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IB DIPLOMA PROGRAMME

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The publisher would like to thank the International Baccalaureate for their kind permission to adapt questions from past examinations and content from the subject guide. The questions adapted for this book, and the corresponding past paper references, are summarized here:

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INTRODUCTION

This book provides full coverage of the IB diploma syllabus in Chemistry and offers support to students preparing for their examinations. The book will help you revise the study material, learn the essential terms and concepts, strengthen your problem-solving skills and improve your approach to IB examinations. The book is packed with worked examples and exam tips that demonstrate best practices and warn against common errors. All topics are illustrated by annotated student answers to questions from past examinations, which explain why marks may be scored or missed.

A separate section is dedicated to data-based and practical questions, which are the most distinctive feature of the syllabus (first assessment in 2016). Numerous examples show how to tackle unfamiliar situations, interpret and analyse experimental data, and suggest improvements to experimental procedures. Practice problems and a complete set of IB-style examination papers provide further opportunities to check your knowledge and skills, boost your confidence and monitor the progress of your studies. Full solutions to all problems and examination papers are given online at **www.oxfordsecondary.com/ib-prepared-support.**

As any study guide, this book is not intended to replace your course materials, such as textbooks, laboratory manuals, past papers and markschemes, the IB Chemistry syllabus and your own notes. To succeed in the examination, you will need to use a broad range of resources, many of which are available online. The authors hope that this book will navigate you through this critical part of your studies, making your preparation for the exam less stressful and more efficient.

DP Chemistry assessment

All standard level (SL) and higher level (HL) students must complete the internal assessment and take three papers as part of their external assessment. Papers 1 and 2 are usually sat on one day and Paper 3 a day or two later. The internal and external assessment marks are combined as shown in the table at the top of page V to give your overall DP Chemistry grade, from 1 (lowest) to 7 (highest).

Overview of the book structure

The book is divided into several sections that cover the internal assessment, core SL and additional higher level (AHL) topics, data-based and practical questions, the four options (A–D) and a complete set of practice examination papers.

The largest section of the book, **core topics**, follows the structure of the IB diploma chemistry syllabus (for first assessment 2016) and covers all *understandings* and *applications and skills* assessment statements. Topics 1–11 contain common material for SL and HL students while topics 12–21 are intended for HL students only. The *nature of science* concepts are also discussed where applicable.

The **data-based and practical questions** section (chapter 22) provides a detailed analysis of problems and laboratory experiments that often appear in section A of paper 3. Similar to core topics, the discussion is illustrated by worked examples and sample scripts, followed by IB-style practice problems. This section also contains a complete list of laboratory experiments and techniques that may be assessed in papers 2 and 3.

The **options** section reviews the material assessed in the second part of paper 3. Each of the four options is presented as a series of SL and AHL subtopics.

The **internal assessment** section outlines the nature of the investigation that you will have to carry out and explains how to select a suitable topic, collect and process experimental data, draw conclusions and present your report in a suitable format to satisfy the marking criteria and achieve the highest grade.

The final section contains IB-style **practice examination papers 1, 2 and 3**, written exclusively for this book. These papers will give you an opportunity to test yourself before the actual exam and at the same time provide additional practice problems for every topic of core and options material.

The answers and solutions to all practice problems and examination papers are given online at **www.oxfordsecondary.com/ib-prepared-support.** Blank answer sheets for examination papers are also available at the same address.

Assessment overview

Assessment	Description	Topics	SL		HL	
			marks	weight	marks	weight
Internal	Experimental work with a written report	—	24	20%	24	20%
Paper 1	Multiple-choice questions	Core: 1–11 (SL) 1–21 (AHL)	30	20%	40	20%
Paper 2	Short- and extended-response questions		50	40%	95	36%
Paper 3	*Section A:* data-based and practical questions	—	15	20%	15	24%
	Section B: short- and extended-response questions	Option of your choice	20		30	

The final IB diploma score is calculated by combining grades for six subjects with up to three additional points from *theory of knowledge* and *extended essay* components.

Command terms

Command terms are pre-defined words and phrases used in all IB Chemistry questions and problems. Each command term specifies the type and depth of the response expected from you in a particular question. For example, the command terms *state, outline, explain* and *discuss* require answers with increasingly higher levels of detail, from a single word, short sentence or numerical value ("state") to comprehensive analysis ("discuss"), as shown in the next table.

Question	Possible answer
State the effect of increasing temperature on the reaction rate.	Rate increases.
Outline how an increase in temperature affects the reaction rate.	For most reactions, the rate approximately doubles when temperature increases by 10 degrees.
Explain why an increase in temperature increases the reaction rate.	As temperature increases, the average speed and thus kinetic energy of particles also increase. The particles collide with one another more frequently and with a greater force. As a result, the frequency of successful collisions increases, so the rate increases.
Discuss the effects of increasing temperature and the presence of a catalyst on the reaction rate.	Both factors increase the rate by increasing the frequency of successful collisions. However, an increase in temperature increases the frequency and intensity of all collisions (successful and unsuccessful) but has no effect on the activation energy. In contrast, a catalyst has no effect on the frequency or intensity of collisions but lowers the activation energy by providing an alternative reaction pathway and thus allowing slow-moving particles to collide successfully. Thus, the same macroscopic effect is achieved by different microscopic changes.

A list of commonly used command terms in Chemistry examination questions is given in the table below. Understanding the exact meaning of frequently used command terms is essential for your success in the examination. Therefore, you should explore this table and use it regularly as a reference when answering questions in this book.

Command term	Definition
Annotate	Add brief notes to a diagram or graph
Calculate	Obtain a numerical answer showing your working
Comment	Give a judgment based on a given statement or result of a calculation
Compare	Give an account of the similarities between two or more items
Compare and contrast	Give an account of similarities and differences between two or more items
Construct	Present information in a diagrammatic or logical form
Deduce	Reach a conclusion from the information given
Describe	Give a detailed account
Determine	Obtain the only possible answer
Discuss	Offer a considered and balanced review that includes a range of arguments, factors or hypotheses
Distinguish	Make clear the differences between two or more items
Draw	Represent by a labelled, accurate diagram or graph, drawn to scale, with plotted points (if appropriate) joined in a straight line or smooth curve

Continued on page VI

Command term	Definition
Estimate	Obtain an approximate value
Explain	Give a detailed account including reasons or causes
Formulate	Express precisely and systematically a concept or argument
Identify	Provide an answer from a number of possibilities
Justify	Give valid reasons or evidence to support an answer or conclusion
Label	Add labels to a diagram
List	Give a sequence of brief answers with no explanation
Outline	Give a brief account or summary
Predict	Give an expected result
Sketch	Represent by means of a diagram or graph (labelled as appropriate), giving a general idea of the required shape or relationship
State	Give a specific name, value or other brief answer without explanation
Suggest	Propose a solution, hypothesis or other possible answer

A complete list of command terms is available in the subject guide.

Preparation and exam strategies

In addition to the above suggestions, there are some simple rules you should follow during your preparation study and the exam itself.

1. **Get ready for study.** Have enough sleep, eat well, drink plenty of water and reduce your stress by positive thinking and physical exercise. A good night's sleep is particularly important before the exam day, as it can improve your score.
2. **Organize your study environment.** Find a comfortable place with adequate lighting, temperature and ventilation. Avoid distractions. Keep your papers and computer files organized. Bookmark useful online and offline material.
3. **Plan your studies.** Make a list of your tasks and arrange them by importance. Break up large tasks into smaller, easily manageable parts. Create an agenda for your studying time and make sure that you can complete each task before the deadline.
4. **Use this book as your first point of reference.** Work your way through the topics systematically and identify the gaps in your understanding and skills. Spend extra time on the topics where improvement is required. Check your textbook and online resources for more information.
5. **Read actively.** Focus on understanding rather than memorizing. Recite key points and definitions using your own words. Try to solve every worked example and practice problem before looking at the answer. Make notes for future reference.
6. **Get ready for the exams.** Practice answering exam-style questions under a time constraint. Learn how to use the Chemistry data booklet quickly and efficiently. Solve as many problems from past papers as you can. Take a trial exam using the papers at the end of this book.
7. **Optimize your exam approach.** Read all questions carefully, paying extra attention to command terms. Keep your answers as short and clear as possible. Double-check all numerical values and units. Label axes in graphs and annotate diagrams. Use exam tips from this book.
8. **Do not panic.** Take a positive attitude and concentrate on things you can improve. Set realistic goals and work systematically to achieve these goals. Be prepared to reflect on your performance and learn from your errors in order to improve your future results.

Key features of the book

Each chapter typically covers one core or option topic, and starts with "**You should know**" and "**You should be able to**" checklists. These outline the *understandings* and *applications and skills* sections of the IB diploma Chemistry syllabus. Some assessment statements have been reworded or combined together to make them more accessible and simplify the navigation. These changes do not affect the coverage of key syllabus material, which is always explained within the chapter. **Chapters contain the features outlined on this page.**

Example

Examples offer solutions to typical problems and demonstrate common problem-solving techniques. Many examples provide alternative answers and explain how the marks are awarded.

Nature of science relates a chemistry concept to the overarching principles of the scientific approach.

ATL **Approaches to learning** gives advice on the development of communication, social, self-management, research or thinking skills.

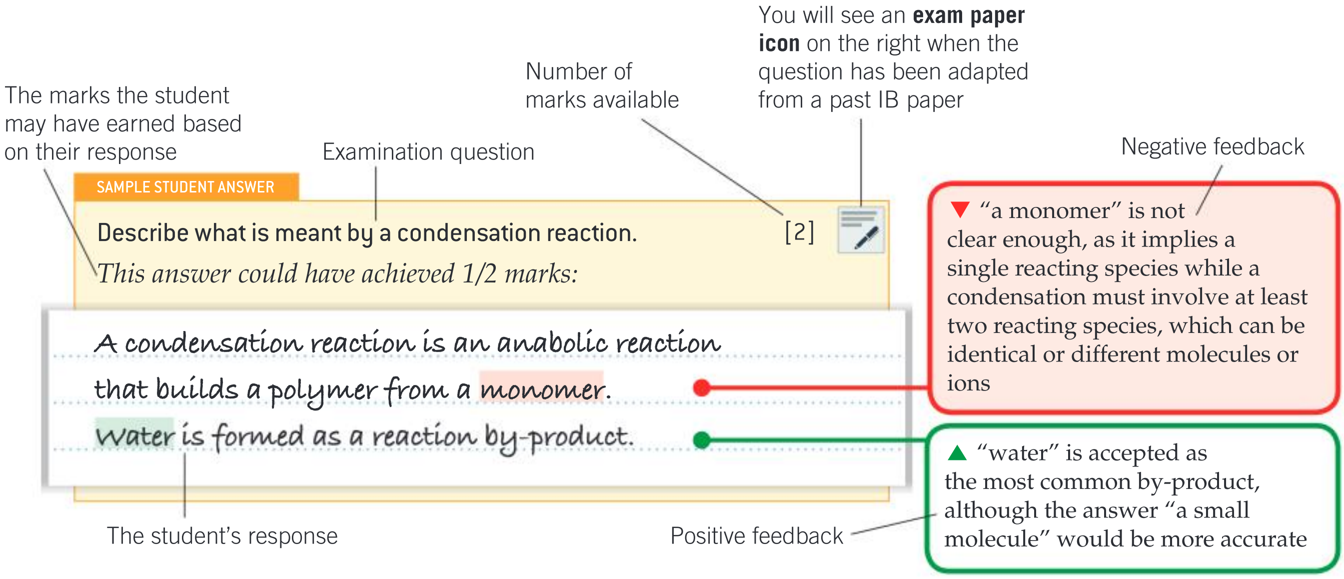
Theoretical concepts and key definitions are discussed at a level sufficient for answering typical examination questions. Many concepts are illustrated by diagrams, tables or worked examples. Most definitions are given in a grey side box like this one, and explained in the text.

Assessment tip

This feature highlights the essential terms and statements that have appeared in past markschemes, warns against common errors and shows how to optimize your approach to particular questions.

Links provide a reference to relevant material, within another part of this book or the IB Chemistry data booklet, that relates to the text in question.

Sample student answers show typical student responses to IB-style questions (most of which are taken from past examination papers). In each response, the correct points are often highlighted in green while incorrect or incomplete answers are highlighted in red. Positive or negative feedback on student's response is given in the green and red pull-out boxes. An example is given below.



SAMPLE STUDENT ANSWER

Describe what is meant by a condensation reaction. [2]

This answer could have achieved 1/2 marks:

A condensation reaction is an anabolic reaction that builds a polymer from a monomer. Water is formed as a reaction by-product.

▼ "a monomer" is not clear enough, as it implies a single reacting species while a condensation must involve at least two reacting species, which can be identical or different molecules or ions

▲ "water" is accepted as the most common by-product, although the answer "a small molecule" would be more accurate

Questions not taken from past IB examinations will not have the exam paper icon.

Practice problems

Practice problems are given at the end of each chapter. These are IB-style questions that provide you with an opportunity to test themselves and improve your problem-solving skills. Some questions introduce factual or theoretical material from the syllabus that can be studied independently.

1 STOICHIOMETRIC RELATIONSHIPS

TOPIC 1.1 INTRODUCTION TO THE PARTICULATE NATURE OF MATTER AND CHEMICAL CHANGE

You should know:

- ✔ atoms of different elements combine in fixed ratios to form compounds, which differ in properties from their constituent elements;
- ✔ a mixture is a combination of two or more substances that retain their individual properties;
- ✔ mixtures can be homogeneous or heterogeneous.

You should be able to:

- ✔ deduce chemical equations from given reactants and products;
- ✔ apply state symbols in equations;
- ✔ explain observed changes in physical properties and temperature during a change of state.

- **Chemical stoichiometry** is the relationship between the amounts of the reactants and products in a chemical reaction.
- **Stoichiometric coefficients** describe the ratios in which amounts of species react with one another.

When substances are mixed together physically, they can be combined in any proportion. Mixtures can be homogeneous (with uniform properties throughout, for example, air) or heterogeneous (in which the composition varies and components may be in different phases, like a mixture of gravel and water). Mixtures can usually be separated by physical processes such as filtration or distillation. However, when substances react to give a chemical compound, their proportions are fixed in a *stoichiometric* ratio and they can only be separated again by a chemical reaction.

Stoichiometric calculations are central to chemistry. For a general stoichiometric equation of the form:

$$a\mathrm{A} + b\mathrm{B} \rightarrow x\mathrm{X} + y\mathrm{Y}$$

in which a moles of A reacts with b moles of B, a, b, x and y are the *stoichiometric coefficients*. These stoichiometric coefficients show the ratios in which chemical species react with one another. An equation with correct stoichiometric coefficients is said to be balanced, with the same number of each type of atom on each side.

To formulate and balance stoichiometric equations quickly, it is useful to memorize the formulas and charges of common ions (table 1.1.1).

Assessment tip

In some questions, state symbols are required and you will be penalized if these are not included. Remember that the state symbol for water in the liquid phase is (l), not (aq): $H_2O(l)$.

Symbols and names of chemical elements can be found in section 5 of the data booklet.

Name	Formula and charge	Name	Formula and charge
ammonium	NH_4^+	nitrite	NO_2^-
carbonate	CO_3^{2-}	nitrate	NO_3^-
hydrogencarbonate	HCO_3^-	sulfite	SO_3^{2-}
ethanedioate (oxalate)	$C_2O_4^{2-}$	sulfate	SO_4^{2-}
phosphate	PO_4^{3-}	thiosulfate	$S_2O_3^{2-}$

▲ **Table 1.1.1** The names, formulas and charges of common polyatomic ions

Chemical equations often include state symbols: solid (s), liquid (l), gas (g) and aqueous solution (aq), which means dissolved in water.

Example 1.1.1.

Formulate a balanced equation, including state symbols, for the reaction of potassium hydroxide, KOH, with phosphoric acid, H_3PO_4, in aqueous solution.

Solution

First, write the formulas of the reactants and products.

$$KOH + H_3PO_4 \rightarrow K_3PO_4 + H_2O$$

Then balance the equation so that the numbers of atoms on both sides are equal. Do this by adjusting the coefficients on each side.

$$3KOH + H_3PO_4 \rightarrow K_3PO_4 + 3H_2O$$

Finally, add the state symbols. Aqueous solutions are involved, so (aq) is used for all species except water.

$$3KOH(aq) + H_3PO_4(aq) \rightarrow K_3PO_4(aq) + 3H_2O(l)$$

Assessment tip

Remember, the chemical formula of a substance should never be changed when balancing chemical equations, only its coefficient.

TOPIC 1.2 THE MOLE CONCEPT

You should know:

- ✔ masses of atoms are measured relative to ^{12}C and expressed as relative atomic mass (A_r) and relative formula/molecular mass (M_r), which have no units;
- ✔ the mole is a measure of the amount of substance, n, and refers to a very large, fixed number of entities (6.02×10^{23});
- ✔ molar mass (mass of one mole of a substance), M, has the derived SI unit g mol^{-1};
- ✔ an empirical formula is the simplest ratio of the atoms of each element in a compound;
- ✔ a molecular formula is the actual number of atoms of each element in a molecule.

You should be able to:

- ✔ calculate the molar masses of atoms, ions, molecules and formula units;
- ✔ solve numerical problems involving the relationships between n, m and M;
- ✔ calculate empirical and molecular formulas and percentage composition by mass from given data.

In order to determine stoichiometric ratios from observations, chemists need a way to calculate the *amount of substance*—the number of atoms, molecules or ions in a known mass of that substance.

The masses of atoms of most elements have been measured with a high degree of accuracy. For example, an atom of carbon has a mass of 1.993×10^{-26} kg. However, it is more convenient to express masses of atoms and molecules as ratios relative to the mass of the ^{12}C atom, which is defined as 12.00 on the relative scale. These ratios are known as *relative atomic mass* (A_r) and *relative molecular mass* (M_r), respectively, and have no units.

The *SI (Système International d'Unités)* is the metric system of measurement. It has seven base units, one of which is the *mole*, the SI unit for *amount of substance*, symbol n. One mole contains 6.02×10^{23} elementary entities, just as one dozen represents a collection of 12 objects. This number is the fixed numerical value of the *Avogadro constant*, N_A.

The mole applies to elementary entities (atoms, molecules, ions, electrons, other particles, or specified groups of such particles).

- **Relative atomic mass** (A_r) is the ratio of the average mass of an atom of a chemical element in a given sample to one-twelfth of the mass of a carbon-12 atom. Since the value is relative, it has no units. The terms **relative molecular mass** and **relative formula mass** (both M_r) are used for molecules and ionic species, respectively.
- The **amount of substance**, n, is the number of atoms, molecules or ions, expressed in moles, in a given quantity of the substance.
- The **mole** (abbreviated to mol) is the SI unit for amount of substance.
- The **Avogadro constant**, N_A, 6.02×10^{23} mol^{-1}, is the number of particles in 1 mol. Without units, it is called the **Avogadro number**.

The carbon-12 atom (^{12}C) is an isotope, a concept discussed in topic 2.1.

