthetic route. Finally, write equations and give reaction conditions.

Analysing synthetic routes

There is often more than one synthetic route for making a given organic compound. Chemists then need to decide which route is best. Points to consider include:

- the cost and availability of the starting materials
- the cost and availability of the reagents required for each step
- the nature of any by-products produced
- hazards associated with each step
- **percentage yield** and **atom economy**.

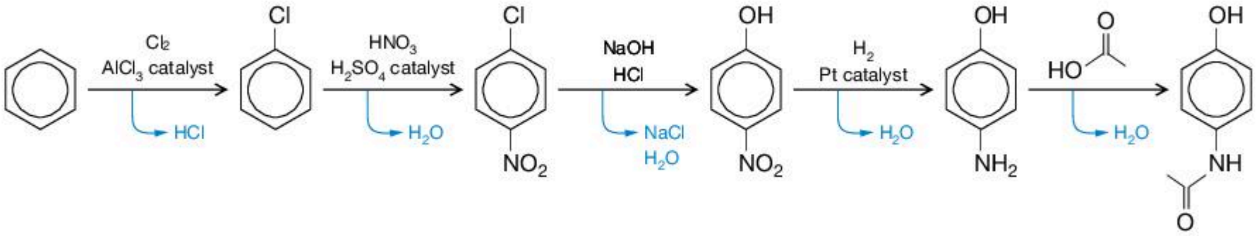
Key terms

Percentage yield : this compares the mass of the desired product obtained with the theoretical maximum possible mass of the product. It is calculated by dividing the actual yield by the theoretical maximum yield and multiplying by 100%.

Atom economy: this expresses the proportion of the starting materials that end up as useful products. It is calculated by dividing the relative formula mass of the desired product by the sum of the relative formula masses of the reactants and multiplying by 100%.

Worked example

One method for the production of paracetamol is outlined below. By-products for each step are shown at the end of curved arrows.



a) Name the starting material in the synthesis.

b) Give the number of steps in the synthesis.

c) Name three by-products of the process.

d) Suggest, in general terms, how chemists might look to improve the synthetic route.

Answer

a) Benzene is the starting material in the synthetic route.

b) The synthesis has five steps.

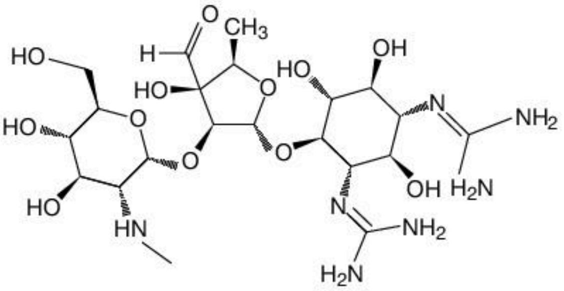
c) The by-products are HCl, water and NaCl.

d) Improvements might include reducing the number of steps, avoiding by-products (in particular acidic HCl) and finding alternatives to the $AlCl_3$ and Pt catalysts.

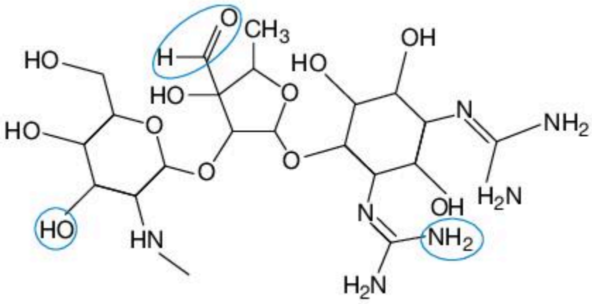
Raise your grade

1 This question is about drugs used to treat tuberculosis.

(a) Streptomycin was the first drug developed to treat tuberculosis.
Its structural formula is given below.



Circle and name three different functional groups in streptomycin. [3]



The top functional group is a carboxylic acid. ✗

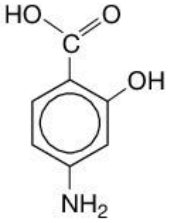
This is actually an aldehyde group. The carboxylic acid functional group is COOH.

The left functional group is an alcohol group. ✓

The right functional group is an amide group. ✗

This is actually an amine group. A amide group is NHC$=$O.

(b) Drug **X** is also a tuberculosis drug. It has the formula below.

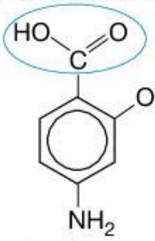


(i) Give the systematic name for drug **X**. [1]

2-amino-4-hydroxybenzoic acid ✗

The candidate has given incorrect numbers. The numbering starts from the carbon atom joined to the carboxylic acid group. This means that the name is 4-amino-2-hydroxybenzoic acid.

(ii) Circle and name one functional group that is present in drug **X** but not in streptomycin. [1]



The functional group is a carboxylic acid. ✓

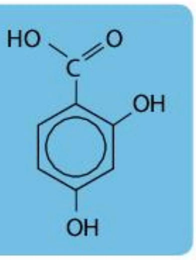
(c) Drug **X** takes part in chemical reactions.

(i) Drug **X** is warmed with nitrous acid, HNO_2.

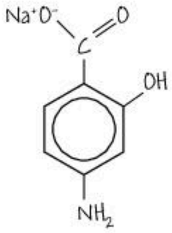
Predict the structural formula of the organic product formed. [1]

✗

This answer is almost correct. However, the candidate has forgotten to include the —OH group that was already attached to the benzene ring. The correct formula is given here.



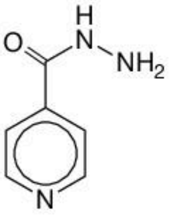
(ii) Sodium carbonate powder is added to a solution of drug **X**.
Predict the formula of the organic product formed, and name the gas produced in the reaction. [2]



✔ ✗

The candidate correctly deduced that the carboxylic acid group reacts in these conditions, forming a salt. However, he did not answer the second part of the question, to name the gas produced. Since the reaction is that of an acid with a carbonate, the gas produced is carbon dioxide.

(d) A third drug used to treat tuberculosis is isoniazid.
Its formula is shown below.



Name one functional group that is present in isoniazid but not in streptomycin or drug **X**. [1]

an amide group ✔

Exam-style questions

1 Give two reasons to explain why, in the synthetic preparation of drug molecules, a single optical isomer is often required. [2]

2 Devise the following syntheses.

For each synthesis, give the reagents and conditions required.

(a) a two-step synthesis to make butan-2-ol from but-2-ene [4]

(b) a two-step synthesis to make benzoic acid from benzene [2]

(c) a three-step synthesis to make ethyl propanoate from propanol. [6]

3 The compound 4-amino-2-hydroxybenzoic acid is a drug used to treat tuberculosis. It can be made in a four-step synthesis.

The starting compound for the synthesis is 2-aminobenzoic acid.

(a) Draw the structural formula of 2-aminobenzoic acid. [1]

(b) In the first step of the synthesis, 2-aminobenzoic acid is converted to 2-amino-4-nitrobenzoic acid.

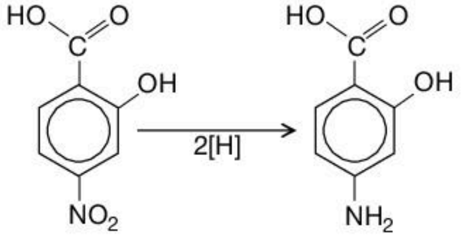
Suggest suitable reagents and conditions for this reaction. [2]

(c) In the second step of the synthesis, 2-amino-4-nitrobenzoic acid is dissolved in cold hydrochloric acid. A solution of cold sodium nitrite is slowly added.

Predict the structural formula of the salt formed. [1]

(d) In the fourth step of the synthesis, 2-hydroxy-4-nitrobenzoic acid reacts with iron and hydrochloric acid to form the drug.

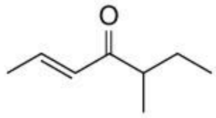
The expression below summarises the reaction that occurs.



Name the type of reaction shown in the equation. [1]

4 The compound with the formula below is known as filbertone.

It is responsible for the smell of hazelnuts.



(a) Circle and name two functional groups in filbertone. [2]

(b) Predict and give the structural formula of the organic products of the reaction of filbertone with the reagents below.

(i) bromine water [1]

(ii) $LiAlH_4$ in dry ethoxyethane [1]

(iii) cold, dilute potassium manganate(VII) [1]

(c) Predict what happens when Fehling's solution is added to filbertone.

Give a reason for your prediction. [1]

(d) Predict what would be observed on adding a few drops of filbertone to 2,4-DNPH. [1]

(e) Filbertone exists as two enantiomers.

(i) Explain what is meant by the term *enantiomer*. [1]

(ii) Draw a * on the one chiral carbon atom in filbertone. [1]

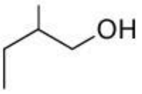
(iii) Draw 3-dimensional structures to show the two enantiomers of filbertone. [2]

(iv) The two enantiomers of filbertone have different smells.

State one other difference in properties between the two enantiomers of filbertone. [1]

(f) In the first step of a laboratory synthesis of filbertone, the alcohol with the formula below was warmed gently with acidified aqueous dichromate(VI).

The product was removed as it was formed.



Predict the skeletal formula of the product of the first step of this synthesis. [1]

24 Practical assessment

Practical work is fundamental to chemistry, and you will have developed your practical skills throughout the course. Papers 3 and 5 assess these skills.

Paper 3

Paper 3 is part of the AS examination. It is a practical exam, with two or three questions, and tests your skills in:

- manipulating apparatus, making measurements and making observations
- presenting data and observations
- analysing results, drawing conclusions and evaluating techniques and results.

In one of the questions, you will perform tests on one or more unknown substances. You will make detailed observations during the tests, and record them carefully. You will then use your observations to draw conclusions about the substances.

In the other question or questions you will make measurements. One question might involve a titration. The other might ask you to investigate reaction rates, or enthalpies of reaction, or mass changes on heating. You will need to draw tables to record your data, and draw graphs to present them. You will then analyse the data, do calculations and draw conclusions.

You are also likely to be asked to evaluate the experiments – perhaps by pointing out sources of error, or by making suggestions for improvement.

The syllabus gives the mark scheme for Paper 3. It shows the number of marks allocated to each skill.

Paper 5

Paper 5 is part of the A Level examination. It is a written exam with at least two questions, and tests your skills in:

- planning an investigation
- analysing results, drawing conclusions and evaluating techniques and results.

One of the questions will ask you to plan how to answer a scientific question, or investigate a problem. You might not be given much guidance, and may be expected to write a detailed plan, draw apparatus, design tables and write equations. You might also be asked to make a prediction.

The other questions might give you some data. You will need to analyse the data, draw conclusions and perhaps evaluate the quality of the data.

The syllabus gives the mark scheme for Paper 5. It shows the number of marks allocated to each skill.

Manipulation, measurement and observation

It is important to collect high-quality data and make observations successfully, making decisions about observations or measurements.

When you are doing the experiments in Paper 3, you must follow the instructions carefully. Read through all the instructions first, before you start doing the practical. Use the correct apparatus, as well as the amounts of substances stated in the questions.

★ **Exam tip**

Always read the introductory information at the start of each question. This might help you to get more marks.

Testing unknown substances

When you do tests on unknown substances, describe each of your observations in detail. The terms below might be useful:

Key terms

Colourless: (not transparent or clear), this term describes a solution that looks like water.

Precipitate: this term describes small pieces of solid mixed with a liquid or solution.

Gelatinous precipitate: a precipitate that looks like jelly.

If a precipitate dissolves on adding more sodium hydroxide solution, for example, the precipitate is **soluble in excess**. If the precipitate does not dissolve, it is **insoluble in excess**.

Effervescence: this term describes the formation of bubbles.

If you are asked to do two tests, one after another, write down your observations for each test. For example, if you are asked to heat gently and then to heat strongly, write down your observations on heating gently and then your observations on heating strongly.

You might notice effervescence in tests on unknown substances. You then need to find out which gas has been made. To do this, follow the steps below:

1. Look at your results so far to see if there are any clues about what the gas might be. Then carry out the test for this gas.
2. If there are no clues, test for the gases listed in the table at the end of the question paper. Start with the ones that are easy to test for, such as hydrogen and oxygen. If these tests are negative, continue with the other gas tests listed until one gives a positive result.
3. In the results table, write down all the tests you did. For each test, state what you observed, and what the observation shows.

✗ Common error

Students sometimes misread questions. For example, a question says 'Add a few drops of sodium hydroxide solution, followed by excess'. Some students add excess solution immediately. This means that they do not record all the results they need.

★ Exam tip

Remember to give the colours of precipitates, and to describe colours in detail. Use phrases like *dark blue* or *light blue* instead of just *blue*, for example.

✗ Common error

Students often write the name of the gas formed, without describing how they tested for it. It is not enough to state 'Carbon dioxide was evolved'. Instead, write something like 'On bubbling the gas that was evolved through limewater, the limewater went milky. This shows that the gas is carbon dioxide.'

Making measurements

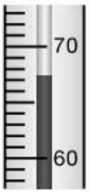
In chemistry, a thermometer is used to measure temperature, and a balance is used to measure mass. Volumes of solutions can be measured with pipettes, burettes and measuring cylinders. Volumes of gases are measured with gas syringes, or measuring cylinders over water.

Worked example

What are the readings on **(a)** the burette (in cm^3) and **(b)** the thermometer (in °C) shown below?

a)

b)



Answer

a) 24.60 cm^3

b) 67.5 °C

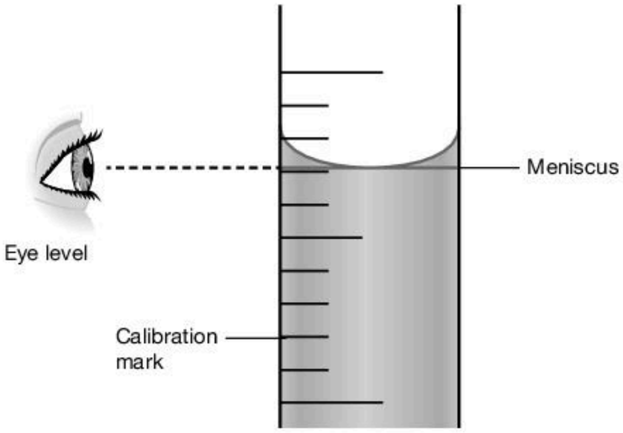
Remember

Give burette readings to the nearest 0.05 cm^3. One drop from a burette has a volume of 0.05 cm^3, so if one more drop leaves the burette shown here in **(a)**, the volume reading will be 24.65 cm^3.

Performing titrations

When doing a titration:

- Use a pipette to measure out the volume of the **aliquot** (the solution in the conical flask at the start of the experiment). The bottom of the meniscus should touch the calibration mark, as shown.



- Do a rough titration to find the approximate end point.
- Carry out repeat titrations until you obtain two titres within 0.10 cm^3.

Key term

Aliquot: a known volume of solution placed in the conical flask in a titration experiment.

★ **Exam tip**

When you have two titres that are within 0.10 cm^3 of each other, stop! Doing more titrations will waste valuable time in the exam.

★ **Exam tip**

Make sure there are no air bubbles in the tip of the burette, or in the pipette.

Rate of reaction experiments

In a rate of reaction experiment, you might be asked to measure the volume of a gaseous product made in a given time. The independent variable could be concentration or temperature.

Worked example

You will investigate how the rate of the reaction shown in the equation below depends on temperature:

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

a) Suggest the number of different temperatures at which to measure rate. Explain your answer.

b) Suggest the range for the temperature values. Explain your answer.

c) Should the experiment be repeated at each temperature? Explain your answer.

Answer

a) The rate should be measured at five temperatures. This means that, when a graph is plotted, it should be possible to decide whether to draw a straight line or smooth curve.

b) A suitable range is from 20 °C to 80 °C. These temperatures span a reasonably wide range of 60 °C and are easily achievable in the lab.

c) Repeating the experiment at each temperature would result in greater accuracy and less experimental error. However, it would take more time. The best strategy is to do the experiment once at each temperature, but to repeat the test if a measurement does not fit the pattern.

★ **Exam tip**

When doing rate experiments, it is important to be well organised. Have all your equipment ready, and write down all measurements immediately.

★ **Exam tip**

While doing an experiment, if you notice that a measurement does not fit the pattern, consider repeating the test for this value of the independent variable.

Key terms

Range: the difference between the highest and lowest values in a set of measurements.

Independent variable: the variable that you change.

Dependent variable: the variable that you observe or measure.

Anomalous result: a result that does not fit the pattern.

Accurate result: a result judged to be close to the true value.

Remember

If a scale on a thermometer shows a mark for every 1.0 °C, then measurements should be recorded to the nearest 0.5 °C. If a scale on a burette shows a mark for every 0.1 cm^3, then the readings should be given to the nearest 0.05 cm^3.

Enthalpy change experiments

In an enthalpy change experiment, you will measure the temperature before and after a reaction. It is important to be consistent in making these readings.

Presentation of data and observations

Recording data and observations

Before collecting any data, you need to draw a table in which to record all your data. As well as columns for the data you collect, you might need to include columns for calculated values or for conclusions.

When preparing a table:

- Put the independent variable in the left column.
- Include both the quantity and unit in the column headings.
- Record all readings to the same **resolution**, or number of decimal places.

Key term

Resolution: the smallest change in the quantity being measured that can be seen on a measuring instrument.

Worked example

A student investigates how the volume of gas collected in 1 minute varies with concentration of acid for a given reaction. Write column headings in the table.

Answer

Concentration of acid /$mol\ dm^{-3}$	Volume of gas collected in 1 minute /cm^3

The independent variable is in the column on the left, and the dependent variable is shown in the column on the right.

Exam tip

Always write a / symbol between the name of the variable and its units. It is not acceptable to write a column heading like this: *Concentration of acid mol dm*$^{-3}$.

Common error

Some students use the symbol *t* in column headings. Do not do this, because *t* could stand for temperature or time.

Displaying your calculations and reasoning

When doing calculations, show each step clearly. You may be awarded marks for doing this. It is also helpful to include units in all steps of a calculation. Make sure you can convert from one unit to another. For example, 1 dm^3 = 1000 cm^3. This means that 25.00 cm^3 is 0.02500 dm^3.

In calculations, be sure to use the correct number of significant figures. You cannot go wrong if you follow the rule below:

> *Give calculated figures to the same number of significant figures, or one more than, the measured quantity with the smallest number of significant figures.*

If you measure a titre volume to four significant figures, such as 23.05 cm^3, then concentration values should be given to four significant figures, such as 1.024 $mol\,dm^{-3}$ or 0.9876 $mol\,dm^{-3}$.

If the concentration of one of the reactants is given to three significant figures, such as 1.00 $mol\,dm^{-3}$, it is best to show the concentration of the other reactant to three significant figures, for example 1.02 $mol\,dm^{-3}$.

If you use your observations or data to make a deduction, show each of the steps in the process you use, as in the worked example below.

Worked example

A candidate has an unknown white salt, **X**. He does the tests and makes the observations shown in the table. Deduce the ions present in **X**.

Test	Observations
To 1 cm depth of a solution of **X** in a test tube, add aqueous sodium hydroxide.	No precipitate formed.
Gently warm a small sample of solid **X**.	Strong sharp smell. Damp red litmus paper went blue.
To 1 cm depth of a solution of **X** in a test tube, add dilute nitric acid followed by silver nitrate solution,	White precipitate formed.
followed by aqueous ammonia.	Precipitate dissolved to form a colourless aqueous solution.

Answer

The sodium hydroxide test, in which no precipitate was formed, shows that the cation is not Al^{3+}, Ca^{2+}, Mg^{2+} or Zn^{2+}. The gas produced when **X** was warmed is ammonia, showing that the cation is NH_4^+. The silver nitrate test shows that the anion is Cl^-. This is confirmed by the addition of aqueous ammonia, in which the precipitate dissolved. Solid **X** must be ammonium chloride.

Data layout – plotting graphs

You often need to present your data on a graph. To get full marks:

- Label the x-axis with the name of the independent variable, and the y-axis with the name of the dependent variable.
- Choose suitable scales for the x- and y-axes:
  - The scales must be even, so that one big square on the paper always represents the same quantity, for example 10 °C.
  - Choose scales that make it easy to read the graph, for example 1, 2, 5 or 10 units to a 2 cm square.
  - The scales must take up at least half the paper in both directions.

    Not all scales must start at zero. If the lowest temperature is 30 °C, start the temperature scale at this temperature, or just below.
- Give the axes the same titles as the column headings, such as *temperature* /°C or *volume* /cm^3.

- Plot the points with a sharp pencil. They can be a small cross × or a dot in a circle ⊙.
- If appropriate, draw a line of best fit. This might be a straight line or a smooth curve. Make sure that there are an equal number of points on each side of the line along its whole length.
- If you think a point is anomalous, label it on the graph. Do not include this point when drawing a line of best fit.

Worked example

A student investigates the reaction shown by the equation below. She makes a hypothesis that, as temperature increases, the rate of reaction will increase because the particles will move more quickly.

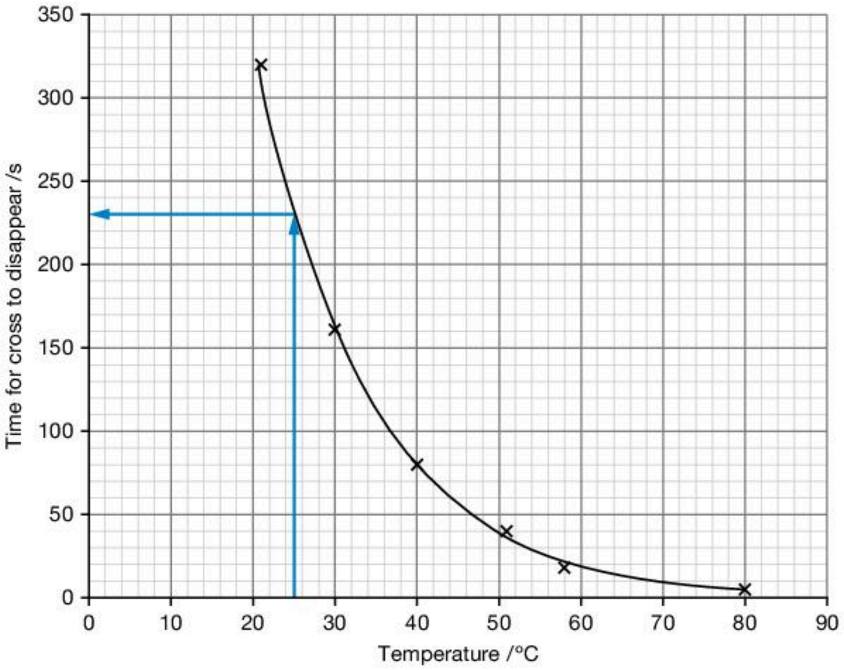
$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$

The student mixes the two solutions in a flask placed over a cross mark. The cross becomes invisible when enough solid sulfur forms. The student measures the time for the cross to disappear at different temperatures. Her results are in the table.

Plot the data in the table on a graph.