The amount of substance, n, is calculated from the mass and the molar mass as follows:

$$n\,(\text{mol}) = \frac{m\,(\text{g})}{M\,(\text{g mol}^{-1})}$$

Assessment tip

Prefixes (e.g., M, k, m, μ, p) are frequently used to form decimal multiples and submultiples of SI units. Do not forget to apply conversion factors when using these prefixes. You should also ensure that your final answer is expressed in the units indicated in the question.

Assessment tip

It is best practice to write relative atomic masses correct to two decimal places, as in the data booklet. For example, A_r for hydrogen is written as 1.01, not 1. Use of integer values can lead to inaccuracies in multi-step solutions to examination questions.

Example 1.2.1.

An extra-strength aspirin tablet contains 500 mg of acetylsalicylic acid, $C_9H_8O_4$. Calculate the number of molecules of acetylsalicylic acid in the tablet.

Solution

Calculate the molar mass, M, of acetylsalicylic acid (using relative atomic masses from the periodic table in section 6 of the data booklet):

$$M = (9 \times 12.01) + (8 \times 1.01) + (4 \times 16.00) = 180.17\ \text{g mol}^{-1}$$

Convert m(acetylsalicylic acid) from mg to g (1 mg = 10^{-3} g):

$$500\ \text{mg} = 500 \times 10^{-3}\ \text{g} = 0.500\ \text{g}$$

Calculate the amount n of acetylsalicylic acid:

$$n = \frac{0.500\ \text{g}}{180.17\ \text{g mol}^{-1}} \approx 2.78 \times 10^{-3}\ \text{mol}$$

Finally, use the relationship: 1 mol $\equiv 6.02 \times 10^{23}$ molecules.

So 2.78×10^{-3} mol $\equiv (6.02 \times 10^{23})(2.78 \times 10^{-3}) \approx 1.67 \times 10^{21}$ molecules of acetylsalicylic acid.

Maths skills

A numerical value should reflect the precision of its measurement. For multiplication or division, the result is expressed based on the measurement with the smallest number of *significant figures* (sf). For addition or subtraction, the result is expressed based on the measurement with the smallest number of *decimal places*.

If the number you are rounding to a certain number of significant figures or decimal places is followed by 5, 6, 7, 8 or 9, round the number up. If it is followed by 0, 1, 2, 3 or 4, round the number down.

This question links topics 1.2, *The mole concept*, and 4.1, *Ionic bonding and structure*. Such linkage is common in IB Chemistry examination papers, especially for stoichiometry.

Example 1.2.2.

Determine the percentage of magnesium present in magnesium phosphate, correct to **three** significant figures.

Solution

First, work out the formula for magnesium phosphate:

The phosphate ion is PO_4^{3-} and the magnesium ion is Mg^{2+} (magnesium belongs to group 2 of the periodic table and loses its two valence electrons when ionized). By balancing the charges, magnesium phosphate will have the chemical formula $Mg_3(PO_4)_2$.

Then calculate the molar mass, M, for $Mg_3(PO_4)_2$:

$$M = (3 \times 24.31) + (2 \times 30.97) + (8 \times 16.00) = 262.87\ \text{g mol}^{-1}$$

Finally calculate the percentage of magnesium in $Mg_3(PO_4)_2$:

$$\%\text{Mg} = \frac{3 \times 24.31}{262.87} \times 100 \approx 27.7\%\ \text{to 3 sf.}$$

Assessment tip

Note that the final mark given for the correct numerical answer would be lost if the answer were not given to the correct number of sf.

Example 1.2.3.

Salbutamol, a drug used to treat asthma, contains carbon, hydrogen, nitrogen and oxygen, and has molar mass $M = 239.35\ \text{g mol}^{-1}$. In a laboratory analysis, the drug was found to contain 65.2% C, 8.9% H and 5.9% N by mass. Deduce the *molecular formula* of salbutamol.

Solution

The mass percent of oxygen in salbutamol can be worked out from $100 - (65.2 + 8.9 + 5.9) = 20.0\%$.

Now we can determine the *empirical formula* of salbutamol:

Element	%	*n* / mol	Divide by smallest value of *n*
C	65.2	$65.2/12.01 \approx 5.43$	$5.43/0.42 \approx 13$
H	8.9	$8.9/1.01 \approx 8.8$	$8.8/0.42 \approx 21$
N	5.9	$5.9/14.01 \approx 0.42$	$0.42/0.42 \approx 1$
O	20.0	$20.0/16.00 \approx 1.25$	$1.25/0.42 \approx 3$

Empirical formula $= C_{13}H_{21}NO_3$

$$M(\text{empirical formula}) = (13 \times 12.01) + (21 \times 1.01) + (14.01) + (3 \times 16.00) = 239.35\ \text{g mol}^{-1}$$

Since M(molecular formula) is also $239.35\ \text{g mol}^{-1}$, the empirical formula for salbutamol is the same as its molecular formula, $C_{13}H_{21}NO_3$.

- **Empirical formula** is the simplest ratio of the atoms of each element in a compound.
- **Molecular formula** is the actual number of atoms of each element in a molecule. For example, for benzene the molecular formula is C_6H_6, but the empirical formula is CH.

Assessment tip

If the subscripts representing the number of atoms in the calculated empirical formula are not integer values, multiply all the subscripts by a factor to generate integer values for the number of atoms. For example, if a subscript is 0.25, multiply all of the subscripts by a factor of 4.

TOPIC 1.3 REACTING MASSES AND VOLUMES

You should know:

- ✔ the amount of limiting reactant controls the amount of product formed in a chemical reaction;
- ✔ the experimental yield is usually lower than the theoretical yield;
- ✔ Avogadro's law states that equal volumes of gases measured at the same temperature and pressure contain equal numbers of molecules;
- ✔ the molar volume of an ideal gas is a constant at a specified temperature and pressure;
- ✔ the molar concentration of a solute, c, is the amount of solute, n, in a given volume, V, of the solution;
- ✔ a standard solution is one with a known concentration of solute.

You should be able to:

- ✔ solve numerical problems involving reacting quantities, limiting reactants, and theoretical, experimental and percentage yields;
- ✔ calculate reacting volumes of gases by applying Avogadro's law;
- ✔ solve problems and analyse graphs involving T, p and V for a fixed mass of an ideal gas;
- ✔ solve numerical problems using the ideal gas equation, $pV = nRT$;
- ✔ explain why real gases deviate from ideal behaviour at high pressure and low temperature;
- ✔ solve problems involving dilution, mixing of solutions and titration.

Mole ratios in chemical equations can be used to calculate reacting ratios by mass, concentration and volume.

When two substances react with each other, the one that is used up completely is called the *limiting reactant*. The reactant that is not entirely consumed is said to be present in *excess*. The expected amount of product from the reaction, the theoretical yield, is calculated from the amount of the limiting reactant, but is rarely obtained in practice because of side reactions and losses on separation and purification. The *percentage yield* can be calculated as follows:

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

- A **limiting reactant** is the reactant that is used up completely, and that limits the amount of product formed in a chemical reaction.
- An **excess reactant** is present in a reaction mixture in a quantity greater than needed to react with another reactant.
- **Percentage yield** = (experimental yield/theoretical yield) × 100%.

Example 1.3.1.

5.25 kg of hydrogen, H_2, reacts with 28.2 kg of nitrogen, N_2, to form 15.5 kg of ammonia, NH_3.

a) Formulate a balanced chemical equation for this reaction, including state symbols.

b) Deduce the limiting reactant.

c) Calculate the theoretical yield of ammonia, in kg, correct to **three** significant figures.

d) Determine the percentage yield of ammonia, correct to **one** decimal place.

Solution

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

b) Step 1: Work out the amount, in mol, of each reactant, $n(H_2)$ and $n(N_2)$.

In the equation $n = \frac{m}{M}$, m is expressed in g. Hence, you need to convert kg to g.

$$n(H_2) = \frac{5.25 \times 10^3}{2 \times 1.01} \approx 2.60 \times 10^3 \text{ mol}$$

$$n(N_2) = \frac{28.2 \times 10^3}{2 \times 14.01} \approx 1.01 \times 10^3 \text{ mol}$$

Step 2: Consider the stoichiometric ratio between $N_2(g)$ and $H_2(g)$.

$$1 \text{ mol } N_2(g) \equiv 3 \text{ mol } H_2(g)$$

$$1.01 \times 10^3 \text{ mol } N_2(g) \equiv 3.03 \times 10^3 \text{ mol } H_2(g)$$

Step 3: $n(H_2)$ reacting with N_2 is 2.60×10^3 mol

$n(H_2)$ needed for complete reaction = 3.03×10^3 mol

Since $n(H_2)$ used < $n(H_2)$ needed, hydrogen is the limiting reactant.

c) Determine the amount, in mol, of ammonia expected from the limiting reactant:

$$3 \text{ mol } H_2(g) \equiv 2 \text{ mol } NH_3(g)$$

$$2.60 \times 10^3 \text{ mol } H_2(g) \equiv \frac{2}{3}(2.60 \times 10^3) \text{ mol } NH_3(g) \approx 1.73 \times 10^3 \text{ mol } NH_3(g)$$

Convert this amount to mass in g, using the expression $n = \frac{m}{M}$:

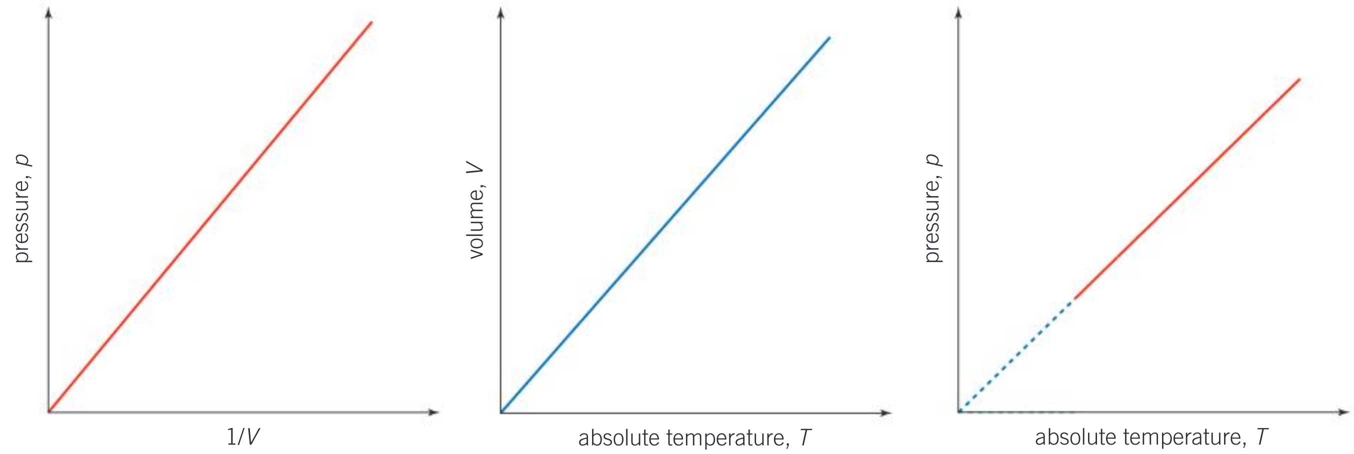
$$m(NH_3) = n \times M = (1.73 \times 10^3 \text{ mol})(17.04 \text{ g mol}^{-1}) \approx 2.95 \times 10^4 \text{ g}$$

Finally, convert the mass into kg and express your answer to 3 sf:

$n(NH_3) = 29.5$ kg

d) Percentage yield $= \frac{15.5 \text{ kg}}{29.5 \text{ kg}} \times 100\% \approx 52.5\%$

The behaviour of *ideal gases* can be described by three laws. Boyle's law states that the pressure of a fixed mass of an ideal gas is inversely proportional to its volume at a constant temperature, $p \propto \frac{1}{V}$. Charles's law states that the volume of a fixed mass of an ideal gas is proportional to its absolute temperature (in kelvin) at constant pressure, $V \propto T$, and finally Gay-Lussac's law states that $p \propto T$ for absolute temperature and a constant volume of gas. Together, these gas laws give the expression: $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$



▲ Figure 1.3.1. The behaviour of ideal gases: Boyle's law (left), Charles's law (middle) and Gay-Lussac's law (right)

For reactions in the gas phase, reacting ratios can be calculated using *Avogadro's law*: equal volumes of gases measured at the same temperature and pressure contain equal numbers of molecules. This proportionality, combined with the gas laws and a constant R, the gas constant, gives the *ideal gas equation*, or *equation of state*:

$$pV = nRT$$

It follows that 1 mol of any ideal gas has the same volume at a specified temperature and pressure. Under standard conditions (STP) of $T = 273$ K (0°C) and $p = 100$ kPa, the *molar volume of an ideal gas* is 22.7 $dm^3\ mol^{-1}$.

- **Avogadro's law** states that equal volumes of gases measured at the same temperature and pressure contain equal number of molecules
- An **ideal gas** is a gas that obeys the equation of state, $pV = nRT$, also known as the **ideal gas equation**. The particles of an ideal gas have negligible volume and collide elastically.

An ideal gas obeys the gas laws exactly, but real gases deviate from ideal gas behaviour because some intermolecular forces of attraction exist between the gaseous particles, slightly altering their speeds and collision behaviour, and because particles in a real gas occupy space. These deviations become noticeable at high pressures and low temperatures:

- At high pressures, the gas is compressed, so the space occupied by gas particles is no longer negligible compared with the volume of the gas, so the volume is larger than that for an ideal gas.
- At low temperatures, gas particles have little kinetic energy to overcome attractive forces between them, so the volume is smaller than that for an ideal gas.

Example 1.3.2.

Calculate the volume of hydrogen gas produced, in cm^3, at 32°C and 90.5 kPa, when 6.55 g of gallium reacts with an excess of hydrochloric acid.

$$2Ga(s) + 6HCl(aq) \rightarrow 2GaCl_3(aq) + 3H_2(g)$$

Solution

Since the question states that hydrochloric acid is in excess, gallium must be the limiting reactant.

Therefore, to deduce the amount of hydrogen gas produced, first calculate the amount of gallium.

The atomic mass of gallium is 69.72 $g\ mol^{-1}$.

$$\text{So, } n = \frac{6.55\ \text{g}}{69.72\ \text{g mol}^{-1}} \approx 0.0939\ \text{mol}$$

Then consider the stoichiometric ratio between gallium and hydrogen:

$$2\ \text{mol Ga(s)} \equiv 3\ \text{mol H}_2\text{(g), so } 1\ \text{mol Ga(s)} \equiv \frac{3}{2}\ \text{mol H}_2\text{(g)}$$

$$\text{Hence, } 0.0939\ \text{mol Ga(s)} \equiv \frac{3}{2}(0.0939)\ \text{mol H}_2\text{(g)} \approx 0.141\ \text{mol H}_2\text{(g)}$$

To calculate the volume V of $H_2(g)$, use the ideal gas equation, $pV = nRT$.

Collect all the required data and ensure that correct units are used:

$n = 0.141$ mol, $R = 8.31\ J\ K^{-1}\ mol^{-1}$, $T = 32 + 273 = 305$ K,
$p = 90.5\ kPa = 9.05 \times 10^4$ Pa

Rearranging the equation and inserting the data gives:

$$V = \frac{nRT}{p} = \frac{0.141\ \text{mol} \times 8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 305\ \text{K}}{9.05 \times 10^4\ \text{Pa}}$$
$$\approx 3.95 \times 10^{-3}\ \text{m}^3$$

Finally convert m^3 to cm^3: $V = 3.95 \times 10^3\ cm^3$

The ideal gas equation can be found in section 1 of the data booklet. The value of the gas constant R is listed in section 2, as is the conversion from m^3 to cm^3: $10^{-3}\ m^3 = 10^3\ cm^3$.

Assessment tip

Remember to convert °C to K for temperature in calculations.

For reactions taking place in solution, quantities can be calculated from concentrations. The *molar concentration of a solute* (dissolved substance), c, in mol dm^{-3}, is related to the amount of the solute, n, in mol and the volume, V, of the solution in dm^3 by the expression:

$$c = \frac{n}{V}$$

Other typical units of concentration, c, are g dm^{-3} and ppm (1 ppm = 1 mg dm^{-3}).

When the concentration of a solute is not known, it can be found by reacting it with a *standard solution* and comparing their reacting volumes, taking into account the stoichiometric equation for the reaction. This is the principle of *titration*.

A **standard solution** is one with a known concentration of a solute.

Example 1.3.3.

Sodium hydroxide reacts with sulfuric acid in aqueous solution to form a salt and water.

a) Formulate a balanced chemical equation for this reaction, including state symbols.

b) Calculate the volume, in dm^3, of 0.350 mol dm^{-3} sodium hydroxide solution that will neutralize 25.0 cm^3 of 0.250 mol dm^{-3} sulfuric acid solution in a titration.

Solution

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

b) $V(H_2SO_4) = 25.0\ cm^3 = 0.0250\ dm^3$

$n(H_2SO_4) = 0.0250\ dm^3 \times 0.250\ mol\ dm^{-3} \approx 0.00625\ mol$

$2\ mol\ NaOH \equiv 1\ mol\ H_2SO_4$, so $n(NaOH) = 2 \times 0.00625\ mol = 0.0125\ mol$

$$V(NaOH) = \frac{0.0125\ mol}{0.350\ mol\ dm^{-3}} \approx 0.0357\ dm^3$$

Titrations involving redox and acid–base reactions are discussed in topics 9.1 and 18.3, respectively. Chemical stoichiometry is also linked to equilibrium calculations in topic 17.1.

Assessment tip

Always ensure that you are using the correct units in numerical questions. In this question, both cm^3 and dm^3 are used, so the calculations involve conversions.

Volume conversion factors are given in section 2 of the data booklet: $1\ dm^3 = 10^3\ cm^3$

SAMPLE STUDENT ANSWER

2.478 g of white phosphorus was used to make phosphine according to the equation:

$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2^-(aq)$

a) Calculate the amount, in mol, of white phosphorus used. [1]

b) This phosphorus was reacted with 100 cm^3 of 5.00 mol dm^{-3} aqueous sodium hydroxide. Deduce, showing your working, which was the limiting reactant. [1]

c) Determine the excess amount, in mol, of the other reactant. [1]

d) Determine the volume of phosphine, measured in cm^3 at standard temperature and pressure, that was produced. [1]

This answer could have achieved 1/4 marks:

a) $n = (2.478)/(4 \times 31) = 0.02$ mol

b) $n(NaOH) = (100 \times 5.00)/(1000) = 0.500$ mol

1 mol $P_4 \equiv 3$ mol OH^-

0.02 mol P_4 used $\equiv 0.06$ mol OH^-

$n(NaOH)$ used $= 0.500$ mol and $n(NaOH)$ needed $=$ 0.06 mol

c) 0.500 mol

d) 1 mol of a gas at STP occupies 22.7 dm^3. Since 1 mol $P_4 \equiv 1$ mol PH_3, 0.02 mol $P_4 \equiv 0.02$ mol PH_3. This is equivalent to (0.02×22.7) $dm^3 = 0.454$ dm^3.