Temperature /°C	Time for cross to disappear /s
21	320
30	161
40	80
51	40
58	18
80	5

Answer



Analysis, conclusions and evaluation

Interpreting data or observations, and drawing conclusions

When you have made observations you need to interpret them and draw conclusions. The worked example on page 216 shows how to explain deductions from tests on unknown substances.

If you have collected data, you might need to calculate the mean value of a set of repeat readings. You might also need to calculate the rate of a reaction, or the volume of a gas, or the mass of a mole of a gas.

You also need to be able to work out the gradient of a graph, or find unknown values from a graph.

Remember

When you calculate the gradient of a graph, choose points on the line that are far apart from each other.

Worked example

The data give three titres for a titration. Calculate the mean titre.

$25.90\,\text{cm}^3$ $25.95\,\text{cm}^3$ $25.85\,\text{cm}^3$

Answer

$$\text{Mean} = \frac{25.90 + 25.95 + 25.85}{3} = 25.90\,\text{cm}^3$$

Worked example

Use the graph on page 217 to predict the time for the cross to disappear at a temperature of 25 °C.

Answer

Time = 230 s. The arrows on the graph show how to find this value.

You also need to draw conclusions from numerical data. A good conclusion includes some, or all, of the features below:

- an description of the main features of the data, including any patterns
- a decision about whether the data support a given **hypothesis**
- a scientific explanation of the data or conclusion.

Key term

Hypothesis: a suggested explanation that can be investigated scientifically.

Worked example

Write a conclusion for the investigation in the worked example on page 217.

Answer

As the temperature increases, the time for the cross to disappear decreases. For every 10 °C increase in temperature, the time for the cross to disappear approximately halves. This pattern shows that the rate of reaction increases with temperature. This supports the hypothesis.

The rate of reaction increases with temperature for two reasons. The first is that, as temperature increases, the particles move faster, so collisions are more frequent. The second is that, as temperature increases, a greater proportion of particles have enough energy to react when they collide.

Exam tip

When you write a conclusion, check that you have included two or three of the features of a good conclusion described above. You only need to refer to a hypothesis if the question asks you to.

Identifying sources of error and suggesting improvements

Some errors are impossible to avoid. For example:

- In some titrations it is difficult to judge the end point.
- In enthalpy titrations some heat is 'lost' (transferred to the surroundings).

Some errors are **systematic**, such as a thermometer always reading 1 °C too low. Some errors are **random**, such as room temperature changing when doors or windows are opened and closed.

You can estimate the size of an error. For example, a burette reading might be $23.05 \pm 0.05\,\mathrm{cm}^3$. A temperature reading might be 56.5 ± 0.5 °C.

You also need to judge which errors are more significant. For example, in an enthalpy experiment errors caused by heat loss are more significant than thermometer reading errors.

You might be asked how to collect more accurate or more precise data. Your suggestions might include:

- repeating readings
- using different apparatus, such as a pH meter instead of indicator paper, or a digital thermometer instead of an alcohol thermometer.

Key terms

Systematic errors: measurement errors caused by measurements differing from the true value by a consistent amount for each measurement that is made.

Random errors: measurement errors caused by measurements varying unpredictably from one measurement to the next.

✗ Common error

Some students state that errors are caused by 'human error'. This gains no marks.

Planning an investigation

In Paper 5 you need to plan an investigation and describe how to carry it out. This might involve:

- identifying independent, dependent and control variables
- making a prediction
- choosing apparatus, drawing a diagram to show how to set it up, and describing how to use it
- suggesting amounts or concentrations of reagents
- describing what to do in the investigation, step-by-step
- describing how to change the independent variable
- describing how to measure the dependent variable
- drawing results tables
- describing how to use data to draw a conclusion, including which graphs to plot.

You also need to identify risks in the investigation and suggest precautions to minimise the risks.

Worked example

The combustion reactions of alcohols are exothermic. You are to plan an investigation to find out how the molar enthalpy of combustion varies with the mass of one mole of a substance.

a) Identify the independent and control variables in the investigation.

b) Draw a labelled diagram showing how to use a spirit burner and other laboratory apparatus to collect data that will enable you to calculate the enthalpy of combustion of ethanol.

c) Describe the risks in the investigation and suggest how to minimise each one.

d) Describe how to use the apparatus in **(b)** to collect data to enable you to calculate the enthalpy of combustion of ethanol.

e) Explain how to use the data, and one piece of data from the data booklet, to calculate the molar enthalpy of combustion of ethanol.

f) **i)** Describe one change that you could make to the apparatus in **(b)** to enable you to collect data for other alcohols.

ii) Suggest how many alcohols to investigate, and give a reason for your suggestion.

g) Identify the control variables in the investigation, and suggest how to control them.

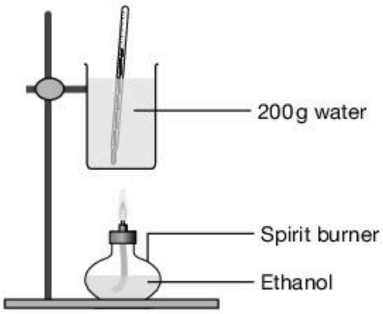
h) Draw a table in which to record the independent variable and the other data needed to carry out the calculations for the different alcohols.

i) Sketch axes for a graph to show how enthalpy of combustion varies with the mass of a mole of alcohol.

Answer

a) The independent variable is the mass of one mole and the dependent variable is the molar enthalpy of combustion.

b)



c) There is the risk of burning from hot apparatus. Minimise this risk by not touching the hot apparatus. There is also the risk of poisoning if combustion is incomplete and carbon monoxide is produced. Minimise this risk by working in a well-ventilated room.

d) Weigh the ethanol and spirit burner together, and measure the temperature of the water. Light the wick and allow the burning ethanol to heat the water. Measure the temperature of the water, and the mass of the ethanol and spirit burner together.

e) Follow the steps below:

- Temperature change of water = ΔT = temperature at end – temperature at start
- Mass of ethanol burned = mass at start – mass at end
- Substitute the temperature change into the equation $\Delta H_c = mc\Delta T$, where m is the mass of the water, c is the specific heat capacity of water, and ΔH_c is the enthalpy change of combustion of ethanol for the amount of ethanol burned.
- Substitute values into the equation below to calculate the molar enthalpy change of combustion of ethanol

$$H_{c,\text{molar}} = H_c \times \frac{\text{mass of 1 mol of ethanol}}{\text{mass of ethanol burned}}$$

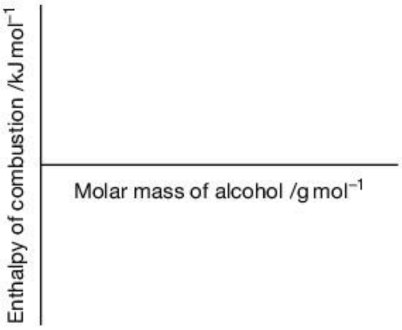
f)
- Use a different spirit burner filled with a different alcohol.
- Use five alcohols, so that a graph can be drawn, and it is clear whether the data show a curve or a straight line.

g) Distance between spirit burner and beaker – do not move the beaker; volume of water – use the same volume each time.

h)

Alcohol	Mass of 1 mol /g	Temperature of water at start /°C	Temperature of water at end /°C	Temperature change of water /°C	Mass of fuel at start /g	Mass of fuel at end /g	Mass change /g

i)



Analysis, conclusions and evaluation

In Paper 5 – as for Paper 3 – you will need to manipulate data, and draw conclusions from data and observations. You will also evaluate methods and data.

Dealing with observations

There is likely to be a question in Paper 5 which provides observations. You will need to interpret these and draw conclusions. The observations could include tests on inorganic substances, as well as for organic functional groups. You might also need to analyse spectra, using them to work out the structure of molecules.

Link

Tests for organic functional groups are given in Units 14 to 20. Unit 22, Analytical techniques, is all about analysing spectra.

Evaluating investigations

If you are asked to evaluate a method, think about the questions below:

- Have readings been repeated enough times?
- Is the range suitable?
- Have control variables been properly controlled?
- Are there any weaknesses in the method?

When evaluating results and conclusions, consider the following questions:

- Are any results anomalous, and if so why? What could be done about these results?
- Does the choice of method, and how it was carried out, allow you to be confident that the results and conclusion are correct?

You might also be asked questions like those below:

- What are the effects on the results of changing concentrations of solutions, or conditions such as temperature?
- What are the effects on the results of using apparatus incorrectly?

Drawing conclusions

As in Paper 3, you will need to draw conclusions from an investigation. You could be asked to give detailed scientific explanations of data and conclusions. You might also be asked to make more predictions.

25 Exam-style questions

Here is a selection of questions similar to those you will be asked in the exams. They are grouped by paper, and include plenty of hints to help you to achieve high marks.

Paper 1 style questions

Paper 1 consists of 40 multiple-choice questions. Questions 1 to 30 in the exam, and questions 1 to 18 in this book, have four possible answers. You have to choose the one correct answer. If you are not sure which answer is correct, draw a tick, cross or question mark next to each one. Then choose the best answer from those with the ticks or question marks.

If you really do not know which answer is correct, have a guess – you might pick up an extra mark!

1 Which isotope has the greatest number of neutrons?

A $^{57}_{26}Fe$

B $^{59}_{27}Co$

C $^{61}_{28}Ni$

D $^{54}_{25}Mn$

★ **Exam tip**

For question 1, you will need to work out the number of neutrons in each isotope shown. Then choose the isotope that has the most neutrons.

2 10 g of propane burned completely in oxygen.

What volume of carbon dioxide was made, at standard temperature and pressure?

A $5.45\,dm^3$

B $9.99\,dm^3$

C $16.4\,dm^3$

D $21.8\,dm^3$

★ **Exam tip**

In question 2 you need to use your knowledge of physical and organic chemistry. Start by writing the formula of propane and the balanced equation for its combustion. Then calculate the number of moles of propane in 10 g, and use the balanced equation to work out how many moles of carbon dioxide are made.

3 Compound **X** has a relative molecular mass of 116.

Its composition by mass is given below.

Carbon	62.07 %
Hydrogen	10.34 %
Oxygen	27.59%

What is the molecular formula of compound **X**?

A C_2H_4O

B C_3H_6O

C $C_4H_8O_2$

D $C_6H_{12}O_2$

★ **Exam tip**

A common error in questions like question 3 is to choose the empirical formula. You need to work out the empirical formula first, and then calculate the relative mass of the empirical formula. Use this, as well as the relative molecular mass and the empirical formula, to work out the molecular formula.

4 What is the electronic configuration of the P^{3-} ion?

A $1s^2\ 2s^2\ 2p^6\ 3s^2$

B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

★ **Exam tip**

For question 4, start by writing the electronic configuration of a phosphorus atom. Then place the extra three electrons in the correct orbitals.

5 Which list below gives the molecules in order of **decreasing** bond angle?

A ethane, methanal, water, beryllium fluoride

B methanal, ethane, water, beryllium fluoride

C beryllium fluoride, methanal, ethane, water

D water, ethane, methanal, beryllium fluoride

★ **Exam tip**

In question 5 you need to bring together your knowledge of organic and physical chemistry. Start by drawing each of the molecules, including any lone pairs. Then mark on their bond angles. The word in bold is important – the molecule with the biggest bond angle should come first.

6 The table gives the properties of some substances.

Which substance could be sodium ethanoate?

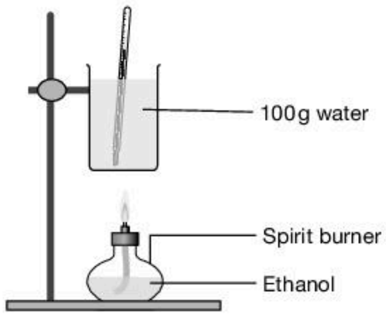
Substance	Melting point /°C	Boiling point /°C	Electrical conductivity of solid	Electrical conductivity of aqueous solution
A	2623	4639	good	good
B	114	184	poor	poor
C	98	883	good	good
D	324	881	poor	good

★ **Exam tip**

To start question 6, think about the bonding in sodium ethanoate. Does it consist of molecules, or is its bonding ionic or metallic?

7 A student set up the apparatus below.

She burned ethanol to heat 100 g of water.



The student recorded the results below.

Mass of ethanol + spirit burner at start = 248.20 g
Mass of ethanol + spirit burner at end = 247.58 g
Temperature of water at start = 26.0 °C
Temperature of water at end = 69.0 °C

★ **Exam tip**

In question 7 you need to do a calculation. Start by writing down the equation you need. Then write out each step of the calculation on rough paper – this will save time if you need to check your answer. In your calculations, you will use two mass values – the mass of water heated, and the mass of ethanol burned. Make sure you use these values correctly.

From these results, what is the calculated value of the enthalpy change of combustion of ethanol?

A 111.9 kJ mol^{-1}

B 1339 kJ mol^{-1}

C 1806 kJ mol^{-1}

D 28 980 kJ mol^{-1}

8 The enthalpy of combustion of carbon, as graphite, is –393.5 kJ mol^{-1}
The enthalpy of combustion of hydrogen, H_2, is –285.8 kJ mol^{-1}
The enthalpy of combustion of but-1-ene is –2716.8 kJ mol^{-1}

What is the standard enthalpy of formation of but-1-ene?

A –0.4000 kJ mol^{-1}

B –286.2 kJ mol^{-1}

C –2037.5 kJ mol^{-1}

D –3396.1 kJ mol^{-1}

★ **Exam tip**

For question 8, start by writing out the equation for the formation of but-1-ene from its elements.

9 The equilibrium constant, K_c, for the equilibrium below is 1.70×10^{-3} at 2300 K.

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

1 mol of nitrogen and 1 mol of oxygen are mixed in a closed container at 2300 K, and allowed to reach equilibrium. What is the concentration of nitrogen monoxide at equilibrium?

A 1.70×10^{-3} mol dm^{-3}

B 4.04×10^{-2} mol dm^{-3}

C 8.24×10^{-2} mol dm^{-3}

D 4.95×10^{3} mol dm^{-3}

★ **Exam tip**

Start question 9 by assuming that $2x$ mol of NO are present at equilibrium, along with $(1 - x)$ mol of nitrogen and $(1 - x)$ mol of oxygen. Then write out an equilibrium expression, substituting the value for K_c. Finally, solve for x.

10 Compound **Y** forms a soluble chloride with the formula YCl_2.

Its nitrate decomposes at a lower temperature than the decomposition temperature of $Ca(NO_3)_2$.

What could be the identity of **Y**?

A aluminium

B barium

C magnesium

D sodium

★ **Exam tip**

There are two pieces of information in question 10. Use the formula YCl_2 to eliminate two answers. Then use the information about the decomposition temperature to choose the correct answer.

11 What are the overall changes in oxidation number of chlorine in its reaction with hot aqueous sodium hydroxide?

A From 0 to –1 and +5

B From 0 to –1 and +1

C From 0 to +1 and +5

D From 0 to +1 and +4

★ **Exam tip**

Start by writing the equation for the reaction in question 11. Then work out the oxidation number of chlorine in each substance.

12 A student investigated compound **Z**, which is a sodium halide.
She added dilute solution of silver nitrate to a solution of **Z**, acidified with dilute nitric acid. Then she added aqueous ammonia.
She wrote down the observations below.

> A yellow precipitate formed, which dissolved in aqueous ammonia.

What can be deduced from these observations?

A Compound **Z** is NaCl.

B Compound **Z** is NaBr.

C Compound **Z** is NaI.

D One of the observations is incorrect.

13 When an alkene is bubbled through bromine water, what is the mechanism of the reaction that occurs?

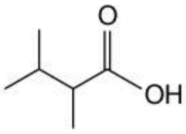
A nucleophilic addition

B nucleophilic substitution

C electrophilic addition

D electrophilic substitution

14 What is the molecular formula of the compound with the skeletal formula below?



A $C_4H_8O_2$

B $C_4H_{10}O_2$

C $C_6H_{10}O_2$

D $C_6H_{12}O_2$

15 What is the main product of the reaction of HCl with 2-methylpropene?

A 1-chloro-1-methylpropene

B 1-chloro-2-methylpropene

C 2-chloro-1-methylpropene

D 2-chloro-2-methylpropene

16 Which equation below shows a termination step in a free radical substitution reaction?

A $CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$

B $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

C $Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$

D $Cl_2 \rightarrow Cl\bullet + Cl\bullet$

★ **Exam tip**

In question 14 you have to translate from one type of formula to another. Remember, there is a carbon atom at the end of every line (except those with the O and OH groups shown), and at every junction. This makes it easy to count carbon atoms, and means that you can quickly eliminate two of the answers.

★ **Exam tip**

Start by drawing the formula of the reactant, 2-methylpropane. Then use Markovnikov's rule to decide the main product of the reaction.

17 Compound **Z** reacts with iodine in the presence of a base to make a yellow precipitate. It does not form a silver mirror when treated with Tollens' reagent.

What could be the identity of **Z**?

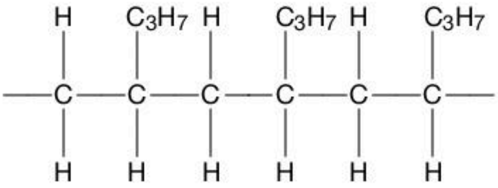
A CH_3OH

B CH_3CH_2CHO

C CH_3CHO

D CH_3COCH_3

18 The formula below shows part of a polymer chain.



What is the name of the monomer from which the polymer is made?

A prop-1-ene

B but-1-ene

C pent-1-ene

D nona-4,5-diene

Exam tip

To work out the monomer in question 18, start by marking the repeating unit on the polymer chain above. Then count the number of carbon atoms in the repeating unit.

Choose your answer to questions 19–27 by selecting on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of responses is used as a correct response.

Exam tip

The last 10 questions in the multiple-choice paper are in the style of questions 19–27 given here. Start by reading the question carefully, and draw a tick, cross or question mark next to each one. Then use the table here to decide whether to mark answer A, B, C or D.

19 Which statements explain why hydrogen bonds form between molecules of ethanol?

1 Its carbon and hydrogen atoms have similar electronegativity values.

2 One hydrogen atom in its molecules is attached to an atom with a high electronegativity.

3 Its molecules include an electronegative atom with unshared pairs of electrons.

Exam tip

In question 19, all the statements are true. However, not all of them are relevant to the question.

20 In the production of nitric acid, ammonia reacts with oxygen to make nitrogen monoxide and water. The reaction takes place at around 850 °C in the presence of a platinum catalyst.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H = -905.6\ \text{kJ mol}^{-1}$$

Which change of conditions is certain to shift the position of the equilibrium towards the right?

1 Decreasing pressure alone.

2 Increasing temperature alone.

3 Increasing temperature and decreasing pressure.

21 A student has four solutions:

W 1.0 mol dm^{-3} HCl

X 0.1 mol dm^{-3} HCl

Y 1.0 mol dm^{-3} CH_3COOH

Z 0.1 mol dm^{-3} CH_3COOH

Which statements about the pH of the solutions are correct?

1 The pH of solution **W** is greater than the pH of solution **X**.

2 The pH of solution **Y** is greater than the pH of solution **W**.

3 The pH of solution **Z** is greater than the pH of solution **Y**.

★ **Exam tip**

Question 21 tests your knowledge about strong and weak acids. You need to know some examples of strong and weak acids, and their formulae.

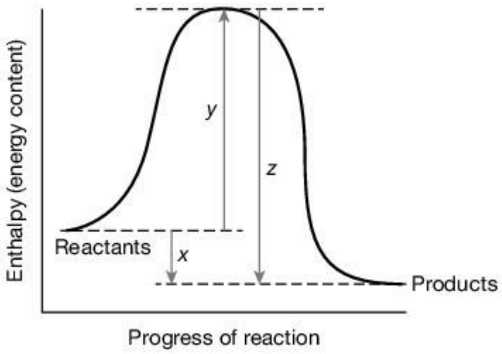
22 The diagram shows the reaction pathway for a reaction.

Which energy changes shown would be changed if a catalyst were used?

1 x

2 y

3 z



23 Why is powdered calcium carbonate powder sometimes added to soil?

1 To neutralise excess soil acidity.

2 To increase soil pH.

3 To ensure that the soil is suitable for growing particular crops.

24 Oxides of nitrogen in the atmosphere act as pollutants. Which statements describe their impacts?

1 They catalyse the oxidation of sulfur dioxide to sulfur trioxide.

2 They contribute to acid rain.

3 They are formed in car engines.

★ **Exam tip**

Statements 1, 2 and 3 are all correct in question 24. It is your task to consider which of them answer the question that is asked.

25 Which of the compounds below could be attacked by a nucleophile?

1 $CH_2{=}CH_2$ **2** $CH_3CH_2CH_2Cl$ **3** $CH_2{=}CH_2CH_2OH$

★ **Exam tip**

Look carefully at the three formulae in question 25. Which molecules include a carbon atom with a δ+ charge?

26 Which substances react to make propanoic acid as one of the products?

1 C_3H_7CHO with MnO_4^-/H^+

2 C_3H_7OH with $Cr_2O_7^{2-}/H^+$

3 $C_2H_5COOC_2H_5$ with HCl

★ **Exam tip**

When answering question 26, count the carbon atoms carefully.

27 Which products could be formed in the catalytic cracking of $C_{11}H_{24}$?

1 $C_{10}H_{24}$ **2** C_9H_{20} **3** C_2H_4

Paper 2 style questions

The questions in Paper 2 are AS structured questions. The questions test your knowledge and understanding of chemistry. They also ask you to handle data and do calculations. In Paper 2 you are likely to be asked to make predictions, to apply knowledge in new situations, and to evaluate information. This means that it is vital to learn what you have been taught thoroughly, and to practise using all these skills in different situations. The questions in this section will help you to do this.

Each question has a **command word**, such as describe, explain or suggest. The tips in the questions below explain what the command words mean.

In the exam, you need to write your answers on the paper, in the spaces provided. Use the number of answer lines to help you to decide how much to write – if there are six answer lines, a one-word answer is not enough.

1 Compound **X** is made up of atoms of carbon, hydrogen and oxygen only. It has a sweet smell, and is used to make glue and as a solvent in nail varnish removers.

On complete combustion, 1.00 g of **X** produced 1.09 dm^3 of carbon dioxide and 0.818 g of water, at room temperature and pressure.

★ **Exam tip**

Read the information at the start of question 1 carefully. It alerts you to the fact that you need to draw on your knowledge of physical and organic chemistry. It also gives you an important clue about the identity of compound **X** – which group of organic compounds includes compounds with sweet smells that are used as solvents?

(a) Calculate the amount, in mol, of carbon dioxide formed in the combustion reaction. [1]

(b) Calculate the amount, in mol, of water formed in the combustion reaction. [1]

(c) **(i)** Calculate the mass of carbon in 1.00 g of **X**. [1]

(ii) Calculate the mass of hydrogen in 1.00 g of **X**. [1]

(d) Use your answers to part c to calculate the mass of oxygen in 1.00 g of **X**. [1]

(e) Deduce the empirical formula of **X**. [3]

★ **Exam tip**

Deduce means that you need to make a logical connection between different pieces of information – in this case, between the masses of the elements in the compound and their relative atomic masses.

(f) The mass of 1 mol of **X** is 88.0 g. Deduce its molecular formula. [2]

★ **Exam tip**

Parts **(e)** and **(f)** show how important it is to learn definitions. You need to know the meanings of the terms *empirical formula* and *molecular formula*, and apply your knowledge to work out the answers.