▲ Correct expression for n ($n = m/M$) and A_r of P correctly multiplied by four, as species is P_4, but exact value for A_r of P (30.97) should have been used

▼ The candidate has ignored significant figures: the correct answer is $n = 0.02000$ mol

▼ Calculation is correct, but the question is not answered, as the limiting reactant (P_4) must be explicitly stated

▼ This is the amount of NaOH used, not the amount in excess; the excess could be calculated as follows:
excess $= 0.500 - 0.0600 = 0.440$ mol

▼ Correct method, but the units of cm^3 were required, so the correct answer is 454 cm^3

Practice problems for Topic 1

Problem 1

Formulate a balanced equation, including state symbols, for the reaction of nitric acid with calcium hydroxide.

Problem 2

Calculate the number of ions present in 0.25 mol of calcium nitrate.

Problem 3

Compound X has an empirical formula CH_2O and a molar mass of 60.06 g mol^{-1}. Deduce the molecular formula of X.

Problem 4

Compound Y is a hydrocarbon and has a molar mass of 86.20 g mol^{-1}. Upon combustion, Y produces 1.75 g CO_2 and 0.836 g H_2O.

Deduce the molecular formula for Y.

Problem 5

1.7 g of $NaNO_3$ ($M_r = 85.00$) is dissolved in water to prepare 0.10 dm^3 of solution. What is the concentration of the resulting solution in mol dm^{-3}?

A. 2.0×10^{-4} **B.** 1.0×10^{-1} **C.** 2.0×10^{-1} **D.** 5.0

Problem 6

4.00 g of propane, C_3H_8, undergoes combustion in 68.2 g of oxygen.

a) Formulate a balanced chemical equation for this reaction, including state symbols.

b) Deduce the limiting reactant.

c) Calculate the theoretical yield, in g, of carbon dioxide formed.

Problem 7

Calculate the volume, in dm^3, of a balloon filled with 0.350 mol of hydrogen gas, at a temperature of 26.0°C and a pressure of 1.15×10^2 kPa.

2 ATOMIC STRUCTURE

TOPIC 2.1 THE NUCLEAR ATOM

You should know:

- ✔ each atom contains a positively charged, dense nucleus composed of protons and neutrons (nucleons);
- ✔ negatively charged electrons occupy the space around the nucleus;
- ✔ mass spectrometry is used to determine the relative atomic mass of an element from its isotopic composition.

You should be able to:

- ✔ deduce the number of protons, neutrons and electrons in atoms and ions from nuclear symbol notation;
- ✔ calculate non-integer relative atomic masses and isotopic abundances from given data, including mass spectra.

- **Protons** are positively charged particles found in the nucleus.
- **Neutrons** are neutral particles found in the nucleus.
- Neutrons and protons are **nucleons**.
- **Electrons** are negatively charged particles with tiny mass found around the nucleus.
- The **atomic number, *Z***, is the number of protons in the nucleus.
- The **mass number, *A***, is the total number of protons and neutrons in the nucleus.
- The **nuclear symbol** includes *A* and *Z* for a particular element, X, and is represented as $^{A}_{Z}X$.

Every chemical reaction can be explained in terms of atoms. Atoms are made up of the subatomic particles listed in table 2.1.1.

Particle	Charge	Mass / amu	Location
proton	+1	~1	nucleus
neutron	0	~1	nucleus
electron	−1	$\frac{1}{1836}$ (negligible)	outside nucleus

▲ **Table 2.1.1.** Particles in atoms and their properties

Atomic number and relative atomic mass, A_r

The numbers of subatomic particles in any atom or ion can be deduced from its *nuclear symbol* and its charge. The nuclear symbol for any element X includes its *mass number*, *A*, its *atomic number*, *Z*, and is represented as $^{A}_{Z}X$. The number of *protons* is given by Z and the total number of *nucleons* is given by *A*, so the number of neutrons is $A - Z$. In a neutral atom the number of *electrons* is equal to the number of protons, while in ions the charge shows the difference between these two numbers.

Example 2.1.1.

Deduce the number of protons, electrons and neutrons present in the species $^{32}_{16}X^{2-}$, and identify element X.

Solution

The first thing to notice is that $^{32}_{16}X^{2-}$ is a nuclear symbol, so has the form $^{A}_{Z}X$. As $Z = 16$, there are 16 protons. Since the species is negatively charged, there are two extra electrons associated with the 2– charge, so there are 18 electrons in total. As $A = 32$, there are $32 - 16 = 16$ neutrons.

Since $Z = 16$, element X is sulfur, S.

In the periodic table provided in the data booklet, the atomic number, Z, is written above the symbol for each element. The number below the symbol is the *relative atomic mass*, A_r. This has no units as it is a ratio of the average mass of the atom to the *unified atomic mass unit*, u.

Isotopes

Isotopes are different forms of the same element that have different numbers of neutrons in their nuclei. The identity of an element is defined by its atomic number, and its chemistry depends on its number of electrons, so isotopes have identical chemical properties. However, as their masses differ slightly, they have different physical properties.

Mass spectra

The *mass spectrometer* is used to determine the relative atomic mass of an element from its isotopic composition. In a mass spectrum the relative abundance of the naturally occurring isotopes may be recorded in two ways. The most abundant isotope can be assigned a value of 100 and the other isotopes recorded as a proportion of this, as in figure 2.1.1. Alternatively, each relative abundance can be expressed as a percentage of the whole.

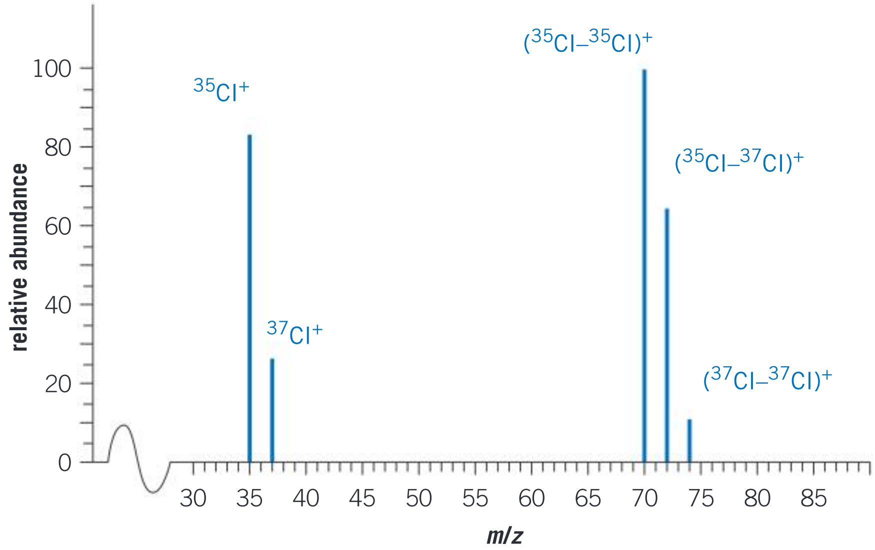


Figure 2.1.1. A mass spectrum of chlorine, Cl_2

Example 2.1.2.

Bromine has two naturally occurring isotopes with the following percentage natural abundances:

Isotope	Natural abundance /%
^{79}Br	50.69
^{81}Br	49.31

Calculate the relative atomic mass of bromine correct to two decimal places.

Solution

The relative atomic mass is the weighted average of the atomic masses of the isotopes and their relative abundance. Therefore:

$$A_r = 79 \times \frac{50.69}{100} + 81 \times \frac{49.31}{100} = 79.9862 \approx 79.99$$

- The **relative atomic mass, A_r**, is the ratio of the average mass of the atom to the unified atomic mass unit and therefore has no units.
- The **unified atomic mass unit** is a non-SI unit of mass, defined as one-twelfth of the mass of a carbon-12 atom in its ground state. $u \approx 1.660540210 \times 10^{-27}$ kg.
- **Isotopes** are different forms of the same element that have the same atomic number, Z, but different mass numbers, A, due to the different numbers of neutrons in their nuclei. They have identical chemical properties but may have different physical properties.

Assessment tip

You should be familiar with the various types of notation that can be used in examination questions. Isotopes are often written with just their mass number, A: for example, $^{35}_{17}Cl$ can be written as ^{35}Cl, chlorine-35 or Cl-35.

A **mass spectrometer** splits molecules into positively charged fragments and records their mass to charge ratios, m/z.

Assessment tip

It is best practice to write relative atomic masses correct to two decimal places as given in the data booklet; for example, A_r for hydrogen is written as 1.01, not 1. Use of integer values can lead to possible inaccuracies in multi-step calculations.

The isotopes of antimony (and many other atoms) have a non-integer relative atomic mass because of the mass defect, covered in additional higher level option C.7.

Example 2.1.3.

Antimony has a relative atomic mass A_r of 121.76 and consists of two naturally occurring isotopes, antimony-121 (A_r = 120.90) and antimony-123 (A_r = 122.90). Calculate the percentages of these isotopes in a naturally occurring sample of antimony.

Solution

Imagine a sample of 100 atoms. Let x = number of ^{121}Sb atoms and $(100 - x)$ = number of ^{123}Sb atoms in the sample.

$$A_r = 121.76 = \frac{120.90x + 122.90(100 - x)}{100}$$

Solve for x:

$$120.90x + 122.90(100 - x) = 12176$$

$$x = 57.00 \text{ and } (100 - x) = 43.00$$

The sample contains 57.00% ^{121}Sb and 43.00% ^{123}Sb.

TOPIC 2.2 ELECTRON CONFIGURATION

You should know:

- ✔ the line emission spectrum of hydrogen provides evidence for the existence of electrons in discrete energy levels, which get progressively closer together at higher energies;
- ✔ emission spectra are produced when electrons fall from higher to lower energy levels, emitting a photon that corresponds to the energy difference between the levels;
- ✔ the main energy level or shell in an atom is given an integer number, n, and can hold up to $2n^2$ electrons;
- ✔ energy levels split into sublevels, s, p, d and f, of progressively higher energy, and each sublevel contains a fixed number of orbitals;
- ✔ an atomic orbital is a region of space where there is a high probability of finding an electron;
- ✔ each orbital has a defined energy state and can hold two electrons of opposite spin.

You should be able to:

- ✔ describe the relationship between colour, wavelength, frequency and energy across the electromagnetic spectrum;
- ✔ distinguish between a continuous spectrum and a line spectrum;
- ✔ describe in detail the line emission spectrum of the hydrogen atom;
- ✔ recognize the shapes of the s and p atomic orbitals;
- ✔ apply the Aufbau principle, Hund's rule of maximum multiplicity and the Pauli exclusion principle to deduce electron configurations for atoms and ions up to Z = 36.

▲ **Figure 2.2.1.** A sodium lamp and its emission spectrum

Line spectra

Atoms absorb and emit energy in the form of electromagnetic radiation, often as visible light. For example, yellow street lamps contain sodium vapour that is excited by an electrical discharge and gives out light. If you put this light through a prism or a spectroscope, it splits not into a continuous spectrum but into a series of coloured lines (figure 2.2.1). This is an *emission spectrum*. An *absorption spectrum* is seen when atoms absorb energy from a continuous spectrum of light, and consists of a series of dark lines against a coloured background. The lines in the emission and absorption spectra of the same element have the same wavelengths.

ATL It may help you remember the principles of emission spectroscopy if you think about the colours observed in a fireworks display, or the colours of various flames observed in flame tests. In fireworks, gunpowder creates a series of redox reactions, generating thermal energy. This energy excites atoms of metal salts in the firework, promoting electrons to higher *energy levels.* A promoted electron will stay in a higher level for a fraction of a second and then drop back down to a lower level, emitting a photon of light. The wavelength of this photon corresponds to the energy difference between the levels and is characteristic for the element (for example lithium—red, sodium—yellow, barium—pale green, copper—blue-green).

Absorption and emission spectra provide evidence for the *Bohr model of the atom*, in which electrons travel around the nucleus in particular orbits with certain energies. The line emission spectrum of hydrogen is shown in figure 2.2.2, along with the corresponding transitions of an electron between the energy levels in the atom. When an electron falls from a higher to a lower energy level, a *photon* is emitted. The photon has a particular wavelength, λ, which depends on the energy difference between the two energy levels.

The relationship between the energy, E, of the photon, its wavelength, λ, and its frequency, v, is given by the expression:

$$E = hv = \frac{hc}{\lambda}$$

where h is Planck's constant $= 6.63 \times 10^{-34}$ J s and c is the speed of light $= 3.00 \times 10^{8}$ m s^{-1}. The energy is inversely proportional to the wavelength, so a photon of red light has less energy than a photon of blue light. Thus, larger differences between energy levels produce shorter wavelengths. The higher energy levels are closer together, so transitions between them produce lower energy photons.

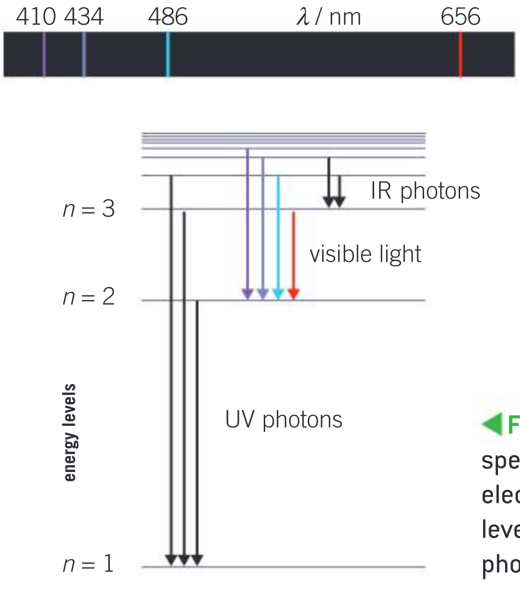


Figure 2.2.2. The emission spectrum of hydrogen (top) and the electron transitions between energy levels that emit the corresponding photons (bottom)

- **Emission spectra** are produced when photons are emitted from excited atoms as electrons return to a lower energy level. When this light is spread out into a spectrum by wavelength, a series of coloured lines is seen against a dark background.
- **Absorption spectra** are seen when atoms absorb energy from a continuous spectrum of light, and consist of a series of dark lines against a coloured background.
- An **energy level** is a quantized (discrete) amount of energy that an electron in an atom may have.
- A **photon** is a quantum of electromagnetic radiation, such as visible light, with a certain amount of energy.

The 1918 Nobel Prize in Physics was awarded to Max Planck "*in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta*". Interestingly, Planck initially thought of quantization as a mathematical trick to force calculations of the amount of energy a body radiates owing to its temperature to agree with observation. However, Albert Einstein suggested in 1905 that quantization was real, and that when an atom emits or absorbs light, the energy transfer is not continuous or smooth but occurs in discrete, tiny packets of energy, termed quanta or photons.

Similarly, our picture of the atom has changed over time. The simple and easily understood Bohr's theory has been replaced by quantum mechanics. Schrödinger's wave equation, formulated in 1926, incorporates the dual (wave and particle) nature of the electron.

Electron energy levels

- An **orbital** is a region of space where there is a high probability of finding an electron.
- A **sublevel** is a part of an energy level, made up of orbitals.
- An **electron configuration** is a notation that describes the arrangement of electrons in the energy levels and sublevels of an atom.

The Bohr model assigns a number *n* to each energy level, with the lowest being $n = 1$. Each energy level, or shell, can hold up to $2n^2$ electrons. For example, the maximum numbers of electrons in the first, second and third energy levels are 2, 8 and 18.

Energy levels split into *sublevels*, with as many sublevels as the value of *n*. The sublevels are s, p, d and f, of progressively higher energy. The first level, with $n = 1$, contains only an s sublevel; the second level, with $n = 2$, contains s and p sublevels, and so on.

Each sublevel contains a fixed number of *atomic orbitals*. Each orbital has a certain energy state for a given electron configuration and chemical environment, and can hold two electrons of opposite spin. The relationship between sublevels and atomic orbitals is shown in figure 2.2.3.

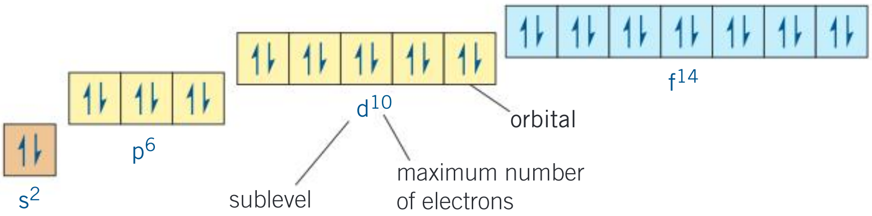
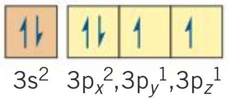


Figure 2.2.3. The s sublevel contains one orbital, with a maximum of two electrons, the p sublevel contains three orbitals, with a maximum six electrons, and so on

You need to be able to deduce the *electron configurations* for atoms and ions of elements up to and including $Z = 36$ (krypton). For example, the electron configuration of sulfur ($Z = 16$) can be represented in three ways:

- full electron configuration: $1s^22s^22p^63s^23p^4$
- condensed (abbreviated) electron configuration, in which the inner electron shells are represented by the noble gas symbol and only the valence (outer energy level) electrons are listed: $[Ne]3s^23p^4$
- orbital diagram: [Ne] 

- The **Aufbau principle** states that electrons fill orbitals of the lowest available energy.
- **Hund's rule of maximum multiplicity** states that for orbitals of the same energy (degenerate orbitals), electrons fill the orbitals singly before pairing.
- The **Pauli exclusion principle** states that any orbital has a maximum capacity of two electrons and these electrons have opposite spins ("up" and "down").

There are some points to remember when working out electron configurations.

- Label all energy levels and sublevels clearly.
- Use the *Aufbau principle, Hund's rule of maximum multiplicity* and the *Pauli exclusion principle.*
- For the first row of the d-block elements the d sublevel is 3d, not 4d.
- Know the electron configurations of chromium and copper, which can be considered as two exceptions within the first 36 elements – Cr: $[Ar]3d^54s^1$ and Cu: $[Ar]3d^{10}4s^1$.
- In cations, electrons are always removed from energy levels with the highest value of *n*. For example, the configuration of Fe^{2+} is $[Ar]3d^6$, **not** $[Ar]3d^44s^2$.

Example 2.2.1.

State the condensed (abbreviated) electron configuration for Co^{3+}.

Solution

First write the condensed electron configuration for the cobalt atom: $[Ar]3d^7 4s^2$.
Co^{3+} is a cation, so three electrons must be removed.
The first two electrons are removed from the 4s level as it has the highest value of *n*. The third electron is removed from the 3d level.
Hence the electron configuration for Co^{3+} is $[Ar]3d^6$.

You need to be able to recognize and sketch both s and p orbitals. The s atomic orbitals are spherically symmetrical and p orbitals are dumbbell-shaped, with one along each of the three Cartesian axes.

Assessment tip

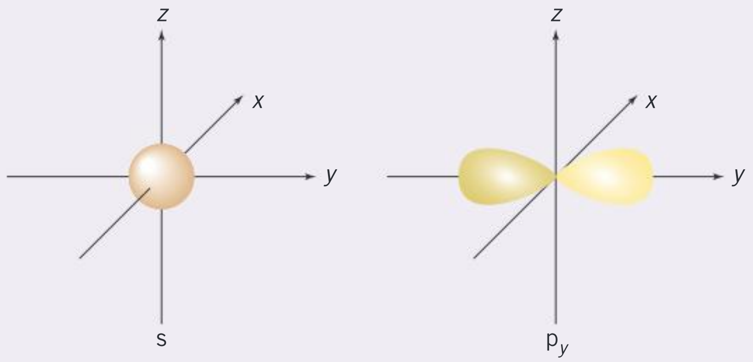
Do not be tempted to rearrange the electron configuration of Co^{3+} to have five electrons in the 3d level. This principle applies only to neutral atoms such as chromium and copper, and not ions.

Since there are four unpaired electrons in the Co^{3+} ion, it is paramagnetic, a property covered in option A.2.

Example 2.2.2.

Sketch the shapes of the s and p_y atomic orbitals.

Solution



Notice that the p_y orbital has the two lobes of electron density lying along the *y*-axis, with a nodal plane at the origin to show that there is never any electron density at the nucleus.

SAMPLE STUDENT ANSWER

a) Describe how the relative atomic mass of a sample of calcium could be determined from its mass spectrum. [2]

b) When calcium compounds are introduced into a gas flame, a red colour is seen; sodium compounds give a yellow flame. Outline the source of the colours and why they are different. [2]

This answer could have achieved 3/4 marks:

a) Different isotopes of calcium will give peaks with different heights. The higher the peak, the greater the percentage of the isotope. To find the A_r of Ca, we can multiply the height of each peak with its m/z value, find the sum of the products and divide the result by 100%.

b) The colours appear when electrons jump from one energy level to another. Ca and Na have different distances between levels, so these jumps produce photons with different energies.

▲ Correct explanation, though note that this method will work only if peak heights show percentage abundances; otherwise the peak of the most abundant isotope must be assigned a relative value of 100 and the sum of the products divided by the sum of all relative abundances instead of 100%

▼ “jump” is not specific enough, as electron transitions can either absorb or emit photons; “fall back” or “move to lower energy levels” would score the mark

▲ The second mark is awarded for “different distances between levels”

Practice problems for Topic 2

Problem 1

What are the numbers of protons, electrons and neutrons in ${}^{42}_{20}\mathrm{Ca}^{2+}$?

A. 42 protons, 40 electrons, 22 neutrons

B. 20 protons, 20 electrons, 42 neutrons

C. 20 protons, 18 electrons, 22 neutrons

D. 20 protons, 20 electrons, 22 neutrons

Problem 2

Which of the following electron transitions in the hydrogen atom would produce light in the ultraviolet region of the electromagnetic spectrum?

A. $n = 5$ to $n = 3$

B. $n = 5$ to $n = 4$

C. $n = 4$ to $n = 1$

D. $n = 4$ to $n = 3$

Problem 3

How many unpaired electrons are there in Cu^{2+}?

A. 0 **B.** 1 **C.** 2 **D.** 11

Problem 4

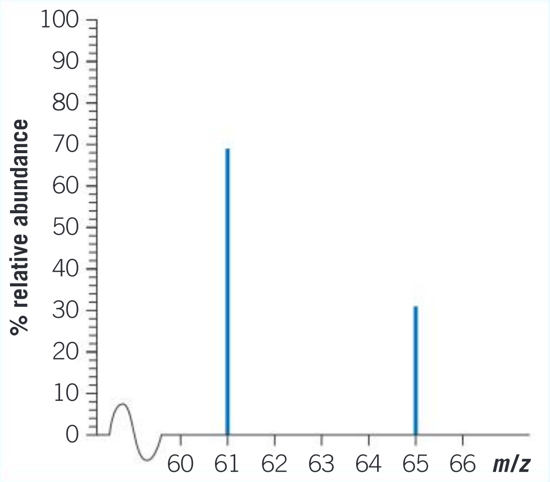
State the structure of the nucleus and the orbital diagram of $^{13}\mathrm{C}$ in its ground state.

Problem 5

The following is the mass spectrum of element X.

a) Calculate the relative atomic mass, A_r, of X.

b) Suggest the identity of element X.



Problem 6

Atoms are often drawn as spheres. Comment why this type of representation might be used in models of the atom.

Problem 7

a) Deduce the full electron configurations for Ga, P^{3-} and V^{2+}.

b) State the condensed electron configuration for Cr^{3+}.

c) Draw orbital diagrams for F and Ni^{2+}.

3 PERIODICITY

TOPIC 3.1 PERIODIC TABLE

You should know:

- ✔ in the periodic table, elements are arranged in order of increasing atomic number, Z;
- ✔ the periodic table consists of groups (columns) and periods (rows);
- ✔ the periodic table is arranged into blocks associated with the sublevels (s, p, d and f);
- ✔ the period number, n, corresponds to the number of energy levels occupied by electrons in the elements.

You should be able to:

- ✔ deduce the electron configuration of an atom from the position of the element in the periodic table, and vice versa;
- ✔ deduce the number of valence (outer-shell) electrons from the group number;
- ✔ identify alkali metals (group 1), halogens (group 17), noble gases (group 18), transition metals (groups 3–11) and lanthanoids and actinoids (the f-block).

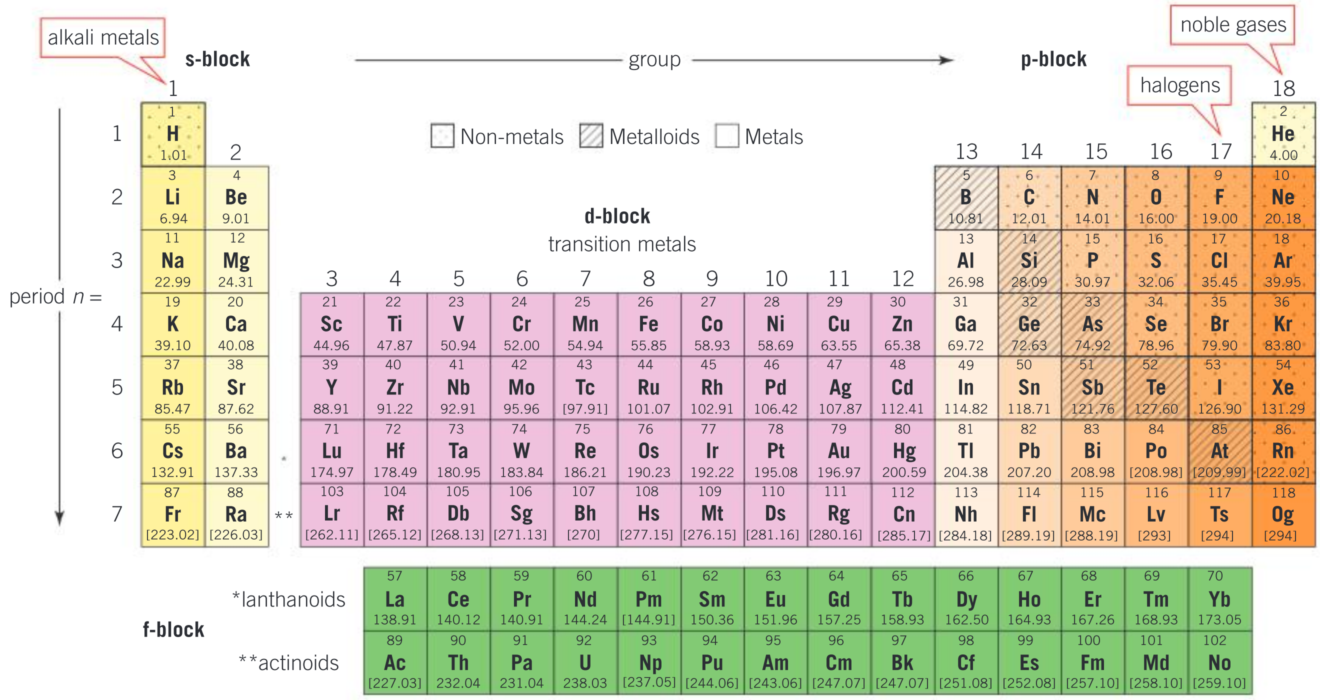
The periodic table can be used to correlate both the physical and chemical properties of elements. Arranging the elements in order of increasing atomic number, Z, and breaking them into rows according to their outer electron energy level, reveals patterns in their properties (figure 3.1.1).

- All elements in a *period* have outer electrons in the same energy level, n, which is equal to the period number.
- All elements in a *group* have the same number of electrons in their outer energy level.
- The periodic table can be split into metals on the left, non-metals on the right and metalloids on the diagonal border between the two.
- The periodic table is naturally divided into blocks of elements with electrons in the same sublevels (the s, p, d and f blocks).

Metal atoms lose electrons (are oxidized) in chemical reactions to form cations (positive ions). Non-metal atoms gain electrons (are reduced) in chemical reactions to form anions (negative ions). Elements that have properties intermediate between metals and non-metals are called metalloids. These elements lie on the boundary between metals and non-metals in the periodic table (figure 3.1.1).

- A **period** is a row in the periodic table; all elements in the same period have outer electrons in the same energy level, n.
- A **group** is a column in the periodic table; all elements in the same group have the same configuration of outer electrons.
- A **transition element** is an element that has an incomplete d-sublevel or that forms cations with an incomplete d-sublevel. For this reason, zinc is not considered a transition element as it has a full 3d sublevel in the elemental state and in all its compounds.

The different ways that an electron configuration (full, condensed and orbital diagram) can be represented are discussed in topic 2.2.



period n =	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.01																		2 He 4.00
2	3 Li 6.94	4 Be 9.01												5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31												13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08		21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62		39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	*	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.20	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	**	103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Nh [284.18]	114 Fl [289.19]	115 Mc [288.19]	116 Lv [293]	117 Ts [294]	118 Og [294]

*lanthanoids	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05
**actinoids	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]

▲ **Figure 3.1.1.** Features of the periodic table

In 1869 the Russian scientist Dimitri Mendeleev published his first periodic table of elements. When elements were arranged in order of atomic weight, some repeating patterns of properties emerged. Mendeleev left gaps in the table to maintain these patterns, predicting that yet undiscovered elements would fill them. In the modern periodic table the elements are arranged in order of increasing atomic number, Z, identified as a physical property by the British physicist Henry Moseley.

Example 3.1.1.

The element bromine is a reddish-brown liquid at room temperature and pressure.

a) State the group number, group name and period to which bromine belongs in the periodic table.

b) State the number of electrons in each principal energy level of bromine.

c) Deduce the condensed electron configuration for bromine and state the number of valence electrons.

Solution

a) Bromine is in group 17, the halogen group, and period 4.

b) 2, 8, 18, 7.

c) $[Ar]\ 3d^{10}4s^{2}4p^{5}$. Since bromine is in group 17, it has 7 valence electrons ($4s^{2} + 4p^{5}$).

TOPIC 3.2 PERIODIC TRENDS

You should know:

- ✔ atomic and ionic radii decrease across a period and increase down a group, while ionization energies and electronegativity values generally increase across a period and decrease down a group, and electron affinity values typically become more negative across a period;
- ✔ oxides change from basic through amphoteric to acidic across a period.

You should be able to:

- ✔ predict and explain the metallic/non-metallic behaviour of an element on the basis of its position in the periodic table;
- ✔ discuss the similarities and differences of elements in group 1 (alkali metals) and group 17 (halogens);
- ✔ construct equations for the reactions of the period 3 oxides $Na_2O(s)$, $MgO(s)$, $P_4O_{10}(s)$, $SO_2(g)$ and $SO_3(l)$ and the period 2 oxide $NO_2(g)$ with water.

General trends

Atomic radii decrease across a period from left to right because the increasing nuclear charge pulls the valence electrons closer to the nucleus. Atomic radii increase down a group, as in each new period the valence electrons enter a new energy level further away from the nucleus. This has a greater effect than the increasing nuclear charge, Z, owing to the shielding effect of the inner electrons.

The radii of cations are smaller than those of their parent atoms, because there are more protons than electrons in the cation, so the outer electrons are more strongly attracted to the nucleus. The radii of anions are larger than those of their parent atoms as the repulsion between the outer electrons increases with their number.

Both *ionization energy* and *electronegativity* increase across a period from left to right, because of the increasing nuclear charge and decreasing atomic radii. Going down a group, both ionization energy and electronegativity decrease because of the increasing atomic radii and the fact that the shielding effect of the core electrons increases faster than the nuclear charge.

Electron affinity values show no consistent trends in periods or groups although the greatest (most negative) values are typical for elements of groups 16 and 17.

Electronegativity is defined and discussed in topic 4.2. Values for atomic radii, ionization energies, electron affinities and electronegativities are given in sections 8 and 9 of the data booklet.

- The first **ionization energy** is the minimum energy required to remove 1 mol of electrons from 1 mol of neutral gaseous atoms in their ground state to give 1 mol of 1+ ions.
- **Electronegativity** is the relative attraction that an atom of an element has for the shared pair of electrons in a covalent bond.
- **Electron affinity** is the energy released when 1 mol of electrons is attached to 1 mol of neutral atoms or molecules in the gas phase.

Chemical trends across periods

Oxides change from basic through amphoteric to acidic across a period from group 1 to group 17 (table 3.2.1). Oxides of group 1 and 2 metals are basic and react with water to form metal hydroxides. Oxides of many other metals are amphoteric and do not react with water. Non-metallic oxides are usually acidic and react with water to form acidic solutions.

Formula of oxide	$Na_2O(s)$	$MgO(s)$	$Al_2O_3(s)$	$SiO_2(s)$	$P_4O_{10}(s)$	$SO_3(l)$ and $SO_2(g)$
Nature of oxide	basic	basic	amphoteric	acidic	acidic	acidic

▲ **Table 3.2.1.** Properties of period 3 oxides

Acid rain, caused by increasing emissions of nitrogen and sulfur oxides, is discussed in topic 8.5, Acid deposition.

The difference between the terms “amphoteric” and “amphiprotic” is explained in topic 8.1. A chemical species that behaves as an acid and base is amphoteric. An amphiprotic species can both donate and accept protons. $Al_2O_3(s)$ does not donate protons so cannot be described as amphiprotic.

Chemical trends down groups

Group 1, the alkali metals, all react with water to form a metal hydroxide, MOH(aq), resulting in an alkaline solution and the release of hydrogen gas, $H_2(g)$:

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$

This is a redox reaction, as the metal atom is oxidized by losing an electron to become an ion.

$$M(s) \rightarrow M^+(aq) + e^-$$

Descending the group, the atomic radius increases and the ionization energy decreases. Because the outer electron is lost more easily, reactions of the alkali metals with water become more vigorous as they get heavier.

Halogens, X_2, react with alkali metals, M(s), to form ionic salts, MX(s):

$$2M(s) + X_2(g) \rightarrow 2MX(s)$$

Halogens easily gain an electron (undergo reduction), but their reactivity decreases down the group, because as the atomic radius increases and the outer electrons are further away from the nucleus, gaining an extra electron becomes less easy.

For the same reason, a lighter halogen can oxidize halide ions formed by a larger, less reactive halogen, for example:

$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

Example 3.2.1.

All period 3 elements have their valence electrons in the third energy level, $n = 3$.

a) Explain why the first ionization energy, IE_1, of magnesium is greater than that of sodium.

b) Outline the acid–base character of the oxides of the period 3 elements from Na to Cl.

c) Describe and explain what you would see if aqueous bromine were added to a solution of potassium iodide and separately to a solution of potassium chloride. Formulate an equation, including state symbols, for any reaction that occurs.

Solution

a) Going from left to right across the periodic table, IE_1 values (as seen in section 8 of the data booklet) increase for two reasons – increasing nuclear charge and decreasing atomic radii.

b) See table 3.2.1.

c) When bromine is added to potassium iodide solution, a dark red/brown solution forms, due to aqueous iodine. This occurs because the oxidizing ability of halogens decreases down the group, so bromine (higher up in the group) can oxidize iodide ions to iodine:

$$Br_2(aq) + 2KI(aq) \rightarrow 2KBr(aq) + I_2(aq)$$

In contrast, when bromine is added to aqueous potassium chloride, no change is observed and no reaction takes place as chlorine is above bromine in group 17 and so the oxidizing ability of bromine is lower than that of chlorine.

Assessment tip

For best practice, physical states of matter, (s), (l), (g) or (aq), should be included in any chemical equation. However, you will not be penalized for omitting them unless they are specifically requested. Remember that the physical state for liquid water is (l), not (aq).

Assessment tip

You may be asked to describe what is observed during a chemical reaction. An observation is something you directly witness, such as a colour change of a solution, the appearance of a solid precipitate or bubbles of gas. "Formation of carbon dioxide" is not an observation.

SAMPLE STUDENT ANSWER

Some oxides of period 3, such as Na_2O and P_4O_{10}, react with water. A spatula measure of each oxide was added to a separate 100 cm^3 flask containing distilled water and a few drops of bromothymol blue indicator. The indicator is listed in section 22 of the data booklet. Deduce the colour of the resulting solution and the chemical formula of the product formed after reaction with water for each oxide. [3]

This answer could have achieved 2/3 marks:

Flask containing	Colour of solution	Product formula
Na_2O	blue	NaOH
P_4O_{10}	yellow	phosphoric acid

▲ Na_2O is a basic oxide that reacts with water:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

the solution is alkaline, therefore the indicator will be blue

▲ P_4O_{10} is an acidic oxide that reacts with water:

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

the solution is acidic, therefore the indicator will be yellow

▼ The question asked for the chemical formula of the product, so the name "phosphoric acid" is not accepted

Practice problems for Topic 3

Problem 1

Which statement is correct?

A. Atomic radius decreases down group 17.

B. First ionization energy decreases down group 1.

C. Atomic radius increases across period 3 from Na to Cl.

D. First ionization energy decreases across period 3 from Na to Cl.

Problem 2

a) State the electron configuration of sulfur and explain why sulfur is found in period 3 and group 16 of the periodic table.

b) Deduce the condensed electron configurations of Cu^{2+} and Zn^{2+} ions and comment why zinc is not considered a transition element whereas copper is.

Problem 3

Classify each of the following elements as metals, metalloids or non-metals: I, Ge, Kr, Ba, Si, H.

Problem 4

Although ionization energy values generally increase across a period, some elements do not follow this trend.

a) Explain why the first ionization energy of boron is lower than the first ionization energy of beryllium.

b) Explain why the first ionization energy of oxygen is lower than the first ionization energy of nitrogen.

4 CHEMICAL BONDING AND STRUCTURE

TOPIC 4.1 IONIC BONDING AND STRUCTURE

You should know:

- ✔ positive ions (cations) form by metals losing valence electrons;
- ✔ negative ions (anions) form by non-metals gaining electrons;
- ✔ an ionic bond is due to the electrostatic attraction between oppositely charged ions;
- ✔ under normal conditions ionic compounds are usually solids with a lattice structure involving a regular arrangement of alternating cations and anions.

You should be able to:

- ✔ deduce the formula and name of an ionic compound from its component ions, including polyatomic ions;
- ✔ explain the physical properties of ionic compounds (volatility, electrical conductivity and solubility) in terms of their structure.