★ **Exam tip**

Show all your working in calculation questions. You might get marks for your working, even if the final answer is wrong.

★ **Exam tip**

You will need to refer to the data booklet to answer parts **(a)** and **(b)**. This gives the molar gas volume (for part **(a)**) and the relative atomic masses of the elements (in the periodic table).

(g) Draw structural formulae of three isomers with the molecular formula deduced in part **(f)**. [3]

★ Exam tip

In part **(g)** you need to draw structural formulae. These must show how the atoms are arranged in a molecule. For example, the structural formula of propan-1-ol is $CH_3CH_2CH_2OH$, not C_3H_7OH. The question does not ask you to draw full displayed formulae, but you will not lose marks if you do.

(h) A separate sample of **X** was boiled under reflux with sodium hydroxide solution.

The products of the reaction, **Y** and **Z**, were separated.

Compound **Y** was then warmed with a mixture of iodine and alkali.

A yellow precipitate was observed.

(i) Give the formula of the yellow precipitate. [1]

(ii) Deduce the name of compound **Y**, and explain your answer. [2]

(iii) Deduce which of the structural formulae you drew in part **(g)** shows compound **X**.

Explain your reasoning. [2]

2 Fingerprints are used to help solve crimes. Many fingerprints are invisible. Invisible fingerprints consist mainly of sweat and oils, which occur along the ridges of the fingerprints.

One way to make fingerprints visible is to allow solid gold to sublime (change directly from a solid to a gas) in a vacuum. The gold deposits as a thin film on the fingerprint.

★ Exam tip

Read the information at the start of question 2 carefully. It describes the context of the question, and explains the meaning of an important word – *sublimation*.

(a) Describe the structure and bonding in solid gold. [2]

★ Exam tip

Part **(a)** asks you to describe two things in solid gold – its structure **and** its bonding.

This means you need to state the particles it is made up of, and how these are attracted to each other. You also need to describe how the particles are arranged.

(b) The enthalpy of sublimation of gold is $+368.4\,kJ\,mol^{-1}$ at 298 K.

(i) Write an equation for the sublimation of gold, including state symbols. [1]

(ii) Explain why the enthalpy of sublimation is endothermic. [1]

(c) Describe the movement and arrangement of the particles in gold vapour. [2]

(d) Gold has one stable isotope, which has the symbol $^{197}_{79}Au$.

Deduce the number of protons, neutrons and electrons in one atom of this isotope of gold. [2]

3 This question is about the properties of the Group 17 elements.

(a) The table gives the boiling points of the Group 17 elements.

Explain the trend shown in the table. [3]

Element	Boiling point /°C
fluorine	−188
chlorine	−34.0
bromine	58.8
iodine	184

(b) The Group 17 elements act as oxidising agents.

(i) Write an equation for the reaction of fluorine with chloride ions, and explain how it shows that fluorine is a stronger oxidising agent than chlorine. [2]

(ii) Explain why fluorine is a stronger oxidising agent than chlorine. Include electronic configurations in your answer. [2]

4 This question is about the elements of Periods 2 and 3.

(a) The table below gives atomic and ionic radius data for some of the elements of the second period of the periodic table.

Element	Atomic radius /nm	Ionic radius /nm
lithium	0.157	0.060
beryllium	0.112	0.031
boron	0.098	0.021
carbon	0.077	
nitrogen	0.075	0.171
oxygen	0.073	0.140
fluorine	0.072	0.136

(i) Describe and suggest an explanation for the trend in atomic radius from lithium to fluorine. [3]

(ii) Suggest an explanation for the trend in ionic radius from lithium to boron. [2]

(iii) Describe and explain the difference in atomic and ionic radii for the non-metals shown in the table. [2]

(b) The graph on the facing page shows the variation in first ionisation energies for the first 20 elements of the periodic table.

(i) Define the term *first ionisation energy*. [1]

(ii) Describe and explain the general trend in ionisation energy across Period 3. [3]

(iii) Explain why the first ionisation energy of magnesium is greater than the first ionisation of aluminium. In your answer, include the electron configurations of the two elements. [2]

(c) Compare the first ionisation energies of the Period 2 elements with the first ionisation energies of the Period 3 elements directly beneath them in the periodic table. Suggest a reason for the difference you describe. [3]

★ **Exam tip**

In your answer to question **3(b)** you need to explain how and why the strength of the intermolecular forces changes down the group. You then need to explain how the strength of the intermolecular forces affects the boiling point.

★ **Exam tip**

Question **(b)(i)** asks you to do two things – write an equation, and give an explanation. You need to answer both parts to obtain two marks.

★ **Exam tip**

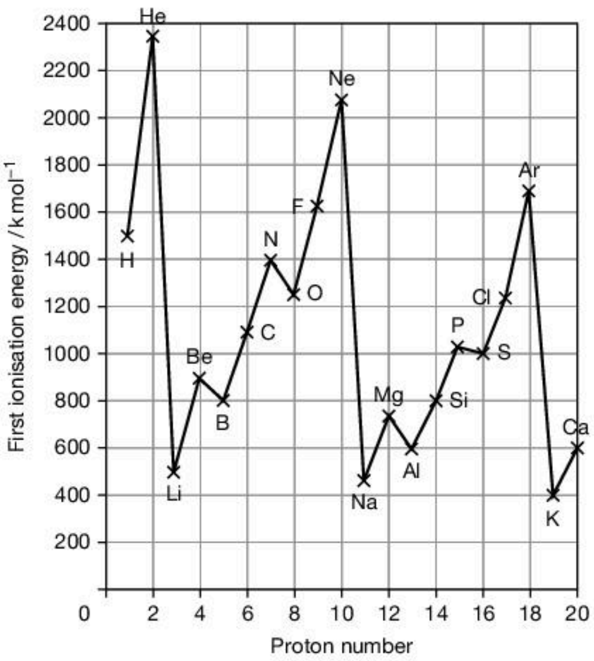
Question **(a)(i)** asks you to do two things – to describe the trend shown in the table, and then to suggest a reason for it. You need to apply your knowledge of Period 3 to a new situation – Period 2.

★ **Exam tip**

It is vital to learn definitions perfectly. If your definition is not exactly right, you will not get the mark.

★ **Exam tip**

The command word **compare** means that you need to describe the similarities and differences.



5 The compound 1-bromopropane is a solvent.

(a) 1-bromopropane is now often used as a dry-cleaning solvent instead of chlorofluoroalkanes. Suggest why. [1]

Exam tip

In question **5(a)** you need to use your knowledge of a problem caused by chlorofluoroalkanes to help you to work out the answer.

(b) 1-bromopropane can be made in the laboratory from an alcohol.

(i) Name the alcohol and the other reactant(s) required for this reaction. [2]

(ii) State the conditions required for the reaction. [1]

Exam tip

Question **(b)(ii)** shows the importance of learning the conditions required for organic reactions. You cannot guess these.

(c) 1-bromopropane can also be made from propene.

(i) Name the reaction mechanism by which propene reacts with hydrogen bromide. [1]

(ii) Two products, 1-bromopropane and 2-bromopropane, are formed when propene reacts with hydrogen bromide. Draw the displayed formulae of these products. [2]

(iii) State which product in part **(ii)** is formed in the greater quantity, and explain in detail why this product is the major product. [3]

Exam tip

Question **(c)(iii)** asks for a detailed explanation. Include all the necessary parts of the explanation, and write about them in a logical order, showing how they connect.

(d) The table shows some data for 1-bromopropane, 2-bromopropane and propane.

Substance	Boiling point /°C	Density /g cm^{-3}
1-bromopropane	71	1.35
2-bromopropane	59	1.31
propane	−42	2.01×10^{-3}

(i) Suggest how **one** of the properties in the table could be used to separate a mixture of 1-bromopropane and 2-bromopropane. [2]

Exam tip

In question **(d)(i)** you need to choose one property, and suggest how it can be used to separate the two substances.

(ii) Explain the difference in boiling point between propane and 1-bromopropane. [2]

6 The compounds hexanoic acid and methyl cinnamate are present in vanilla.

(a) Draw the skeletal formula of hexanoic acid. [1]

★ Exam tip

In question **6(a)** start by writing the structural formula. Then convert this to a skeletal formula. Remember, there is a carbon atom at the end of each line, and at each bend and junction.

(b) Hexanoic acid is a weak acid.

(i) Explain the meaning of the term *weak acid*. [1]

★ Exam tip

Question **(b)(i)** is a reminder of the importance of learning definitions carefully. If you get the meaning wrong, you will not get the mark.

(ii) State how the pH of a weak acid differs from the pH of a strong acid of the same concentration. [1]

(c) Sodium carbonate solution is added to hexanoic acid.

(i) Predict and explain what would be observed in the reaction. [1]

(ii) Write an equation for the reaction. [1]

(d) LiAlH$_4$ in ethoxyethane is added to hexanoic acid, followed by dilute sulfuric acid.

(i) Draw a dot-and-cross diagram to show the bonds in the AlH$_4^-$ ion. [1]

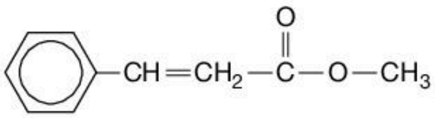
★ Exam tip

In question **(d)(i)** you will need to apply your learning about bonding in molecules and ions to a new situation. Start by drawing the outer electrons around the central aluminium atom. Then work out how electrons are shared in bonds between the aluminium atom and the four hydrogen atoms. There is a single negative charge on the ion, so the number of electrons in the ion is one more than the number of protons.

(ii) Sketch the shape of the AlH$_4^-$ ion. [1]

(iii) Predict the name and formula of organic product of the reaction of LiAlH$_4$ with hexanoic acid. [2]

(e) The formula of methyl cinnamate is shown below.



(i) Name the two functional groups present in methyl cinnamate. [1]

(ii) Predict the structural formula of the compound formed when methyl cinnamate is heated with hydrogen in the presence of a nickel catalyst. [1]

(f) Methyl cinnamate is heated under reflux with dilute hydrochloric acid.

An equilibrium mixture results.

(i) Write an equation for the reaction. [1]

(ii) Write an expression for the equilibrium constant for the reaction. [1]

★ Exam tip

In question **(e)(i)** you need to give the *names* of the functional groups – you will not get any marks for writing *double bond* or *COO group*.

(iii) Deduce the units of the equilibrium constant. [1]

(iv) Describe and explain how the position of the equilibrium will change if more methyl cinnamate is added to the equilibrium mixture. [2]

★ Exam tip

When answering questions about the position of an equilibrium, refer to Le Chatelier's principle.

★ Exam tip

Question **(f)(iii)** asks you to deduce units. Write the units for each concentration in the equilibrium expression, and then cancel out as necessary to find the units of K_c.

7 PVC is an important polymer. Its monomer is chloroethene.

★ Exam tip

Throughout question 7 you will need to apply learning from different sections of the syllabus to new situations. The key to success in questions like these is to keep calm, read all the information carefully, and think about how you can use your knowledge to answer the questions.

(a) (i) Give the systematic name of PVC. [1]

(ii) Draw the repeat unit of PVC. [1]

(b) The monomer, chloroethene, can be manufactured from hydrogen chloride and ethyne, C_2H_2. The structure of ethyne is H—C≡C—H. There is a triple bond between the two carbon atoms.

(i) Predict the bond angle in ethyne. [1]

(ii) Deduce the equation for the reaction of hydrogen chloride and ethyne to make chloroethene. The reactants and products are in the gas phase. [1]

(iii) Predict the type of reaction mechanism for the reaction in part **(ii)**, and explain your prediction. [2]

★ Exam tip

To answer question **(b)(iii)**, consider the triple bond. The triple bond consists of three pairs of electrons – what is the most likely mechanism for its reactions?