- An **ion** is a charged species.
- An **ionic bond** is the electrostatic attraction between ions with opposite charges.
- A **cation** is a positively charged ion, usually formed when a metal atom loses one or more valence (outer) electrons.
- An **anion** is a negative ion, usually formed when a non-metal gains one or more electrons.
- An **oxoanion** is a polyatomic anion containing oxygen.

A table listing some polyatomic ions appears in topic 1.1.

Periodic trends (ionic radii, metallic and non-metallic character and some chemical properties of the alkali metals and the halogens) are discussed in topic 3.2.

Solid ionic compounds are held together by *ionic bonds*, due to the strong electrostatic attraction between the *cations* and *anions*. These *ions* occupy regular alternating positions in a lattice structure. The high strength of the electrostatic attractions results in a high melting point and very poor electrical conductivity in the solid state. Molten ionic compounds can conduct electricity, because the ions are able to move and act as charge carriers. The mobile ions are still bound by strong electrostatic attractions, so ionic compounds have low volatility and high boiling points. Most ionic substances are soluble in polar solvents such as water, but insoluble in non-polar solvents like hexane.

Elements in the s- and p-blocks of the periodic table tend to lose or gain electrons to form a full outer energy level, so the charges on their ions can be predicted from their group numbers (table 4.1.1).

Group	Electrons lost	Charge on ion	Example
1	1	1+	Na$^+$, K$^+$
2	2	2+	Mg^{2+}, Ca^{2+}
3	3	3+	Al^{3+}

Group	Electrons gained	Charge on ion	Example
15	3	3–	N^{3-}
16	2	2–	O^{2-}
17	1	1–	Cl$^-$, Br$^-$

▲ **Table 4.1.1.** Relationship between group number and ionic charge

Assessment tip

A common misunderstanding is the idea that ionic bonds form *only* between metals and non-metals. In fact, this is not always the case. For example, ammonium chloride, $[NH_4]Cl$, contains ammonium cations, $[NH_4]^+$, and chloride anions, Cl^-, but no metal ions.

Example 4.1.1.

Deduce the formula for the compound formed by magnesium and nitrogen.

Solution

Magnesium is a group 2 (alkaline earth) metal, so loses its two outer electrons to form the cation Mg^{2+}. Nitrogen is a group 15 non-metal and gains three electrons to form the anion N^{3-}. In the compound the charges need to balance, so the formula of magnesium nitride will be Mg_3N_2.

TOPIC 4.2 COVALENT BONDING

You should know:

- ✔ covalent bonds are formed by the electrostatic attraction between a shared pair of electrons and the positively charged nuclei;
- ✔ single, double and triple covalent bonds involve one, two and three shared pairs of electrons, respectively;
- ✔ bond strength: triple > double > single, and bond length: single > double > triple.

You should be able to:

- ✔ deduce the polar nature of a covalent bond from electronegativity values.

Shared pairs of electrons

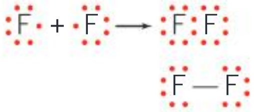
Like ionic bonding, a *covalent bond* is caused by electrostatic attraction, but instead of ions of opposite charges, covalent bonding involves positively charged nuclei attracted to one or more shared electron pairs.

When atoms form covalent bonds, they share electrons in their outermost energy level and tend to form as many bonds as will fill that energy level.

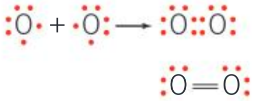
Lewis (electron dot) structures show all the electrons (either bonding or non-bonding) in molecules or ions. Dots, crosses or lines can be used to represent electrons in Lewis structures to permit easy visualization of the outer electrons. Figure 4.2.1 represents the sharing of two electrons, one from each atom, between two fluorine atoms. The effect is as if each atom had a full outer shell.

More than one pair of electrons can be shared, as for example in the oxygen molecule (Figure 4.2.2). A double bond, like the one in the oxygen molecule, is stronger and shorter than a single bond between the same atoms, and a triple bond (for example, in N_2) is stronger and shorter than a double bond.

A single **covalent bond** is the electrostatic attraction between a pair of electrons shared between atoms and their positively charged nuclei.



▲ **Figure 4.2.1.** The formation of a single covalent bond between two fluorine atoms



▲ **Figure 4.2.2.** The formation of a double covalent bond between two oxygen atoms

Polar bonds and electronegativity

Some covalent molecules contain *polar covalent bonds*, in which the shared electrons spend more time closer to one nucleus than the other. As a result, one atom carries a partial positive charge and the other a partial negative charge (for example, $H^{\delta+}F^{\delta-}$). Such bonds are intermediate between pure covalent (non-polar) and ionic.

In **polar covalent bonds** one atom has a partial positive charge and the other has a partial negative charge.

Electronegativity (χ) is the relative attraction that an atom of an element has for the shared pair of electrons in a covalent bond.

Electronegativity values are provided in section 8 of the data booklet. Periodic trends in electronegativity are described in topic 3.2.

Bond polarity can be characterized by the difference in *electronegativity* values (χ) of the bonded atoms. Electronegativity ranges from 0.8 for heavy alkali metals up to 4.0 for fluorine, the most reactive halogen. The larger the difference in electronegativity $\Delta\chi$, the greater the polarity of the bond (table 4.2.1).

Bonding type	$\Delta\chi$	Example
non-polar ("pure") covalent	0	F–F
polar covalent	0–1.8	$H^{\delta+}$–$F^{\delta-}$
ionic	> 1.8	Na^+Cl^-

▲ Table 4.2.1. Bonding type depends on the difference in electronegativities of the two atoms, $\Delta\chi$

Example 4.2.1.

Deduce whether the bond in the interhalogen compound ICl is ionic, pure covalent (non-polar) or polar covalent.

Solution

Calculate $\Delta\chi$, using the electronegativity values in section 8 of the data booklet, and then compare the answer with the electronegativity values in table 4.2.1.

$\Delta\chi = 3.2 - 2.7 = 0.5$, so ICl has a polar covalent single bond, $I^{\delta+}Cl^{\delta-}$ (note that chlorine is more electronegative than iodine).

TOPIC 4.3 COVALENT STRUCTURES

You should know:

- ✔ Lewis (electron dot) structures show all the valence electrons in covalently bonded species;
- ✔ atoms tend to achieve a valence shell containing eight electrons (the octet rule);
- ✔ some atoms (boron, beryllium) form stable compounds despite having incomplete electron octets;
- ✔ resonance structures occur when there is more than one possible position for a double bond in a molecule or anion;
- ✔ carbon and silicon form covalent network structures.

You should be able to:

- ✔ deduce the Lewis (electron dot) structure of a molecule or ion with up to four electron pairs on each atom;
- ✔ predict the electron domain and molecular geometries using VSEPR theory for up to four electron domains;
- ✔ predict and explain variations in bond angles from electron domains;
- ✔ predict the polarity of a molecule by considering both bond polarity and molecular geometry;
- ✔ deduce resonance structures;
- ✔ explain the properties of covalent network compounds in terms of their structures.

Shared and lone pairs of electrons

The bonding within covalent molecules can be predicted by means of Lewis (electron dot) structures, which are two-dimensional representations of the shared and unshared electrons (topic 4.2). In a Lewis structure each pair of electrons can be represented by two dots (••), two crosses (××) or a line (–). In the examples in figure 4.3.1, shared pairs of electrons – the bonding pairs – are shown as lines, and the *lone pairs* are shown as pairs of dots. The central atom in each of these species has four electron pairs (shared and lone), giving a total of eight electrons. This is the *octet rule*.

A **lone pair** of electrons belongs to a single atom, so it is not involved in covalent bonding.

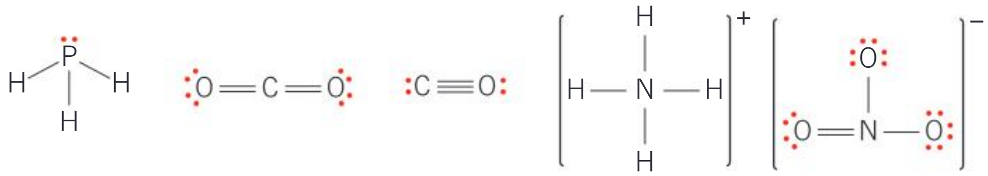
Assessment tip

Make sure to include all the valence electrons on every atom when drawing a Lewis structure. Each terminal atom should have a full octet of eight electrons surrounding it, with the exception of H, which has a maximum of two electrons surrounding it. Remember to include square brackets, [ ], and the charge (placed outside the square brackets) for any Lewis structure representing an ion.

Other exceptions to the octet rule are boron and beryllium, which can both form stable compounds with incomplete octets of electrons, for example, BCl_3 and $BeCl_2$.

- The **octet rule** refers to the tendency of atoms to gain a full valence shell with a total of eight electrons (four electron pairs, lone or bonding).
- A **coordinate bond** is a covalent bond in which both shared electrons are provided by the same atom.

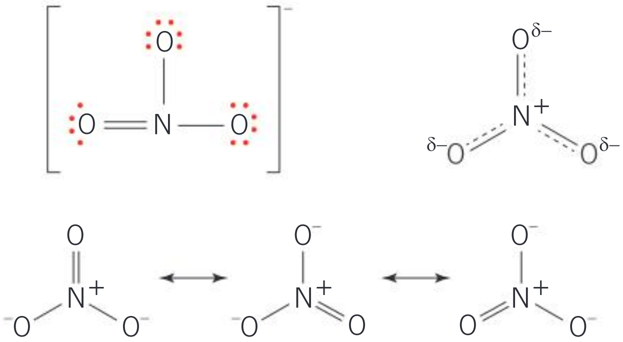
In the case of ammonium nitrate, NH_4NO_3 (figure 4.3.1), the ions are held together by ionic bonds, but the atoms within each polyatomic ion are bonded together covalently. Note that one of the four covalent N–H single bonds in the ammonium ion, NH_4^+, is formed when an ammonia molecule, NH_3, shares its lone pair of electrons with a hydrogen ion, H^+. Such a bond is called a *coordinate bond*.



▲ Figure 4.3.1. Lewis structures for PH_3, CO_2, CO and NH_4NO_3

The carbon dioxide and carbon monoxide structures in figure 4.3.1 contain multiple bonds, which are shorter and stronger than single bonds (topic 4.2). However, in the nitrate ion (the last Lewis structure in figure 4.3.1) all the bonds between the nitrogen and oxygen atoms have the same length, intermediate between a single N–O and a double N=O bond. The electrons in these bonds are delocalized, as illustrated in figure 4.3.2. Such *resonance structures* occur when there is more than one possible position for a double bond in a molecule or anion, and all contribute to the actual structure. Note that when drawing resonance structures, a double-headed arrow is used (↔).

Resonance structures are the different possible structures of a molecule or ion in which a double bond can occupy different positions. The electrons of the double bond are delocalized over all the possible positions, increasing the stability of the species.



▲ Figure 4.3.2. Lewis (top left), delocalized (top right) and contributing resonance (bottom) structures for the nitrate anion, $[NO_3]^-$

More details about resonance structures and the nature of single and double bonds will be discussed in topic 14.1.

Shapes and VSEPR theory

Lewis structures do not represent three-dimensional shapes of molecules and ions. These shapes can be deduced by means of *valence shell electron pair repulsion (VSEPR) theory*. The simple rules of VSEPR theory are:

- electron domains are regions of increased electron density, such as bonding or lone electron pairs

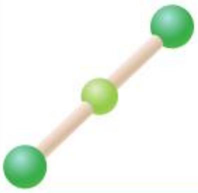
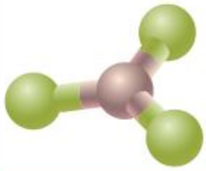
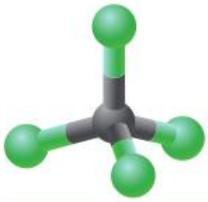
- double and triple bonds each count as one domain
- electron pairs repel one another to be as far apart as possible in space
- lone pairs have a greater repulsive effect than bonding pairs.

The electron domain geometry is the underlying geometry, where both the bonding pairs and the lone pairs are considered. The molecular geometry is the actual shape of the molecule: for example, ammonia, NH_3, has four electron domains and thus a tetrahedral electron domain geometry, but its molecular geometry of three covalent bonds is trigonal pyramidal. Molecular geometries based on two, three and four electron domains are shown in table 4.3.1.

Because lone pairs of electrons occupy more space near the central atom than bonding pairs, the order of repulsion between types of electron pairs is:

lone–lone > lone–bonding > bonding–bonding

Thus, the presence of lone pairs reduces bond angles: for example, in water, H_2O, an AB_2E_2 system, the bond angle is reduced from the ideal tetrahedral value of 109.5° to 104°. The exact bond angles in species with lone pairs cannot be deduced using VSEPR theory alone. Some bond angles for species containing lone pairs are shown in table 4.3.2.

Number of electron domains	**Molecular geometry**	**Bond angle**	**Examples of molecules or ions having this shape**
two	linear, AB_2 	180°	$BeCl_2$, CO_2
three	trigonal planar, AB_3 	120°	BF_3, $[NO_3]^-$
four	tetrahedral, AB_4 	109.5°	CH_4, $[NH_4]^+$, $[ClO_4]^-$

▲ **Table 4.3.1.** Molecular geometries based on two, three, and four electron domains

Electron domains	**Electron domain geometry**	**Molecule geometry**	**Bond angle**
three	trigonal planar (AB_2E)	V-shaped (bent)	<120°
four	tetrahedral (AB_3E)	trigonal pyramidal	<109.5°
four	tetrahedral (AB_2E_2)	V-shaped (bent)	<109.5°

E = lone pair of electrons

▲ **Table 4.3.2.** Geometries involving lone pairs based on three and four electron domains

Assessment tip

Many factors affect the bond angle, such as lone pairs, multiple bonds and electronegativity. For example, the bond angle in the trigonal pyramidal molecule NH_3 is 107° (AB_3E system) but the bond angle in PF_3, also trigonal pyramidal, is 96°, owing to the larger size of the lone pair on phosphorus and the high electronegativity of fluorine contributing to a large electronegativity difference, $\Delta\chi$.

VSEPR theory is a simple model used for the qualitative deduction of the shapes of covalent species (molecules and polyatomic ions). Like many models in chemistry, VSEPR theory has its limitations. It cannot predict the degree to which bond angles will deviate from their ideal values, it provides no information on exact bond lengths and it cannot be used to deduce the structures of species containing transition metals with incomplete d sublevels. However, as a model, VSEPR theory does give a qualitative explanation for the observed deviations from ideal molecular geometries.

Polar molecules

Knowing the polarity of individual bonds and the shape of a molecule, it is possible to predict whether the molecule as a whole will be polar or not. For example, in carbon dioxide the two C=O bonds are polar ($\Delta\chi = 0.8$), but since the molecule is symmetrical and linear, the two dipoles, although equal in magnitude, point in opposite directions and so cancel each other out. As a result, CO_2 is a non-polar molecule. In contrast, carbonyl sulfide, OCS, also a linear molecule, is polar. The two bond dipoles are not equal in magnitude, owing to electronegativity differences ($\Delta\chi = 0.8$ for C=O and 0 for C=S, so the carbon-to-sulfur bond is essentially non-polar). Hence, due to the asymmetrical arrangement, the molecule has a net dipole moment. Similarly, the two S–Br bonds in the SBr_2 molecule are polar ($S^{\delta+}$–$Br^{\delta-}$) because $\Delta\chi = (3.0 - 2.6) = 0.4$. Since SBr_2 is a bent molecule, the dipoles of the two bonds do not cancel out, so the molecule itself is also polar.

Covalent network structures

In addition to the simple covalent molecules discussed above, covalent network structures are possible, such as those formed by carbon and silicon (table 4.3.3).

	Structure	Shape	Bond angles
diamond (C)	each C atom is bonded to four others	C atoms in a tetrahedral arrangement	109.5°
graphite (C)	each C atom is bonded to three others in **parallel** sheets	C atoms in a trigonal planar arrangement	120°
graphene (C)	each C atom is bonded to three others in a **single** layer		
silicon (Si)	each Si atom is bonded to four others	Si atoms in a tetrahedral arrangement	109.5°
silicon dioxide (SiO_2)	each Si atom is bonded to four O atoms; each O atom is bonded to two Si atoms		109.5° (O–Si–O)

▲ **Table 4.3.3.** Covalent network structures

Carbon also forms simple but large C_{60} molecules in the shape of a soccer ball, called fullerenes, in which each carbon atom is bonded to three others, similar to graphite.

SAMPLE STUDENT ANSWER

Phosphine (IUPAC name phosphane) is a hydride of phosphorus, with the formula PH_3.

a) Draw a Lewis (electron dot) structure of phosphine. [1]

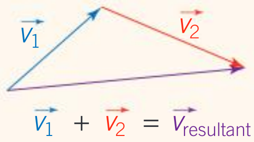
b) Outline whether you expect the bonds in phosphine to be polar or non-polar, giving a brief reason. Use the values in section 8 of the data booklet. [1]

c) Explain why the phosphine molecule is not planar. [2]

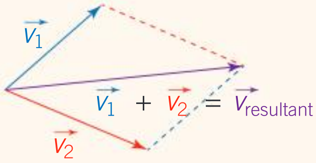
Maths skills

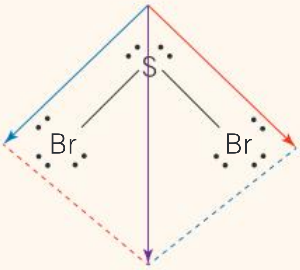
Each polar bond ($A^{\delta+}$–$B^{\delta-}$) creates a vector dipole $\vec{v}$. These vectors can be added, over the geometrical arrangement of the molecule, by vector addition (triangle law or parallelogram law).

triangle law



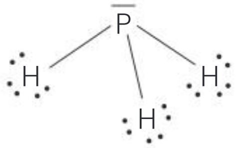
parallelogram law





This answer could have achieved 2/4 marks:

a)



b) Non-polar, due to the presence of the one lone pair.

c) There are four electron domains. The electron domain geometry is tetrahedral and the molecular geometry is trigonal pyramidal.

▼ The only error in the Lewis structure is that each H atom should not have any lone pairs

▼ The reason given is incorrect: each P–H bond is non-polar because P and H have the same electronegativity value ($\chi = 2.2$) so $\Delta\chi = 0$

▲ “four electron domains” is correct

▲ and the actual shape of phosphine is trigonal pyramidal

TOPIC 4.4 INTERMOLECULAR FORCES

You should know:

- ✔ intermolecular forces are weaker than covalent bonds;
- ✔ given comparable molar mass, the relative strengths of the different intermolecular forces are usually:
  London (dispersion) forces < dipole–dipole forces < hydrogen bonding.

You should be able to:

- ✔ deduce the type of intermolecular force(s) present in substances from their structure and chemical formula;
- ✔ explain various physical properties of a covalent compound, such as boiling point, electrical conductivity and solubility, in terms of its structure and intermolecular forces.

- **London (dispersion) forces** are instantaneous dipole–induced dipole forces due to temporary asymmetries in electron distribution. All molecules experience London forces.
- **Dipole–dipole forces** are an attraction between the positive end of one permanent dipole and the negative end of another permanent dipole on an adjacent molecule.
- A **hydrogen bond** is an electrostatic attraction between a hydrogen atom with a partial positive charge and a more electronegative atom, N, O or F, with a full or partial negative charge.
- **Van der Waals forces of attraction** include London (dispersion), dipole–dipole and dipole-induced dipole forces.

The bulk physical properties of molecular substances result from the different types of forces of attraction between their molecules.

In order of increasing relative strength, intermolecular forces of attraction are *London (dispersion) forces < dipole–dipole forces < hydrogen bonding*, assuming the molar masses are similar.

London (dispersion) forces and dipole–dipole forces are both *van der Waals forces*, which are characterized by weak electrostatic attractions.

London forces

All molecules experience *London forces*, which are short-lived electrostatic attractions between an instantaneous dipole in one molecule and an induced dipole in another. All molecules contain a cloud of negatively charged electrons, which are constantly changing position. Over time, the average distribution of the electrons is symmetrical, but at any given moment one part of the molecule might have slightly higher electron density than another part, producing a temporary (instantaneous) dipole. This instantaneous dipole will induce dipoles in other adjacent molecules. The oppositely charged ends of these dipoles will attract one another, holding the molecules together. In contrast, when regions of temporarily increased electron density within two molecules approach each other, the mobile electrons tend to be dispersed, so the repulsion is minimized. These effects are temporary, but in the next instant a different pattern of induced dipoles will emerge.

London forces depend on the number of electrons and the size of the electron cloud—the larger the cloud and the further the valence electrons are from the nucleus, the more easily the electron cloud can be polarized. Moreover, a long molecule with a large contact area will experience larger London forces than a spherical molecule with a small surface area.

Dipole–dipole forces

Dipole–dipole forces occur in all polar molecules with a permanent (not instantaneous) dipole moment. An attraction between the positive end of one permanent dipole and the negative end of another permanent dipole on an adjacent molecule provides a weak intermolecular force to keep such polar molecules together.

Hydrogen bonding

The strongest intermolecular force, *hydrogen bonding*, occurs between molecules in which an F–H, O–H or N–H bond is present. This bond is polar, and the larger atom has a lone pair of electrons. Such a lone pair in one molecule is attracted to the partially positively charged hydrogen atom in another, forming a hydrogen bond.

Assessment tip

A common misunderstanding is to think of the O–H, F–H or N–H bonds in molecules as hydrogen bonds. This is incorrect – these are polar covalent bonds. There is a clear difference between *intramolecular forces of attraction* (covalent bonds that hold atoms together *within* a molecule) and *intermolecular forces of attraction* (interactions *between* molecules).

Example 4.4.1.

Identify the intermolecular forces of attraction present in Ne, CH_2F_2 and $CH_3CH_2NH_2$.

Solution

Ne: Only London (dispersion) forces.

CH_2F_2: There are London and dipole–dipole forces (since CH_2F_2 is a polar molecule). Although a highly electronegative fluorine atom is present, hydrogen bonding is not possible: both hydrogen atoms are bonded to carbon, and the low polarity of the C–H bond is insufficient to produce a large $\delta+$ charge on hydrogen.

$CH_3CH_2NH_2$: The molecule is polar and there is an N–H bond, so all three forces of attraction are present: London, dipole–dipole and hydrogen bonding.

TOPIC 4.5 METALLIC BONDING

You should know:

- ✔ metallic bonding is the electrostatic attraction between a lattice of metal cations and their delocalized electrons;
- ✔ the strength of metallic bonding depends on the charge and radius of metal ions;
- ✔ an alloy is a mixture of a metal with other metals or non-metals.

You should be able to:

- ✔ explain the electrical conductivity and malleability of metals;
- ✔ explain the trends in melting points of metals in the s and p blocks of the periodic table;
- ✔ explain the properties of alloys.

Metals occur on the left side of the periodic table. For metals in the solid state, atoms lose one or more outer electrons and form a lattice of metal cations surrounded by a "sea" of delocalized electrons. The electrostatic attraction between these cations and electrons is known as *metallic bonding*.

Metals conduct electricity because their delocalized electrons can move freely in the solid or liquid states and thus carry electric charge.

Metallic bonding involves the electrostatic attractions between the lattice of metal cations and the "sea" of delocalized electrons that surrounds it.

Metals are malleable because there are no directional bonds to be broken—the ions can slide past each other when a force is applied.

The strength of metallic bonding depends on three factors: the number of valence electrons that can be delocalized, the charge on the metal cation and its ionic radius. Across periods, the number of valence electrons and the ionic charge increase, so the strength of metallic bonding and the melting points of metals generally increase. Down a group, the strength of metallic bonding and hence the melting points of metals decrease because of the increasing ionic radii: the larger size weakens the attraction between the cations and the delocalized electrons.

The properties of metals can be altered by alloying (mixing) them with other metals or non-metals. Alloys often have greater mechanical strength than their individual components, as ions of different sizes form a less regular lattice in which it is more difficult for the cations to slide past each other. They may also have greater resistance to corrosion or enhanced magnetic properties.

Practice problems for Topic 4

Problem 1

Deduce which of the bonds in the following binary compounds are ionic, non-polar covalent or polar covalent: PCl_3, HCl, MgF_2.

Problem 2

Which molecule has the shortest carbon-to-oxygen bond length?

A. CO **B.** CO_2

C. HCOOH **D.** $(CH_3)_2CO$

Problem 3

Which species have a coordinate covalent bond?

I. H_2O

II. $[NH_4]^+$

III. CO

A. I and II only **B.** I and III only

C. II and III only **D.** I, II and III

Problem 4

a) Consider the species $[BF_4]^-$, H_2S, BF_2Cl and CO_3^{2-}. For each species:

- **i)** draw its Lewis (electron dot) structure
- **ii)** state its electron domain geometry
- **iii)** state its molecular geometry
- **iv)** predict its bond angle(s).

b) Deduce whether H_2S and BF_2Cl are polar or non-polar molecules.

c) Draw the resonance structures of the carbonate anion, CO_3^{2-}, and comment on the bond lengths in this ion.

Problem 5

Draw the hydrogen bonds formed between propanoic acid, CH_3CH_2COOH, and water.

Problem 6

Deduce which species has the higher boiling point, HF or HCl.

Problem 7

Consider the following three compounds: methanal, CH_2O, hydrogen peroxide, H_2O_2, and fluoromethane, CH_3F.

a) Draw the full structural formula for each substance.

b) Deduce which substance is a liquid at 298 K.

Problem 8

Explain the difference in the melting point between sodium (melting point = 97.79°C) and magnesium (melting point = 650.0°C).

5 ENERGETICS/ THERMOCHEMISTRY

TOPIC 5.1 MEASURING ENERGY CHANGES

You should know:

- ✔ total energy is conserved in chemical reactions;
- ✔ heat, q, is a form of energy, and temperature, T, is a measure of the average kinetic energy of particles;
- ✔ enthalpy change, ΔH, is expressed in kJ mol^{-1} and usually under standard state conditions, $\Delta H^{\ominus}$;
- ✔ in an exothermic reaction, heat is transferred from the system to the surroundings ($\Delta H < 0$) and in an endothermic reaction, heat is transferred from the surroundings to the system ($\Delta H > 0$).

You should be able to:

- ✔ calculate the heat change when the temperature of a pure substance is changed, using $q = mc\Delta T$;
- ✔ design and evaluate calorimetry experiments to determine the enthalpy of a reaction.

Thermochemistry involves the measurement of temperature changes and the calculation of heat absorbed or released when a chemical or physical change occurs. At constant pressure, this heat is equal to the *enthalpy change*, ΔH, of the reaction or change of state.

The *first law of thermodynamics* states that energy cannot be created or destroyed, but is only converted from one form to another. A change of state or a chemical change will always absorb or release the same amount of energy under the same conditions. This energy can be determined by measuring the amount of heat transferred between the *system* and the *surroundings*.

Heat, temperature and specific heat capacity

When the same amount of *heat* is transferred to a beaker of water and a block of copper of the same mass, the *temperature* rise of the copper is ten times greater than that of the water. The two substances have different *specific heat capacities*, c; that is, more energy, in the form of heat, q, is needed to raise the temperature, T, of the water than that of the block of copper. The heat and the temperature change are related as follows:

$$q = mc\Delta T$$

Heat, q, is a form of energy (SI unit: J).

Temperature, T, is a measure of the average kinetic energy of particles (SI unit: K).

Specific heat capacity, c, is the amount of heat (in J) required to raise the temperature of 1 g of a substance by 1 K. It may also be expressed in kJ kg^{-1} K^{-1}.

- **Thermochemistry** is the study of the heat absorbed or released in chemical or physical changes.
- **Enthalpy change,** ΔH, in a system refers to the heat absorbed or released by the system at constant pressure. The enthalpy change of a chemical reaction is associated with the breaking and forming of chemical bonds.
- A **system** is all the reactants, products and solvents involved in the change of interest.
- The **surroundings** are everything else in the universe outside the system.
- An **open system** can exchange matter and energy across its boundary with the surroundings.
- A **closed system** can exchange energy but not matter across its boundary with the surroundings.
- An **isolated system** cannot exchange matter or energy with the surroundings.

The equation $q = mc\Delta T$ is given in section 1 of the data booklet and the specific heat capacity of water is provided in section 2.

Assessment tip

Note that the temperature *change* has the same value when expressed in K or °C.

- In an **exothermic reaction** heat is transferred from the system to the surroundings ($\Delta H < 0$).
- In an **endothermic reaction** heat is transferred from the surroundings to the system ($\Delta H > 0$).
- **Standard enthalpy change, $\Delta H^\ominus$**, of a reaction is the heat transferred to a closed system during a chemical reaction under standard state conditions. It is usually expressed in kJ.
- **Standard conditions for gases** are a temperature of 273.15 K and pressure of 100 kPa.
- **Standard state** refers to the most stable state of a substance at 100 kPa. For standard enthalpy changes all species are in their standard state, unless specified otherwise. Temperature is not a part of the definition of standard state, but 298 K is commonly given as the temperature of interest.
- **Standard state conditions** typically refer to a substance in its standard state at a pressure of 10^5 Pa (= 100 kPa) and the temperature of interest, usually 298 K.

Example 5.1.1.

A block of aluminium of mass $m = 34.5$ g whose initial temperature $T_i = 23.5$°C, absorbs 650 J of heat, q. Calculate the final temperature of the block, T_f, in °C.

Specific heat capacity, c, of Al is 0.903 J g^{-1} K^{-1}.

Solution

Use the equation $q = mc\Delta T$.

$\Delta T = T_f - T_i$, so $mc(T_f - T_i) = q$

Rearranging the equation gives:

$$T_f - T_i = \frac{q}{mc}, \text{ so } T_f = \frac{q}{mc} + T_i.$$

$$T_f = \frac{650 \text{ J}}{34.5 \text{ g} \times 0.903 \text{ J g}^{-1} \text{ K}^{-1}} + 23.5 = 44.4°\text{C}.$$

Enthalpy changes of reaction

Exothermic reactions give out energy while *endothermic reactions* absorb energy. The resulting temperature changes can be measured and used to calculate the enthalpy change, ΔH, of the reaction. So that enthalpy changes can easily be compared, they are often stated for the change occurring with all species in their *standard states* at a pressure of 100 kPa (*standard state conditions*).

Example 5.1.2.

To measure the enthalpy change of combustion of ethanol, ΔH_c, an IB student heated a copper calorimeter containing 0.100 dm^3 of water. The following data were recorded:

Initial temperature of water, T_i = 18.0°C

Final temperature of water, T_f = 81.4°C

Mass of ethanol combusted, m = 1.00 g

Density of water, ρ = 1.00 g cm^{-3}

a) Calculate the enthalpy change of combustion of ethanol, ΔH_c, in kJ mol^{-1}.

b) Compare your answer with the ΔH_c value for ethanol from section 13 of the data booklet, giving **two** reasons for the difference.

c) Sketch and annotate a diagram for the experimental setup.

Solution

a) First calculate q, the heat evolved when the ethanol was combusted, from $q = mc\Delta T$.

$\Delta T = T_f - T_i = 81.4 - 18.0 = 63.4$ K

0.100 dm^3 of water = 100 cm^3

$m(H_2O) = \rho \times V = 1.00 \text{ g cm}^{-3} \times 100 \text{ cm}^3 = 100$ g

$q = mc\Delta T = 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 63.4 \text{ K} \approx 2.65 \times 10^4 \text{ J} = 26.5$ kJ

Next deduce the amount of ethanol, using the expression $n = \frac{m}{M}$.

$M(CH_3CH_2OH) = (2 \times 12.01) + (6 \times 1.01) + (16.00) = 46.08$ g mol^{-1}

$$n = \frac{1.00 \text{ g}}{46.08 \text{ g mol}^{-1}} \approx 0.0217 \text{ mol}$$

Finally calculate $\Delta H_c = \dfrac{-26.5\text{ kJ}}{0.0217\text{ mol}} \approx -1.22 \times 10^3\text{ kJ mol}^{-1}$.

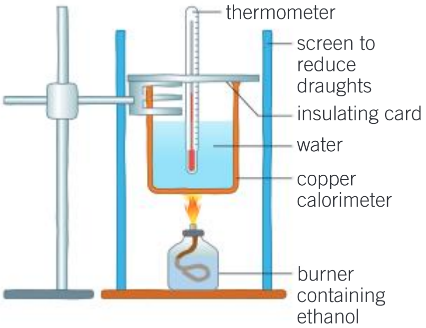
Note that combustion is exothermic, so $\Delta H_c < 0$, hence the negative sign.

b) ΔH_c for ethanol is given as -1367 kJ mol^{-1} in the data booklet. There are three potential reasons for the difference in the two values:

1. Heat was lost to the surroundings.
2. Heat absorbed by the copper calorimeter was not accounted for in calculations.
3. The combustion of ethanol was incomplete.

All of these reasons would cause the experimental ΔH_c value to be lower than the true value. You need only mention two of these reasons to score full marks.

c) See figure 5.1.1.



▲ **Figure 5.1.1.** Answer to part c) of Example 5.1.2

TOPIC 5.2 HESS'S LAW

You should know:

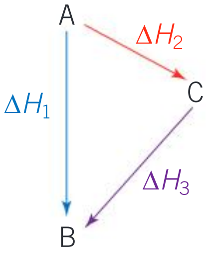
- ✔ Hess's Law states that the sum of the enthalpy changes for a reaction that is carried out in a series of steps equals the enthalpy change for the same reaction carried out in a single step.

You should be able to:

- ✔ apply Hess's Law to calculate enthalpy changes;
- ✔ calculate $\Delta H^\ominus_r$ from $\Delta H^\ominus_f$ data or using enthalpy cycles to sum other reactions with known ΔH values.

Many products can be made from the same reactants by more than one route. In figure 5.2.1, B can be made directly from A (ΔH_1), or A can first be converted to C (ΔH_2) and then C can be converted to B (ΔH_3). In this energy cycle, $\Delta H_1 = \Delta H_2 + \Delta H_3$. This is the basis of *Hess's Law*, which states that, regardless of the route by which a chemical reaction proceeds, the enthalpy change will always be the same provided that the initial and final states of the system are identical. Hess's Law is particularly useful in calculating enthalpy changes that cannot be directly determined experimentally. It can also be used to calculate the enthalpy change of any reaction, $\Delta H^\ominus_r$, from the *standard enthalpy change of formation* of reactants and products.

$$\Delta H^\ominus_r = \Sigma[\Delta H^\ominus_f(\text{products})] - \Sigma[\Delta H^\ominus_f(\text{reactants})]$$



▲ **Figure 5.2.1.** Two routes from reactant A to product B

- **Hess's Law** states that, regardless of the route by which a chemical reaction proceeds, the enthalpy change will always be the same provided that the initial and final states of the system are identical.
- The **standard enthalpy of formation,** $\Delta H^\ominus_f$, for a pure compound is the enthalpy change when 1 mol of the compound in its standard state is formed from its constituent elements in their standard states. For a pure element in its standard state, $\Delta H^\ominus_f = 0$.

Enthalpy, H, is a state function, that is, a property of a system that is independent of the way the system has reached a particular state in which it shows that particular property. We can only measure enthalpy changes, ΔH, and cannot determine the absolute enthalpy, H. Therefore, it is convenient to set a zero enthalpy baseline, so by definition the standard enthalpy of formation of a pure *element* in its standard state is zero. This is similar to arbitrarily setting a value of zero altitude for sea level. By fixing this value, any change in altitude from the baseline set at sea level can be measured. In a similar way, all enthalpy changes can be measured relative to the enthalpy of pure elements in their standard states.

Example 5.2.1.

Consider the following reactions:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H^\ominus_1 = -116.2$ kJ

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\Delta H^\ominus_2$

a) Calculate the standard enthalpy change $\Delta H^\ominus_2$, in kJ, using data from section 12 of the data booklet.

b) Using your answer to part (a), calculate the standard enthalpy change, $\Delta H^\ominus_3$ in kJ, for the reaction between carbon monoxide, CO(g), and nitrogen dioxide, $NO_2(g)$:

$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$ $\Delta H^\ominus_3$

Solution

a) $\Delta H^\ominus_2 = \Sigma[\Delta H^\ominus_f(\text{products})] - \Sigma[\Delta H^\ominus_f(\text{reactants})]$

$= [2 \times (-393.5)] - [2 \times (-110.5) + 2 \times 0] = -566.0$ kJ

b) Chemical equations can be combined in the same way as mathematical equations. To produce the third equation, we need to subtract the first equation from the second and divide all stoichiometric coefficients by two:

$\cancel{2}CO(g) + \cancel{O_2(g)} - \cancel{2}NO(g) - \cancel{O_2(g)} \longrightarrow \cancel{2}CO_2(g) - \cancel{2}NO_2(g)$

$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$

The enthalpy changes of the reactions must be combined in the same way as the equations. Therefore:

$\Delta H^\ominus_3 = 0.5 \times (\Delta H^\ominus_2 - \Delta H^\ominus_1) = 0.5 \times [-566.0 - (-116.2)] = -224.9$ kJ

Assessment tip

Note that $O_2(g)$ is an elementary substance in its standard state, so its $\Delta H^\ominus_f$ value is zero.

Assessment tip

When combining equations, note the position of each species. The equations with the desired reactants on the left (or products on the right) will be used as is, or added together. The equations with the desired reactants on the right (or products on the left) will be reversed, or subtracted from other equations.

TOPIC 5.3 BOND ENTHALPIES

You should know:

- ✔ bond-breaking requires energy (is endothermic) and bond-forming releases energy (is exothermic);
- ✔ the average bond enthalpy is the energy needed to break 1 mol of a particular covalent bond in a gaseous molecule, averaged over similar compounds.

You should be able to:

- ✔ calculate $\Delta H^\ominus_r$ using known bond enthalpy (BE) values and compare the result with the experimental $\Delta H^\ominus_r$;
- ✔ sketch potential energy profiles for chemical reactions or changes of state;
- ✔ evaluate potential energy profiles to determine whether reactants or products are more stable and whether the reaction is exothermic or endothermic;
- ✔ discuss the bond strength in ozone, O_3, compared with oxygen, O_2, in relation to the importance of ozone in the atmosphere.