(c) Scientists have recently discovered that gold, in the solid state, is a good catalyst for the reaction of ethyne gas with hydrogen chloride gas.

(i) Define the term *catalyst*. [1]

(ii) State whether the catalyst is homogeneous or heterogeneous, and explain your decision. [1]

★ Exam tip

Question parts **(c)(i)** and **(iii)** ask for definitions. You just need to write down the definitions to answer these questions – but they must be word perfect.

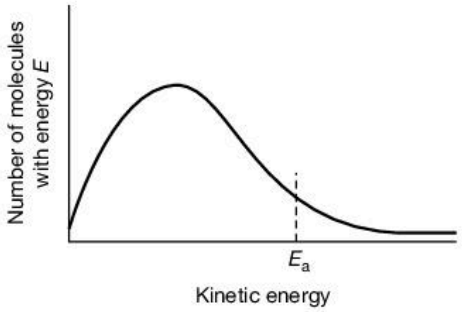
★ Exam tip

You can work out the answer to question **(c)(ii)** by reading the information at the start of part **(c)** very carefully. The catalyst and reactants are in different states.

(iii) Define the term *activation energy*. [1]

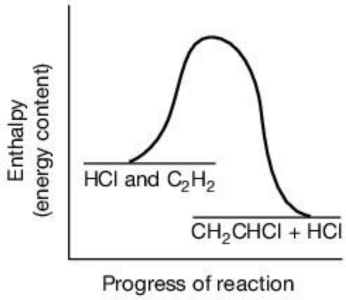
(iv) The diagram overleaf shows a Boltzmann distribution of the kinetic energy of the molecules in a mixture of ethyne and hydrogen chloride gases.

The activation energy, E_a, is marked.



On a copy of the diagram, mark a possible position for the activation energy of the catalysed reaction. [1]

(v) The diagram below shows the reaction pathway for the uncatalysed reaction.



On a copy of the diagram, sketch another curve to show a possible pathway for the catalysed reaction. Label the activation energy. [1]

(d) Chloroethene can also be manufactured by the two-step process shown by the equations below.

$CH_2{=}CH_2(g) + Cl_2(g) \rightarrow ClCH_2CH_2Cl(l)$ **Reaction 1**

$ClCH_2CH_2Cl(l) \rightarrow CH_2{=}CHCl(g) + HCl(g)$ **Reaction 2**

(i) Give the name of the product of Reaction 1. [1]

(ii) Use bond energy values from the data booklet to estimate the enthalpy change of Reaction 1. [2]

★ **Exam tip**

In question **(d)(ii)**, start by drawing displayed formulae for all the reactants and products in the equation. Then work out which bonds are broken and which are made in the reaction.

(iii) State what is meant by the term *enthalpy change of formation*. [1]

(iv) The values for enthalpy of formation of the substances involved in Reaction 2 are given in the table below. Use the enthalpy of formation values to estimate the enthalpy change of Reaction 2. [2]

Substance	Standard enthalpy of formation /kJ mol^{-1}
$ClCH_2CH_2Cl(l)$	−165
$CH_2{=}CHCl(g)$	−22.09
$HCl(g)$	−92.3

Paper 3 style questions

Paper 3 is a practical paper. You will be given instructions for three practicals, which you must carry out. You need to record your results and observations carefully, and answer the questions about each practical.

At the end of Paper 3 there is a section called *Qualitative analysis notes*. This describes the reactions of aqueous cations and anions, as well as gas tests. Read this section in a past exam paper, or the specimen paper, and make sure you are familiar with the information it contains.

The methods for the practicals in the questions in this section of the book are less detailed than those in Paper 3, since you are not expected to carry out the practicals described here. Sample results are given so that you can answer the questions that follow.

1 Sodium thiosulfate reacts with dilute hydrochloric acid according to the equation below.

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$

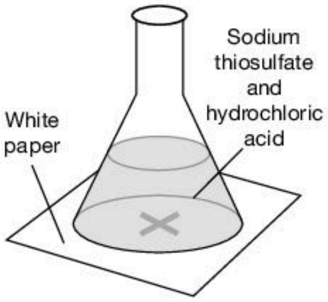
The reaction can be investigated by measuring the time for the precipitate to obscure a cross placed beneath the flask.

(a) Method

- Draw a black cross on a piece of scrap paper.
- Use a measuring cylinder to measure out 50 cm³ of sodium thiosulfate solution, and pour into a conical flask. Place the flask on the cross.
- Measure out 5 cm³ of dilute hydrochloric acid.
- Add the acid to the solution in the flask, swirl to mix, and start the timer.
- Record the time for the cross to become invisible.
- Use a thermometer to measure the temperature of the mixture.
- Repeat the experiment at four more temperatures between 20 °C and 60 °C. For each temperature, use a Bunsen burner to heat the sodium thiosulfate in the flask to a temperature of about 5°C above the required temperature. Measure the temperature of the mixture just after the cross becomes invisible. [3]

★ Exam tip

In the practical exam, read the whole method before you start.



Results

Temperature at end of reaction/°C	Time for cross to become invisible/s
21	79
30	60
39	41
52	18
60	10

(b) (i) Plot a graph of time for the cross to become invisible against temperature. [2]

(ii) Draw a line of best fit, and circle any anomalous points. [1]

★ Exam tip

In question **(b)**, follow the instructions carefully. Temperature is on the *x*-axis, and time for the cross to become invisible is on the *y*-axis. Don't forget to include units in the axis labels, and make sure the scales are even.

(iii) Describe what can be deduced from the shape of the line of best fit, and explain in detail why the factor investigated changes the rate of reaction in the way that it does. [3]

★ **Exam tip**

Question **(b)(iii)** requires you to use your theoretical knowledge of reaction rates to explain the shape of the graph. There are three marks for this question – one to describe what the graph shows, and two to explain why increasing the temperature increases the reaction rate.

(c) **(i)** Suggest why the temperature recorded is the one that is measured just after the cross becomes invisible, *not* the temperature of sodium thiosulfate in the flask before the reaction. [1]

(ii) Identify two factors you kept constant so as to ensure the test is fair. [2]

(iii) Suggest one possible inaccuracy that cannot be completely eliminated from the experiment, and explain why it cannot be eliminated. [1]

★ **Exam tip**

To answer question **(c)(iii)** think about how you judged the end point of the reaction – was it easy to judge the exact time to stop the timer? Why?

★ **Exam tip**

You will need to use your experience of practical work to answer question **(c)(i)**. Think about what will happen to the temperature of hot sodium thiosulfate when hydrochloric acid (at room temperature) is added to it.

2 Some people take iron tablets. One type of iron tablet contains iron(II) sulfate.

You will do a titration with potassium manganate(VII) solution to find the mass of iron in one tablet.

The equation for the reaction is:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

You are provided with:

- five iron tablets
- dilute sulfuric acid
- $0.010\,mol\,dm^{-3}$ potassium manganate(VII) solution.

(a) **Method**

- Find the mass of five iron tablets.
- Dissolve the tablets in about $100\,cm^3$ of warm dilute sulfuric acid in a conical flask.
- Pour the solution into a $250\,cm^3$ standard flask, and make up to the mark with distilled water. Stopper and shake.
- Use a pipette to transfer $25.00\,cm^3$ of the solution into a clean conical flask.
- Fill the burette with potassium manganate(VII) solution.
- Perform a rough titration and record your burette readings in a suitable table.
- Carry out several more accurate titrations, until your results are consistent. Record all your readings in a table.

	Rough	Run 1	Run 2	Run 3
Reading on burette at start/cm³	0.00	0.50	1.50	20.50
Reading on burette at end/cm³	26.50	25.95	26.90	45.85
Titre/cm³	26.50	25.45	25.40	25.35

[8]

(b) From the titration results, obtain a titre value to use in your calculations.

Show your working. [1]

(c) Calculation

★ Exam tip

Remember to show all your working at all stages of the calculation. You can get marks for correct methods, even if your answers are incorrect. If you make a mistake in one part, the examiner will follow through your error and give you marks for the next part if you have used the correct method.

(i) Calculate the number of moles of $KMnO_4^-$ in the titre. [1]

(ii) Calculate the number of moles of Fe^{2+} in 25.00 cm³ of solution. [1]

★ Exam tip

To answer **(c)(ii)**, you will need to refer to the equation for the reaction.

(iii) Calculate the number of moles of Fe^{2+} in 250 cm³ of solution. [1]

(iv) Calculate the number of moles of Fe^{2+} in one tablet. [1]

(v) Calculate the mass of Fe^{2+} in one tablet. [1]

(vi) Give all your answers to a suitable number of significant figures. [1]

3 Qualitative analysis

Do the tests in the table. At each stage, record any colour changes seen. Write down whether precipitates are formed, and if they are soluble in excess. If a gas is evolved, do tests to find out what it is. Write down the results of these tests.

★ Exam tip

It is vital that you follow these instructions carefully. Write down all your observations, and describe gas tests and their results carefully.

You are given solid **X**. Solid **X** is a mixture of two salts, and it contains two cations and two anions. Carry out the tests below, and complete the table.

(a)

Test		**Observations**
1	To 1 spatula measure of **X** in a test tube, add 1 cm depth of dilute hydrochloric acid.	Bubbles of gas. On bubbling through limewater, the limewater went milky, showing that the gas is carbon dioxide.
2	Place 1 spatula measure of **X** in a boiling tube, and warm gently.	Smell of ammonia. Damp red litmus paper was placed in the top of the boiling tube. This went blue, confirming that the gas is ammonia.
3	Add about 50 cm^3 distilled water to all of **X** that remains. Stir.	Solid X dissolves, showing that both salts are soluble in water.
4	To a 1 cm depth of your solution of **X**, add 1 cm depth of dilute nitric acid. Then add a few drops of silver nitrate solution,	A yellow or cream precipitate forms – it is hard to tell which.
	followed by 1 cm depth of concentrated aqueous ammonia.	The precipitate does not dissolve.
5	To 1 cm depth of your solution of **X**, add 1 cm depth of aqueous sodium hydroxide,	A white precipitate forms.
	followed by excess aqueous sodium hydroxide.	The white precipitate dissolves.

[5]

(b) From Test 2, identify one of the cations present in solid **X**. [1]

(c) The results of Test 5 suggest two further possible cations that might be present in solid **X**.

(i) Name these cations. [1]

(ii) Choose a reagent that can be used to distinguish between these two cations, and use it to carry out an extra test on solution **X**. [1]

★ **Exam tip**

You can use the 'Qualitative analysis notes' at the end of the question paper to help you to work out which reagent to use.

Aqueous ammonia.

(iii) Carry out the test, and record your results. [2]

A white precipitate formed. It was insoluble in excess ammonia.

(d) Use all your observations to deduce the identities of the two cations and two anions present in solid **X**. Give reasons for all your deductions. [4]

★ **Exam tip**

To gain full marks in part **(d)**, you need to give a reason for each deduction you make. Include as much detail as possible.

Paper 4 style questions

The questions in Paper 4 are on A Level structured chemistry. As for Paper 2, the questions test your knowledge and understanding of chemistry. They also ask you to use data, to apply knowledge in new situations, and to evaluate information. The questions in this section will help you to practise and develop these skills.

1 Ethanedioic acid is used to fix dyes to fabrics.

(a) Ethanedioic acid is oxidised by warming with acidified potassium manganate(VII).

(i) Write a half-equation for the oxidation of ethanedioic acid. [1]

★ Exam tip

The products of the half-reaction in part **(a)(i)** include CO_2 and H^+.