Enthalpy change of reaction and average bond enthalpies

Energy is absorbed when chemical bonds are broken and released when bonds are formed. The balance between bond breaking and bond formation determines whether a chemical reaction is exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$).

The *average bond enthalpy* (BE) is the energy needed to break 1 mol of a particular covalent bond in a gaseous molecule. This bond enthalpy value is a mean obtained by averaging the slightly different values for the BE in various molecules. Experimentally measured enthalpy changes of reaction will differ from calculated values.

$\Delta H^\ominus_r = \Sigma(\text{BE bonds broken}) - \Sigma(\text{BE bonds formed})$

The **average bond enthalpy** is the energy needed to break 1 mol of a particular covalent bond in a gaseous molecule, averaged over similar compounds.

Bond enthalpy values are listed in section 11 of the data booklet.

Bond strengths are discussed in topic 4.2. Bond strength: triple > double > single.

Example 5.3.1.

a) Calculate the standard enthalpy change for the complete combustion of ethane, in kJ mol^{-1}.

b) Compare your answer to part (a) with the value given in section 13 of the data booklet.

Solution

a) First, write a balanced chemical equation for the complete combustion of ethane:

$C_2H_6(g) + 3.5O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

List the bonds that are broken and the bonds that are formed, with the BE values from section 11 of the data booklet:

Bonds broken:

$(1 \times C–C) + (6 \times C–H) + (3.5 \times O{=}O)$

$\Delta H = 1 \times 346 + 6 \times 414 + 3.5 \times 498 = 4573$ kJ

Bonds formed:

$(4 \times C{=}O) + (6 \times O–H)$

$\Delta H = 4 \times 804 + 6 \times 463 = 5994$ kJ

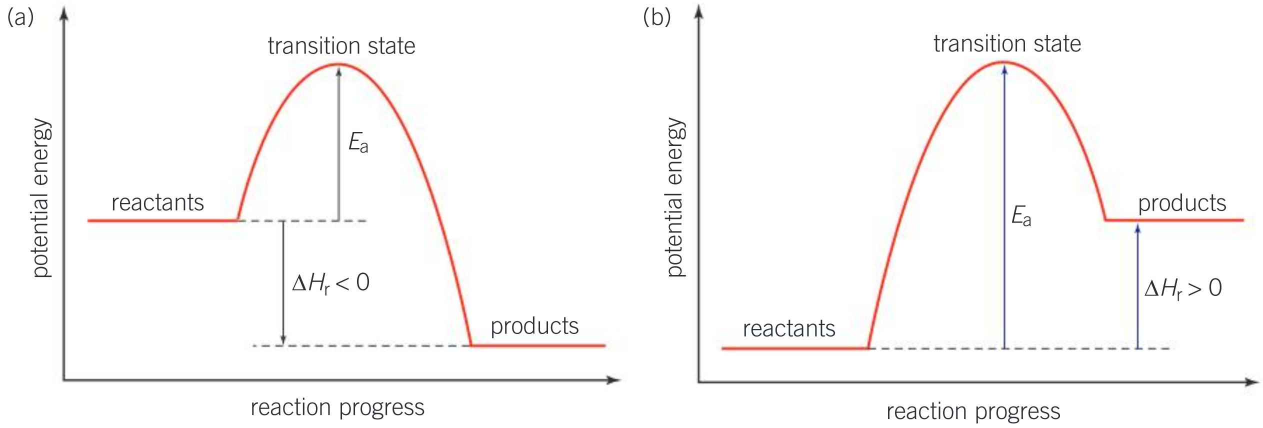
$\Delta H_c^{\ominus} = \Sigma(\text{BE bonds broken}) - \Sigma(\text{BE bonds formed}) = 4573 - 5994 = -1421$ kJ mol^{-1}

b) $\Delta H_c^{\ominus} = -1561$ kJ mol^{-1} from section 13 of the data booklet, measured under standard state conditions of 298 K and 100 kPa. There are two reasons for the difference in the two values. First, all BE values are averaged over many compounds, so bond enthalpies for a specific compound (ethane) can differ slightly. Second, the combustion of ethane under standard state conditions produces liquid water, $H_2O(l)$, while BE values used in part (a) refer to gaseous species, such as $H_2O(g)$.

Potential energy profiles

A potential energy profile is a sketch of the potential energy as a function of the reaction progress (figure 5.3.1). Low potential energy is equivalent to high stability, so an exothermic reaction yields products that are more stable than reactants. The upwards 'bump' in energy from the reactants represents the *activation energy*, E_a.

Activation energy (E_a) is the minimum kinetic energy of colliding particles required for a successful collision.



▲ **Figure 5.3.1.** Potential energy profile for **(a)** an exothermic reaction; **(b)** an endothermic reaction

Assessment tip

Ensure that you know the difference between a *potential energy profile* (discussed here) and a *Maxwell–Boltzmann energy distribution* (topic 6.1). Mixing up these two graphs and their axis labels is a common error.

	Potential energy profile	**Maxwell–Boltzmann energy distribution**
x-axis	reaction progress	kinetic energy
y-axis	potential energy	fraction of particles

Activation energy is discussed in more detail in topic 6.1. Potential energy profiles for a catalysed and an uncatalysed reaction are given in the sample problem at the end of the same topic.

The structure of ozone, O_3, involves delocalization (see example 14.1.3), so ozone has a bond order of 1.5, whereas oxygen, O_2, has a bond order of 2. Bond order is discussed in topic 14.1.

Ozone

The double bond in the oxygen molecule, O_2, is stronger than the oxygen to oxygen bonds in ozone, O_3. The BE of the oxygen molecule, O=O, is 498 kJ mol^{-1}, whereas the BE of each oxygen–oxygen bond within ozone is 362 kJ mol^{-1}. Hence radiation of shorter wavelength (greater energy) is needed to break the stronger bond in oxygen.

The ultraviolet (UV) radiation from the Sun has three forms: UV-A (λ = 320–400 nm), UV-B (λ = 280–320 nm) and UV-C (λ < 280 nm). The high-energy UV-C causes the oxygen molecule to dissociate into two oxygen radicals:

$$O_2(g) \xrightarrow{UV\text{-}C} 2O\cdot(g)$$

Ozone in the stratosphere is broken down mainly by UV-B (lower energy) to form an oxygen radical and oxygen gas:

$$O_3(g) \xrightarrow{UV\text{-}B} O\cdot(g) + O_2(g)$$

This absorption of UV photons by both oxygen (UV-C) and ozone (UV-B) prevents these harmful types of radiation from reaching the Earth's surface, where such radiation could damage living species. Most of the UV radiation reaching the Earth is low-energy UV-A, which is not as dangerous as UV-C or UV-B. Depletion of the ozone layer is hence a cause of major concern.

SAMPLE STUDENT ANSWER

a) Determine the enthalpy change of reaction, ΔH_r, in kJ, when 1.00 mol of gaseous hydrazine decomposes to its elements. Use bond enthalpy values in section 11 of the data booklet. [3]

$N_2H_4(g) \rightarrow N_2(g) + 2H_2(g)$

b) The standard enthalpy of formation of $N_2H_4(l)$ is +50.6 kJ mol^{-1}. Calculate the enthalpy of vaporization, ΔH_{vap}, of hydrazine in kJ mol^{-1}. [2]

This answer could have achieved 3/5 marks:

a) Bonds broken:

$(1 \times N{-}N) + (4 \times N{-}H) = 158 + 4 \times 391 = 1722$ kJ

▲ Correct Σ(BE bonds broken)

Bonds formed:

$(1 \times N{\equiv}N) + (2 \times H{-}H) = 945 + 2 \times 436 = 1817$ kJ

▲ Correct Σ(BE bonds formed)

$\Delta H_r = 1817 - 1722 = 95$ kJ

▼ The subtraction is reversed; correct ΔH_r value is –95 kJ

b)

$$\begin{tikzcd}
N_2H_4(l) \arrow[rr, "\Delta H_{vap}"] & & N_2H_4(g) \arrow[dl, "\Delta H_r"] \\
& N_2(g) + 2H_2(g) \arrow[ul, "\Delta H_f"] &
\end{tikzcd}$$

▲ Correct diagram

$\Delta H_{vap} = \Delta H_r + \Delta H_f = 95 + 50.6$

$= 145.6$ kJ mol^{-1}

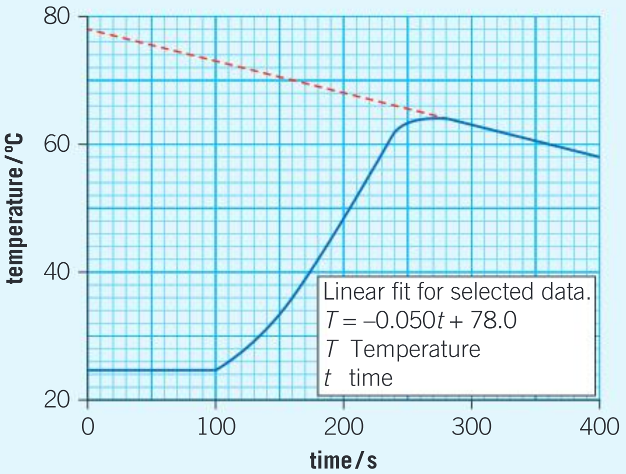
▼ $\Delta H_r + \Delta H_f$ gives ΔH for the process $N_2H_4(g) \rightarrow N_2H_4(l)$, while the vaporization is the reverse process; also, an incorrect value of ΔH_r (+95 kJ instead of –95 kJ) is used; correct answer: $\Delta H_{vap} = -(\Delta H_r + \Delta H_f) = -(-95 + 50.6) \approx +44$ kJ

Practice problems for Topic 5

Problem 1

50.0 cm^3 of 1.00 mol dm^{-3} copper(II) sulfate solution was placed in a polystyrene cup, and zinc powder was added after 100 seconds. Temperature–time data were recorded and graphed, and a line fitted as shown.

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



a) The heat produced by the reaction can be calculated from the temperature change, ΔT, using the expression below.

Heat change = mass of solution × specific heat capacity of $H_2O \times \Delta T$

Describe **two** assumptions made in using this expression to calculate the heat change.

b) i) Deduce the temperature change, ΔT, which would have occurred if the reaction had taken place instantaneously with no heat loss.

ii) State the assumption made in part (b)(i).

iii) Calculate the heat, in kJ, produced during the reaction. Use the expression given in part (a).

c) After the addition of zinc metal, the blue solution of copper(II) sulfate became colourless. Deduce the amount, in mol, of zinc that reacted in the polystyrene cup.

d) Calculate the enthalpy change, in kJ, for this reaction.

Problem 2

Consider the following reactions:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\quad \Delta H = +182.6$ kJ

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\quad \Delta H = -116.2$ kJ

Calculate ΔH, in kJ, for the reaction:

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

Problem 3

Consider the thermite reaction:
$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$

a) Calculate the standard enthalpy change for the reaction, $\Delta H^{\ominus}$, in kJ, using $\Delta H_f^{\ominus}$ values for $Al_2O_3(s)$ and $Fe_2O_3(s)$ of –1675.7 and –824.2 kJ mol^{-1}, respectively.

b) Deduce whether the reaction is exothermic or endothermic.

Problem 4

a) Calculate the standard enthalpy change for the complete combustion of ethanol, in kJ mol^{-1}, using bond enthalpy data from section 11 of the data booklet.

b) Suggest why the value obtained in part (a) differs from the $\Delta H_c^{\ominus}$ value for ethanol given in section 13 of the data booklet.

Problem 5

Calculate the wavelength, λ, in nm, of the ultraviolet radiation required to break the covalent bond in ozone, using sections 1 and 2 of the data booklet.

Bond enthalpy of ozone = 362 kJ mol^{-1}.

6 CHEMICAL KINETICS

TOPIC 6.1 COLLISION THEORY AND RATES OF REACTION

You should know:

- ✔ chemical changes occur when colliding particles have sufficient energy and proper orientation;
- ✔ activation energy (E_a) is the minimum energy required for a successful collision;
- ✔ a catalyst increases the reaction rate by lowering E_a and is not consumed in that reaction;
- ✔ reaction rate is the change in concentration of a reactant or product per unit time;
- ✔ concentration changes can be monitored by changes in mass, volume or colour.

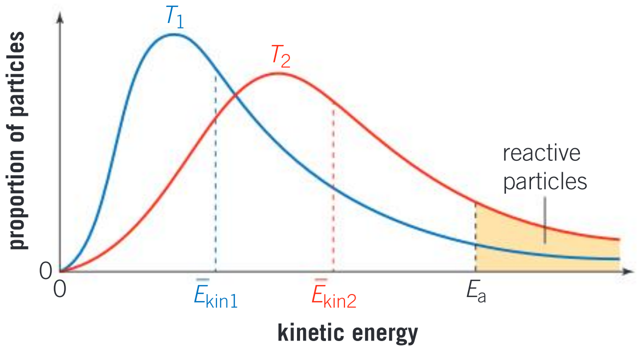
You should be able to:

- ✔ describe the kinetic theory of gases in terms of the movement and collisions of particles;
- ✔ explain the effects of temperature and catalysts on the probability of successful collisions by constructing Maxwell–Boltzmann energy distribution curves;
- ✔ sketch and explain reaction energy profiles with and without catalysts;
- ✔ explain the effects of temperature, concentration, pressure and particle size on reaction rates;
- ✔ analyse graphical and numerical data from rate experiments.

Activation energy and temperature

According to the *kinetic theory*, gas particles move randomly, have negligible sizes and collide elastically; their average kinetic energy ($\bar{E}_{kin}$) is proportional to the absolute temperature (T) in kelvins. The *collision theory* states that chemical changes are caused by *successful collisions* between reacting particles. Successful collisions occur when the particles have the required mutual orientation and combined kinetic energy $E_{kin} \geq E_a$, where E_a is the *activation energy* (figure 6.1.1). Each reaction has a specific E_a and a certain range of acceptable orientations for colliding particles, which explains why different chemical reactions proceed at different rates under the same conditions.

- **Kinetic theory** describes a gas as a large number of randomly moving particles and explains macroscopic properties of gases, such as temperature and pressure, in terms of their molecular composition and motion.
- A **successful collision** is a collision between particles that leads to a chemical reaction.
- **Activation energy** (E_a) is the minimum kinetic energy of colliding particles required for a successful collision.
- **Collision theory** explains the kinetics of chemical reactions in terms of the activation energy and mutual orientation of colliding particles.



▲ **Figure 6.1.1.** Maxwell–Boltzmann energy distribution curves for gas particles at $T_1 < T_2$

Example 6.1.1.

Explain why an increase in temperature increases the reaction rate.

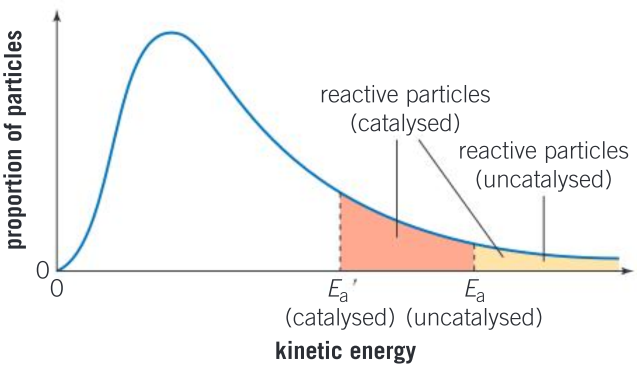
Solution

In figure 6.1.1, the shaded area represents the number of particles with $E_{kin} > E_a$. The shaded area under the curve for the higher temperature, T_2, is greater than that under the curve for T_1. This means that the proportion of particles with $E_{kin} \geq E_a$ and thus the proportion of successful collisions increases with temperature. In addition, at higher temperatures particles move faster and collide with each other more frequently, which further increases the reaction rate.

Catalysis

A *catalyst* is a substance that increases the rate of a chemical reaction but is not consumed in that reaction. Unlike temperature, a catalyst does not affect $\bar{E}_{kin}$, but lowers E_a by providing an alternative pathway for the reaction. The effect of a catalyst on the reaction rate can be represented using a Maxwell–Boltzmann curve (figure 6.1.2) or a reaction energy profile, as shown in the sample student answer at the end of this topic.

A catalyst forms an unstable compound (an *intermediate*) with a reactant. This intermediate then transforms into the reaction product, releasing the catalyst in an unchanged form. Therefore, the catalyst is both a reactant and product of the same reaction.



▲ **Figure 6.1.2.** The effect of a catalyst on the proportion of reactive particles

Assessment tip

When sketching Maxwell–Boltzmann curves for $T_1 < T_2$, make sure that the peak for T_2 is lower and lies to the right of that for T_1. Both curves must begin at the origin and they should not touch the *x*-axis at high E_{kin}. Finally, the *x*-axis must show *kinetic* energy, not just energy.

Assessment tip

It is important to mention both factors (greater *proportion* of particles with $E_{kin} \geq E_a$ and greater *frequency* of collisions). Note that answers like "more reactive particles" or "more collisions" are not specific enough and thus will not be accepted.

- A **catalyst** increases the reaction rate without being consumed in that reaction.
- An **intermediate** is an unstable species formed temporarily during a reaction.

Assessment tip

Liquids and solids are almost incompressible, so pressure has no effect on reactions that do not involve gaseous reactants. Concentration affects the rates of reactions in solution or the gas phase, while surface area is only applicable to heterogeneous mixtures.

Heterogeneous and homogeneous mixtures are covered in topic 1.1.

Assessment tip

A reaction rate cannot be negative, so it must be calculated using the absolute value (modulus) of the concentration change.

Check whether the question requires specific units for the reaction rate. If not, express the rate in mol dm^{-3} s^{-1}.

Other factors affecting rate

In addition to temperature and catalysts, other factors that affect reaction rates are the concentration, pressure and surface area of reactants. An increase in any of these parameters increases the frequency of collisions between reacting species and thus the reaction rate, while a decrease has the opposite effect.

Expressing rates of reaction

The rate of a chemical reaction can be expressed quantitatively in several ways. The *average reaction rate* (v_{avr}) is the change in concentration (Δc) of a reactant or product per unit time (Δt):

$$v_{avr} = \frac{|\Delta c|}{\Delta t}$$

The *instantaneous reaction rate* (v_{inst}) is the concentration change (dc) over an infinitesimally small period of time (dt):

$$v_{inst} = \frac{|dc|}{dt}$$

The *initial reaction rate* (v_{init}) is the instantaneous rate measured at $t = 0$.

These reaction rates can be calculated for particular species, or for the reaction. If a species has a stoichiometric coefficient other than 1, the overall reaction rate can be found by dividing the relative reaction rate for that species by its stoichiometric coefficient:

$$aA + bB \rightarrow xX + yY$$

$$v_{inst} = \frac{1}{a}\left|\frac{dc_A}{dt}\right| = \frac{1}{b}\left|\frac{dc_B}{dt}\right| = \frac{1}{x}\left|\frac{dc_X}{dt}\right| = \frac{1}{y}\left|\frac{dc_Y}{dt}\right|$$

Example 6.1.2.