(ii) Write a half-equation for the reduction of acidified potassium manganate(VII) to make Mn^{2+}. [1]

(iii) Use the half-equations you wrote in parts **(i)** and **(ii)** to construct a redox equation for the reaction of ethanedioic acid with acidified potassium manganate(VII). [1]

★ Exam tip

If you cannot remember the half-equation required for part (a), use the data booklet.

(b) Use standard electrode potential data from the data booklet, as well as the value given below, to show that the reaction in part **(a) (iii)** is feasible. [2]

Standard electrode potential for the oxidation of ethanedioic acid = –0.49 V

(c) Ethanedioic acid dissociates in aqueous solution according to the equations below.

Equilibrium 1 $HO_2CCO_2H(aq) \rightleftharpoons H^+(aq) + HO_2CCO_2^-(aq)$

Equilibrium 2 $HO_2CCO_2^-(aq) \rightleftharpoons H^+(aq) + O_2CCO_2^{2-}(aq)$

(i) Write an expression for K_a for Equilibrium 1. [1]

(ii) The value of K_a for Equilibrium 1 is $5.37 \times 10^{-2}\,mol\,dm^{-3}$.

Calculate pK_a for Equilibrium 1. [1]

(iii) The value of pK_a for Equilibrium 2 is 4.27.

Explain what the difference in pK_a values for Equilibrium 1 and Equilibrium 2 shows about the difference in positions of the two equilibria. [1]

★ Exam tip

Remember that pK_a is equal to $-\log_{10}K_a$. Some candidates forget to change the sign once they have used their calculator to find the log of K_a.

(iv) The value of pK_a for ethanoic acid is 4.76.

Suggest a reason for the difference between this value and the pK_a value for Equilibrium 1. [2]

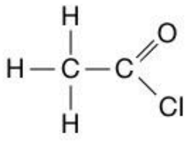
(v) Predict which solution has a higher pH: $1.0\,mol\,dm^{-3}$ ethanedioic acid or $1.0\,mol\,dm^{-3}$ ethanoic acid.

Explain your prediction. [1]

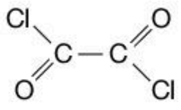
★ Exam tip

To answer part **(c)(v)** you need to know that the greater the value of pK_a, the weaker the acid, and the greater the pH for a solution of given concentration.

2 This question is about the compounds with the formulae below.



A



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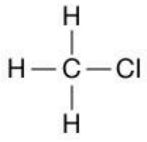

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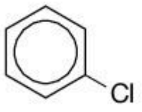


D

(a) Give the names of compounds **A** and **D**. [2]

(b) Write an equation for the reaction of compound **A** with methanol, and name the organic product of the reaction. [2]

(c) Compound **A** reacts vigorously with water.

(i) Write an equation for the reaction of compound **A** with water. [1]

(ii) Describe the observations that would be made during the reaction. [1]

Exam tip

Candidates often make mistakes in naming compounds. Make sure you practise naming organic compounds again and again, until you always get them correct.

(d) Compounds **A** and **C** react with sodium hydroxide solution.

(i) Write equations for the reaction of **A** and **C** with sodium hydroxide solution. [1]

(ii) Explain why the reaction of **A** with sodium hydroxide solution is more vigorous than the reaction of **C** with sodium hydroxide solution. [2]

(iii) Explain why compound **D** does not react with sodium hydroxide solution. [2]

Exam tip

In question **(d)(ii)**, the command word *explain* means that you need to give a reason for the difference.

(e) Compound **B** reacts with water as shown in the equation below:

$$(COCl)_2(l) + H_2O(l) \rightarrow 2HCl(g) + CO_2(g) + CO(g)$$

(i) Copy the structural formula of **B**. Mark with a * the two atoms that are most likely to be attacked by water molecules. Explain your decision. [2]

(ii) Define the term *entropy*. [1]

(iii) Predict whether the entropy change for the reaction is positive or negative. Explain your prediction. [1]

Exam tip

Make sure you learn definitions carefully. You will only get the mark if your definition is exactly correct.

Exam tip

To answer question **(e)(iii)** look at the states of the reactants and products. Which have higher standard entropies in general, substances in the solid, liquid or gas states?

(iv) Select data from the table to calculate the entropy change for the reaction. [2]

Substance	Standard entropy /J mol^{-1} K^{-1}	Standard enthalpy of formation /kJ mol^{-1}
$(COCl)_2$ (l)	174.4	–367.6
H_2O (l)	69.9	–285.5
HCl(g)	186.8	–92.3
CO_2(g)	213.6	–393.5
CO (g)	197.6	–110.5

(v) Select data from the table to calculate the enthalpy change for the reaction under standard conditions. [2]

(vi) Use your answers to parts **(iv)** and **(v)** to calculate $\Delta G^\ominus$ for the reaction of compound **B** with water at 298 K. [2]

★ Exam tip

To answer part **(e)(v)** start by writing out the equation for the reaction. Then write the standard enthalpies of formation under each reactant and product.

★ Exam tip

In calculations involving entropy, be careful to use units consistently. In the table, the units for entropy include J, but the units for enthalpy are given in kJ mol^{-1}.

(vii) Use your answer to part **(vi)** to predict whether the reaction of compound **B** with water occurs spontaneously at 298 K. Explain your decision. [1]

3 Dinitrogen pentoxide, N_2O_5, exists in different forms.

(a) In the solid state, N_2O_5 is a salt. It is made up of NO_2^+ and NO_3^- ions.

(i) Suggest, giving reasons, the type of structure and bonding in solid N_2O_5. [2]

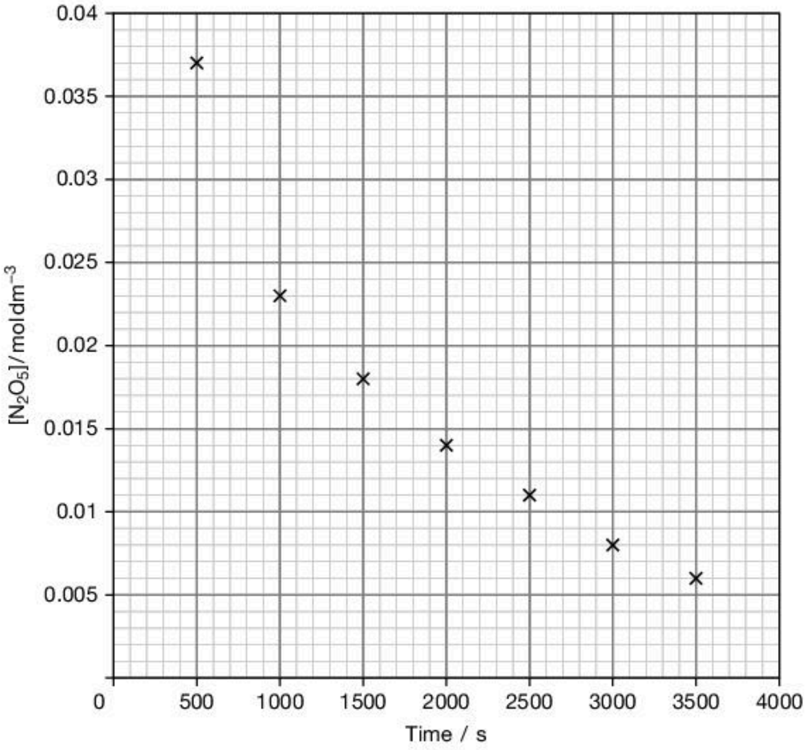
(ii) N_2O_5 exists in the solid state at room temperature. Use ideas about structure and bonding to explain why. [1]

(b) N_2O_5 exists as molecules in the gas state, and when it is dissolved in tetrachloromethane. The molecules decompose according to the equation below.

$$2N_2O_5\ (\text{solution}) \rightarrow 4NO_2\ (\text{solution}) + O_2(g)$$

Give the oxidation state of nitrogen in N_2O_5 and in NO_2, and state whether the nitrogen is oxidised or reduced in the decomposition reaction. [1]

(c) The graph shows the change in concentration of N_2O_5 over time as it decomposes at a fixed temperature.



(i) Draw a smooth curve on a copy of the graph. [1]

(ii) Select data from the graph to show that the reaction is first order with respect to N_2O_5. [2]

(iii) Write a rate equation for the reaction. [1]

(iv) The rate constant for the reaction is $4.80 \times 10^{-2}\ \text{s}^{-1}$ at that temperature.

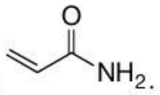
Calculate the initial rate of the reaction. [2]

(v) Use the value of the rate constant given above to calculate the half-life for the reaction. Compare your value to a value obtained from the graph, and suggest a reason for any difference. [3]

★ **Exam tip**

To answer part **(c)(ii)**, consider using the half-life of the reaction. The time taken for the concentration to fall from 0.030 mol dm^{-3} to 0.015 mol dm^{-3} should be the same as the time taken for the concentration to fall from 0.02 mol dm^{-3} to 0.01 mol dm^{-3}, for example.

4 Acrylamide is made when starchy foods such as potatoes are cooked at high temperature.

The skeletal formula of acrylamide is 

(a) Give the systematic name of acrylamide. [1]

(b) On a copy of the skeletal formula:

(i) Draw a ring around each of the two functional groups in the molecule. [1]

(ii) Give the names of the functional groups. [1]

(c) Pure acrylamide is a white solid at room temperature. It dissolves in water to form a colourless solution.
A sample of aqueous acrylamide is shaken with bromine water.

(i) Predict one observation that would be made. [1]

(ii) Give the structural formula of the product formed. [1]

(iii) Describe the mechanism of the reaction. [3]

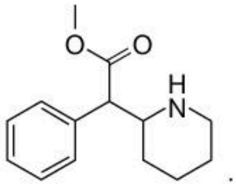
★ **Exam tip**

When describing an observation, state the colour both before and after the reaction.

★ **Exam tip**

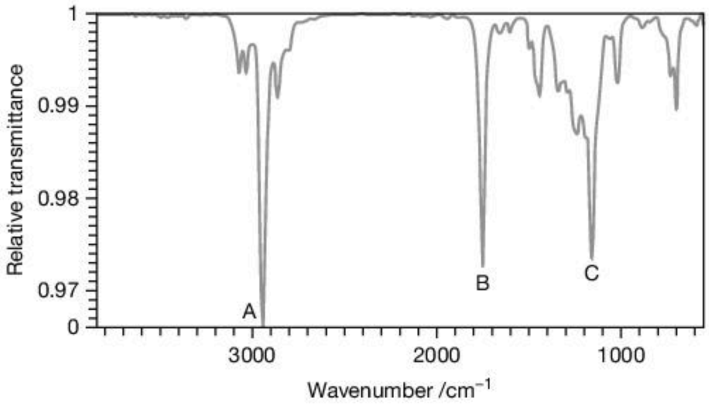
There are two marks for question part **(c)(iii)**. This means that you need to describe the mechanism in detail, not just give the name of the reaction mechanism. Use curly arrows in your answer. Remember, a curly arrow represents the movement of an electron pair, so the arrow must start on a lone pair or on an electron pair in a bond.

5 Methylphenidate is used to treat attention deficit hyperactivity disorder (ADHD).

The formula of methylphenidate is  .

The infra-red spectrum of methylphenidate is shown below.

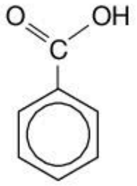
Identify the bonds and functional groups that result in peaks A, B and C. [2]



★ **Exam tip**

To answer question 5, you will need to use the data booklet.

6 Benzoic acid is used to make sodium benzoate, which is added to food and drink as a preservative. The formula of benzoic acid is:



(a) Benzoic acid can be made from methylbenzene.

Give the names of the reagents, and the conditions required for the reaction. [2]

★ Exam tip

You cannot work out the answer to part **(a)** – you need to learn the conditions and reagents for the organic reactions in the syllabus.

(b) Benzoic acid reacts with sodium.

(i) Write a balanced equation for the reaction. [1]

(ii) Name the organic product formed. [1]

★ Exam tip

In part **(b)(ii)** you will need to use your learning about the properties of ethanoic acid, and apply it to benzoic acid. Sodium reacts with ethanoic acid to make sodium ethanoate, so the products of the reaction of sodium with benzoic acid are…

(c) Benzoic acid reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid at 50 °C.

(i) State the name of the mechanism of the reaction. [1]

(ii) Draw the structural formula of the product. Use the data booklet to help you. [1]

(d) A chemist makes 500 cm^3 of a solution of benzoic acid, using octan-1-ol as the solvent. The chemist then adds 500 cm^3 of pure water, and shakes the mixture.

Two layers of solution result, with the octan-1-ol layer on top.

(i) The pH of the aqueous solution is 2.94.

Calculate the concentration of hydrogen ions in this layer. [1]

(ii) The acid dissociation constant, K_a, for benzoic acid is 6.3×10^{-5} mol dm^{-3}.

Calculate the concentration of benzoic acid in the aqueous solution. [2]

(iii) Benzoic acid is more soluble in octan-1-ol than in water.

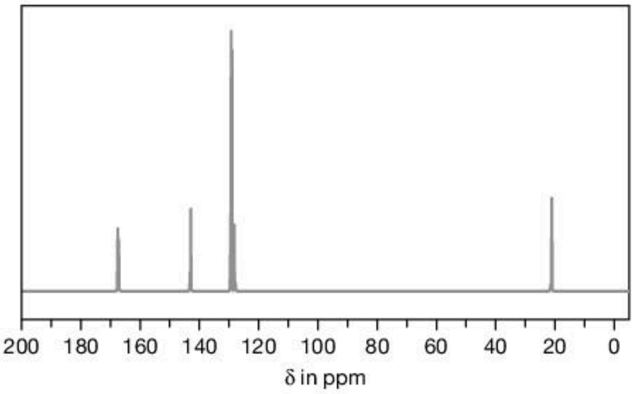
The value of the partition coefficient for the octan-1-ol/water system is 79.4.

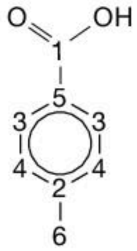
Calculate the concentration of benzoic acid in the octan-1-ol layer. [2]

(e) The carbon-13 NMR spectrum of 4-methylbenzoic acid is shown on the next page.

The structural formula numbers each carbon atom so that the carbon atoms can be identified.

You will need to use your data booklet in this question part.





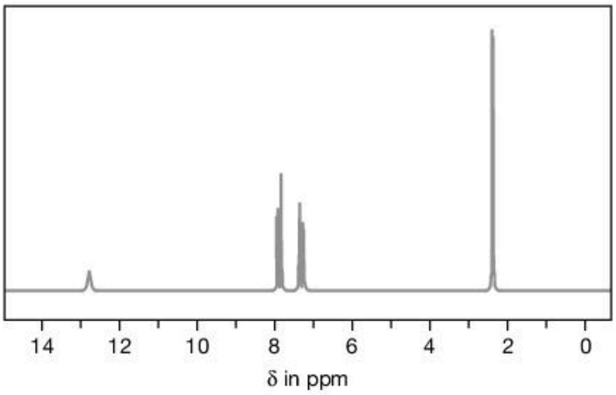
(i) Give the number of the carbon atom responsible for the peak at $\delta = 21$ ppm. [1]

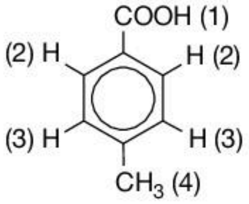
(ii) Deduce which peak results from carbon atom 1. [1]

(iii) Explain why the spectrum shows four peaks, even though 4-methylbenzoic acid has 8 carbon atoms. [2]

(iv) Predict how the C-13 NMR spectrum of benzoic acid is different from that of 4-methylbenzoic acid. [1]

(f) The proton NMR spectrum of 4-methylbenzoic acid is shown below.





The structural formula numbers each hydrogen atom so that the hydrogen atoms can be identified.

You will need to use your data booklet in this question part.

(i) Identify the hydrogen atom or atoms responsible for the peak at $\delta = 2.4$ ppm. [1]

(ii) Identify the hydrogen atom or atoms responsible for the peak at $\delta = 12.8$ ppm. [1]

(iii) Explain the difference in height of the peaks at $\delta = 2.4$ ppm and $\delta = 12.8$ ppm. [1]

Paper 5 style questions

In Paper 5 you have the opportunity to demonstrate your skills in planning, analysis and evaluation. The paper is set in the context of two investigations. You will not actually carry out these investigations in the exam, but will use your experiences in the lab to help you to answer the questions.

1 Hydrogen peroxide decomposes in the presence of a catalyst to produce water and oxygen gas. The equation below shows the reaction.

$$2H_2O_2\ (aq) \rightarrow 2H_2O\ (l) + O_2\ (g)$$

You will plan some investigations to study the factors that affect the rate of the reaction.

(a) One scientific question that could be investigated is:

How is the volume of oxygen gas collected in 1 minute affected by the use of different catalysts?

(i) Identify the independent variable in an investigation to answer the question. [1]

(ii) Identify the dependent variable in an investigation to answer the question. [1]

(iii) State two control variables in the investigation. [1]

(iv) Choose *one* of the control variables you identified in **(iii)**, and describe how to control this variable. [1]

★ **Exam tip**

Question **(a)** is about variables. Remember, the independent variable is the one that you change, the dependent variable is the one that you observe or measure, and the control variables are those that you must control or keep the same.

(b) **(i)** Draw and label a diagram to show how you could set up the apparatus listed below to answer the scientific question in **(a)**. You may include extra apparatus in your diagram. [2]

- conical flask
- test tube
- measuring cylinder
- trough or bowl
- glass and rubber tubing
- clamp

(ii) Describe how to use the apparatus to investigate the scientific question in **(a)**. Include the measurements you need to make. [3]

★ **Exam tip**

Sketch a rough diagram first. Then use a pencil and ruler to draw a clear, labelled diagram of the apparatus set up. Think about how you will collect the gas (perhaps over water) and how you can avoid the gas escaping as it travels from the reaction vessel (the conical flask) to the collection vessel (the measuring cylinder).

(c) Five groups of students carried out investigations to answer the question in **(a)**.

Their results are in the table below.

Catalyst	Volume of oxygen gas collected in 1 minute /cm³				
	Group A	Group B	Group C	Group D	Group E
MnO_2	28.5	29.0	14.0	1.5	29.5
CuO	1.0	1.5	0.5	29.0	1.0
PbO_2	30.0	30.5	14.5	31.0	32.0
ZnO	0	0	0	0	0
Catalase	48.5	50.0	26.0	49.0	48.0

(i) Deduce which group used a more dilute hydrogen peroxide solution than the other groups. Explain your deduction. [1]

★ **Exam tip**

To answer question **(c)(i)** think about what you are looking for in the results table. Will the volumes of oxygen gas collected be higher or lower for the group that used the more dilute solution?

(ii) Deduce which group muddled up two of the catalysts. Explain your deduction. [1]

(iii) State what type of chart should be used to display the results in the table.

Explain your answer. [1]

(iv) List the catalysts in order of increasing effectiveness. [1]

(v) Catalase is found in liver and celery.

What is the name given to a catalyst found in living organisms? [1]

(d) Another group of students carried out an investigation to answer the scientific question:

How does the rate of decomposition of hydrogen peroxide depend on the concentration of the hydrogen peroxide solution?

The students used a manganese(IV) oxide catalyst.

They collected the data below.

$[H_2O_2]$ /mol dm^{-3}	Time to collect 25 cm^3 of oxygen gas /s	Rate of reaction /cm^3 s^{-1}
0.2	27.00	
0.4	9.05	
0.6	8.85	
0.8	4.60	
1.0	4.60	

(i) Calculate the rate of reaction in cm^3 s^{-1} for each of the concentrations in the table. [1]

★ Exam tip

To answer question **(d)(i)** you can use the units given for the rate of reaction to help you to decide how to do the calculation. The units show that you need to divide volume by time.

(ii) Plot a graph of rate of reaction against $[H_2O_2]$. [3]

(iii) Draw a line of best fit on your graph, and circle the anomalous result. [1]

(iv) Suggest one mistake the students might have made that led to the anomalous result. [1]

★ Exam tip

To answer question **(d)(iv)** look carefully at the data. The times to collect 25 cm^3 of oxygen for both the 0.8 mol dm^{-3} solution and the 1.0 mol dm^{-3} solution are the same. What mistake does this suggest that the students made?

(v) Use your graph to predict the rate of reaction when $[H_2O_2]$ is 0.5 mol dm^{-3}. [1]

(vi) Use your graph to deduce the order of the reaction with respect to $[H_2O_2]$. [1]

(vii) Suggest how the students could improve the reliability of the investigation. [1]

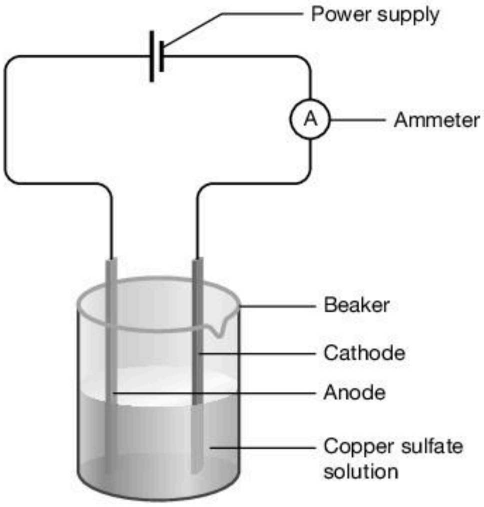
★ Exam tip

$[H_2O_2]$ is on the *x*-axis and the rate of reaction is on the *y*-axis. Remember to use even scales on both axes.

★ Exam tip

Question **(d)(vi)** requires you to use your knowledge of reaction rates. Does the shape of the graph show that the reaction is zero, first or second order with respect to $[H_2O_2]$?

2 Some students decide to investigate the factors that affect the mass of copper deposited on the cathode in an electrolysis investigation. They set up the apparatus below.



(a) The students obtain the results shown in the table below.

Current/A	Mass of copper deposited/g
0.4	0.06
0.6	0.10
0.8	0.14
1.0	0.20
1.2	0.22

(i) Identify the independent and dependent variables in the investigation. [2]

(ii) Suggest one control variable in the investigation. [1]

(b) Plot the data on a graph, and draw a line of best fit. [2]

(c) Write a conclusion for the investigation. [1]

★ **Exam tip**

To write the conclusion for part (c), look back to the information at the start of the question and at the table. The students are investigating the factors that affect the mass of copper deposited. The table shows that the students looked at just one factor – current. This means that the conclusion should state how changing the current affects the mass of copper deposited.

(d) Use your graph to predict the mass of copper deposited when the current is 0.9 A. [1]

(e) The students calculate the theoretical mass of copper deposited at each current.

They find that all their actual mass values are less than the theoretical values.

Suggest one possible reason for this difference. [1]

★ **Exam tip**

To answer this question you will need to draw on your experience of practical work. Does all the copper stay on the cathode, or does some of it fall off, when you take it out of the solution?

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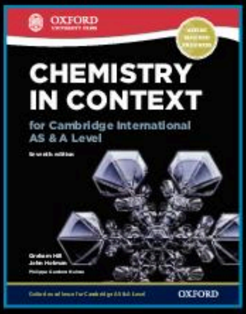
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