A sample of calcium carbonate, $CaCO_3$(s), was added to excess hydrochloric acid, HCl(aq). The concentration of the acid during the experiment was monitored by titrating small samples of the solution every 20 seconds (table 6.1.1).

▼ **Table 6.1.1** Concentration of hydrochloric acid over time

t / s	0	20	40	60	80	100	120	140	160
c(HCl) / mol dm^{-3}	0.500	0.320	0.236	0.190	0.162	0.140	0.122	0.112	0.104

a) Draw a graph of the concentration of hydrochloric acid against time on graph paper.

b) Determine the average reaction rate with respect to HCl(aq) between 0 and 100 s.

c) Determine the initial reaction rate and the instantaneous reaction rate with respect to HCl(aq) at $t = 100$ s.

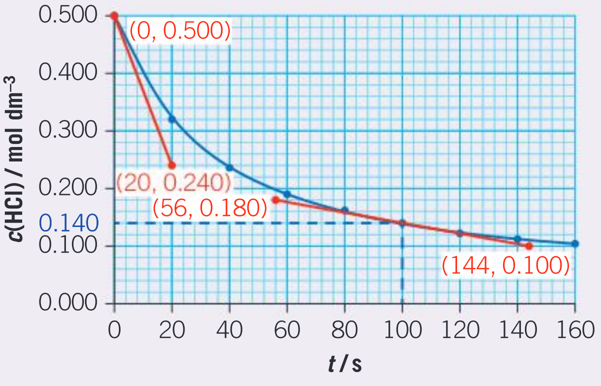
d) Calculate the overall instantaneous reaction rate at $t = 100$ s.

e) Explain the relationship between the reaction rate and the concentration of HCl(aq).

f) Suggest a method other than titration for monitoring the reaction progress.

Solution

a)



▲ **Figure 6.1.3.** The plot of [HCl(aq)] against time using the data from table 6.1.1

b) The average rate can be found either from table 6.1.1 or from figure 6.1.3:

$$v_{avr} = \frac{|0.140 - 0.500|}{100 - 0} = 3.60 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

c) To find v_{init} and $v_{inst}(100)$, we draw tangents to the curve at $t = 0$ s and $t = 100$ s, respectively, and then find their gradients from any two points on each line (figure 6.1.3):

$$v_{init} = \frac{|0.240 - 0.500|}{20 - 0} = 1.3 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$v_{\text{inst}}(100) = \frac{|\,0.100 - 0.180\,|}{144 - 56} \approx 9.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

d) The equation for the overall reaction is:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The stoichiometric coefficient before HCl(aq) is 2, so the overall reaction rate will be half the relative reaction rate with respect to HCl(aq):

$$v_{\text{inst}}(100)\ \text{overall} = \frac{9.0 \times 10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}}{2}$$

$$\approx 4.5 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

e) As c(HCl) decreases, the rate decreases as collisions between the reactant particles become less frequent.

f) The reaction consumes acid and produces gaseous carbon dioxide. Therefore, the reaction progress could be monitored by using a digital pH probe or an electrical conductivity probe. Alternatively, the mass or volume of the evolved gas could be measured.

Assessment tip

The mass of a gas evolved from a reaction can be determined by placing the reaction vessel on a digital balance, setting the balance to zero and recording the mass loss. The volume of a gas can be monitored by collecting the gas in a gas syringe or (if it is poorly soluble) an upturned measuring cylinder filled with water. The concentration of a coloured compound can be monitored by colorimetry or UV-vis spectroscopy.

For more on measurement of pH and electrical conductivity, see topics 8.3 and 8.4, respectively. UV-vis spectroscopy is described in topic B.7.

SAMPLE STUDENT ANSWER

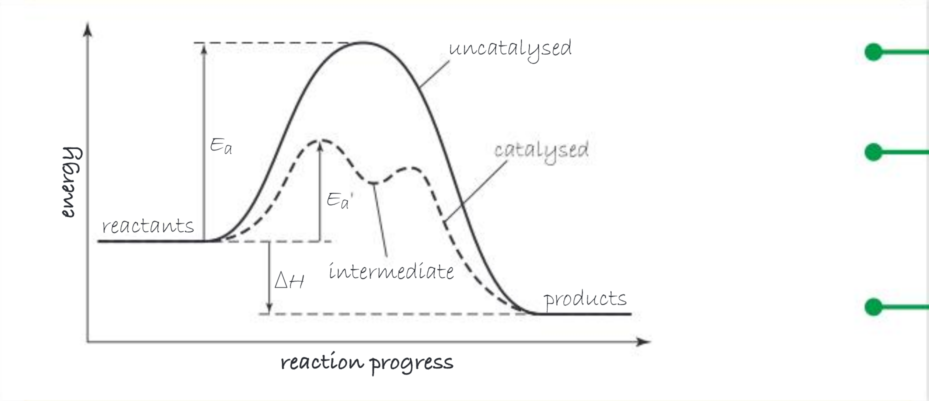
Phosgene, $COCl_2$, is usually produced by the reaction between carbon monoxide and chlorine according to the equation:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H = -108\ \text{kJ}$$

a) Sketch the potential energy profile for the synthesis of phosgene, indicating both the enthalpy of reaction and the activation energy. [2]

b) This reaction is normally carried out using a catalyst. Draw a dotted line labelled "catalysed" on the diagram to indicate the effect of the catalyst. [1]

This answer could have achieved 3/3 marks:



▲ Correct energy profile for the uncatalysed reaction

▲ Positive E_a (upward arrow) and negative ΔH (downward arrow) are shown correctly

▲ Correct energy profile for the catalysed reaction showing that $E_a' < E_a$; note that the labels for the intermediate and E_a' are not required for the mark

Assessment tip

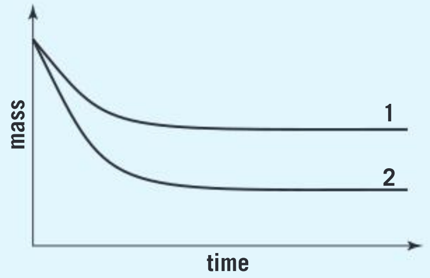
The command term "sketch" in a question means draw a labelled diagram or graph freehand. The sketch should clearly show the required shape or relationship, with any relevant features.

The command term "draw" requires a labelled, accurate graph or diagram drawn to scale and using a ruler. Points should be plotted and joined with a best-fit line or smooth curve.

Practice problems for Topic 6.1

Problem 1

Excess magnesium powder was added to a beaker containing dilute hydrochloric acid. The mass of the beaker and its contents was recorded and plotted against time (curve 1).



Which change could produce curve 2?

A. Increasing the temperature
B. Using the same mass of Mg ribbon
C. Doubling the mass of powdered Mg
D. Using the same volume of concentrated HCl(aq)

Problem 2

The questions below refer to the experiments described in problem 1 above.

a) Explain the shape of curve 1 in terms of the collision theory.

b) Using the same graph, sketch the third curve that would be produced if the original experiment were run at a lower temperature.

c) Using a different graph, sketch the concentration of $Mg^{2+}(aq)$ against time for experiments 1 and 2.

Problem 3

The rate of the acid-catalysed reaction between iodate, $IO_3^-(aq)$, and iodide, $I^-(aq)$, ions can be followed by measuring the concentration of molecular iodine, $I_2(aq)$, in the solution.

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

a) Suggest how the change of iodine concentration could be monitored.

b) A student investigated the kinetics of this reaction and obtained the following data:

t / s	0	5	10	20	30	40	50	60
c(I_2) / mmol dm^{-3}	0	0.54	0.90	1.32	1.55	1.69	1.80	1.89

i) Plot the concentration of iodine, $I_2(aq)$, against time on graph paper.

ii) Determine the average reaction rate with respect to $I_2(aq)$, in mol dm^{-3} s^{-1}, during the first 30 seconds of the experiment.

iii) Determine the initial reaction rate and the instantaneous reaction rate with respect to $I_2(aq)$ at $t = 30$ s.

iv) Calculate the overall initial reaction rate.

7 EQUILIBRIUM

TOPIC 7.1 EQUILIBRIUM

You should know:

- ✔ chemical equilibrium is a dynamic state in which the forward and reverse reactions occur at equal rates;
- ✔ the position of chemical equilibrium is characterized by the equilibrium constant (K_c), which is defined by the equilibrium law;
- ✔ Le Châtelier's principle states that a system at equilibrium counteracts any changes in reaction conditions by shifting the equilibrium position;
- ✔ changes in concentration, pressure or volume may affect the equilibrium position but not the K_c value, which depends only on temperature and the nature of the reacting species;
- ✔ a catalyst increases the rates of forward and reverse reactions equally, so it has no effect on the equilibrium position or the K_c value.

You should be able to:

- ✔ describe the characteristics of systems at equilibrium;
- ✔ deduce the K_c expression from an equation of a homogeneous reaction;
- ✔ derive new K_c expressions for equations with altered stoichiometric coefficients or combined equations;
- ✔ calculate the K_c value or an unknown concentration from the K_c expression;
- ✔ apply Le Châtelier's principle to predict how the equilibrium position and the K_c value for a given process will be affected by changes in temperature, pressure and concentration.

Reversible reactions

When the rates of the forward (left to right) and reverse (right to left) processes in a *reversible reaction* are equal to each other, the overall quantities of reactants and products do not change and the system is said to be at *equilibrium*.

- **Reversible reactions** proceed in both directions at the same time.
- **Equilibrium** is a dynamic state in which the reactants and products are constantly interconverted but their concentrations remain unchanged.

Assessment tip

When a reversible process is represented by an equation, the equilibrium sign ($\rightleftharpoons$) must be used instead of the reaction arrow ($\rightarrow$). Many students lose marks by forgetting this simple rule.

Equilibrium constants

The position of chemical equilibrium is characterized by the equilibrium constant (K_c), which is the ratio of the equilibrium concentrations of reactants and products raised to the power of their stoichiometric coefficients:

$$aA + bB \rightleftharpoons pP + qQ \qquad K_c = \frac{[P]^p[Q]^q}{[A]^a[B]^b}$$

This is the equilibrium law expression. The equilibrium concentrations of all species are denoted by square brackets.

Microscopic changes at equilibrium can be revealed by isotopic labelling, when an isotope introduced into one species appears in other species participating in the reaction.

Certain species, such as water in aqueous solutions (topic 8.3) or solids in heterogeneous equilibria (topic A.10) are excluded from K_c expressions.

Example 7.1.1.

Sulfur(VI) oxide is produced on an industrial scale from sulfur(IV) oxide and molecular oxygen:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

a) Deduce the K_c expression for this reversible reaction.

b) At a certain temperature, equilibrium was achieved at $[SO_2] = [SO_3] = 0.10 \text{ mol dm}^{-3}$ and $[O_2] = 0.24 \text{ mol dm}^{-3}$. Calculate the K_c value at that temperature.

Solution

a) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

Note that the product appears in the numerator while the reactants appear in the denominator. The states of reacting species in K_c expressions can be omitted.

b) $K_c = \dfrac{0.10^2}{0.10^2 \times 0.24} \approx 4.2$

Assessment tip

In calculations, the K_c values are treated as unitless quantities. However, all equilibrium concentrations must still be expressed using appropriate units (typically, mol dm^{-3}).

Each K_c expression refers to a specific equation. When the equation is altered, the K_c value changes accordingly (table 7.1.1).

▼ **Table 7.1.1.** The equilibrium constant and reaction stoichiometry

Change in the equation	Effect on the K_c value
coefficients halved	$K_c' = \sqrt{K_c}$
coefficients doubled	$K_c' = K_c^2$
equation reversed	$K_c' = \dfrac{1}{K_c}$
two equations added together	$K_c' = K_{c1} \times K_{c2}$

Reaction quotients

The reaction quotient (Q) is calculated in the same way as K_c but from the concentrations of reacting species at a given point in the reaction instead of at equilibrium. The forward reaction is favoured when $Q_c < K_c$, while the reverse reaction is favoured when $Q_c > K_c$. If $Q_c = K_c$, the rates of both reactions are equal, so the system is at equilibrium.

Example 7.1.2.

The Haber process involves the following reaction:

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

At 475 K, the K_c value for this reaction is 0.59. Determine the favoured process in a mixture of nitrogen, hydrogen and ammonia at 475 K if the concentration of each species is 0.50 mol dm^{-3}.

Solution

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.59$$

$$Q_c = \frac{0.50^2}{0.50 \times 0.50^3} = 4.0$$

$Q_c > K_c$, so the reverse reaction is favoured.

Le Châtelier's principle

A system at equilibrium counteracts any change in the reaction conditions by shifting the equilibrium position (*Le Châtelier's principle*). Changes in concentration, pressure or volume may affect the equilibrium position, though not the K_c value, which depends only on temperature and the identity of reacting species (table 7.1.2). A catalyst increases the rates of the forward and reverse reactions equally, so it has no effect on the equilibrium position or the K_c value.

Le Châtelier's principle states that a system at equilibrium counteracts any change in the reaction conditions by shifting the equilibrium position.

▼ **Table 7.1.2.** The effects of reaction conditions on equilibrium position and K_c value

Change in condition	Shift of equilibrium	K_c
c(reactant) increases*	to the right (towards products)	no change
c(product) decreases*		
c(reactant) decreases*	to the left (towards reactants)	
c(product) increases*		
pressure increases	to the side with fewer gas molecules	
volume decreases		
pressure decreases	to the side with more gas molecules	
volume increases		
temperature increases	$\Delta H^\circ < 0$: to the left $\Delta H^\circ > 0$: to the right $\Delta H^\circ = 0$: no change	$\Delta H^\circ < 0$: decreases $\Delta H^\circ > 0$: increases $\Delta H^\circ = 0$: no change
temperature decreases	$\Delta H^\circ < 0$: to the right $\Delta H^\circ > 0$: to the left $\Delta H^\circ = 0$: no change	$\Delta H^\circ < 0$: increases $\Delta H^\circ > 0$: decreases $\Delta H^\circ = 0$: no change
catalyst is added	no change	no change

**c*(substance) refers to a non-equilibrium concentration.

SAMPLE STUDENT ANSWER

Ethane-1,2-diol can be formed according to the following reaction:

$$2CO(g) + 3H_2(g) \rightleftharpoons HOCH_2CH_2OH(g)$$

a) Deduce the equilibrium constant expression, K_c, for this reaction. [1]

b) State how increasing the pressure of the reaction mixture at constant temperature will affect the position of equilibrium and the value of K_c. [2]

This answer could have achieved 1/3 marks:

a) $K_c = \frac{(HOCH_2CH_2OH)}{(CO)^2(H_2)^3}$

b) Position of equilibrium: Shifts towards the products, as there are fewer gas molecules on the right.

K_c: Increases, as the product concentration increases, while the reactant concentrations decrease.

▲ Correct relative positions of concentrations (products over reactants)

▼ Round brackets are used instead of square brackets

▲ Correct statement about the equilibrium position, although the explanation is not required (note the command term "state")

▼ The K_c value is not affected by pressure or concentrations

SAMPLE STUDENT ANSWER

Ammonia reacts reversibly with water:

$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Explain the effect of adding $H^+(aq)$ ions on the position of the equilibrium. [2]

This answer could have achieved 1/2 marks:

Equilibrium will shift left as OH^- ions will react with H^+ ions to produce water.

▼ When OH^- ions react with H^+ ions, $[OH^-]$ decreases, so the equilibrium position shifts to counteract this effect, to the right, not to the left

▲ Hydroxide ions are correctly identified as a species that will react with H^+ ions

Practice problems for Topic 7

Problem 1

For a reversible reaction, the reaction quotient is 0.12 and the equilibrium constant is 0.28. What is correct at this stage of the reaction?

A. The forward and reverse reactions proceed at the same rate.

B. The rate of the forward reaction is greater than the rate of the reverse reaction.

C. The rate of the forward reaction is lower than the rate of the reverse reaction.

D. At equilibrium, all reactants and products have equal concentrations.

Problem 2

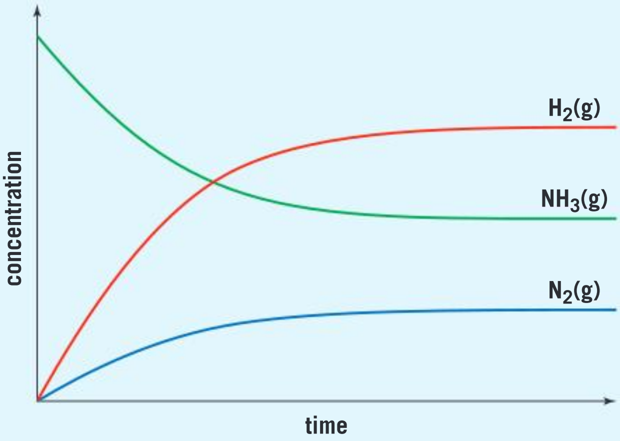
At high temperature, ammonia decomposes into nitrogen and hydrogen:

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

a) Deduce the K_c expression for this reaction.

b) State the sign of the standard enthalpy change for this reaction if its K_c value increases with temperature.

c) The progress of this reaction under certain conditions without a catalyst is shown below.



On the same graph, sketch the changes in concentrations of $NH_3(g)$, $N_2(g)$ and $H_2(g)$ over time for the same reaction under the same conditions in the presence of a catalyst.

8 ACIDS AND BASES

TOPIC 8.1 THEORIES OF ACIDS AND BASES

You should know:

- ✔ a Brønsted–Lowry acid is a proton donor and a Brønsted–Lowry base is a proton acceptor;
- ✔ amphiprotic species can act as both Brønsted–Lowry acids and bases;
- ✔ a pair of species differing by a single proton is called a conjugate acid–base pair.

You should be able to:

- ✔ deduce Brønsted–Lowry acids and bases in chemical reactions;
- ✔ deduce the conjugate acid or conjugate base for a given species.

Acids and bases have opposing properties and neutralize each other when mixed together. The concepts of acidity and basicity can be extended to all classes of chemical compounds, including salts and oxides.

According to the Arrhenius theory, acids produce protons (H^+ ions) and bases produce hydroxide (OH^-) ions in aqueous solutions. The more general Brønsted–Lowry theory defines acids as proton donors and bases as proton acceptors. For example, aqueous hydrogen chloride is both an Arrhenius and a Brønsted–Lowry acid:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Gaseous ammonia is a Brønsted–Lowry base but not an Arrhenius base, as it can accept protons (for example, from hydrogen chloride) but does not contain oxygen and thus cannot produce hydroxide ions:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

When an acid loses a proton, it forms its *conjugate base*, while a base forms its *conjugate acid* by accepting a proton.

The Lewis theory of acids and bases is discussed in topic 18.1.

Assessment tip

A free proton, H^+, cannot exist in aqueous solutions, as it immediately forms a coordinate bond with water and produces a hydronium ion, H_3O^+. However, the $H^+(aq)$ symbol is often used as a shorthand equivalent of $H_3O^+(aq)$. In the IB examinations, chemical equations involving H^+ or H_3O^+ ions are equally acceptable.

Example 8.1.1.

The ionization of hydrogen cyanide in water proceeds as follows:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

a) Identify the Brønsted–Lowry acids and Brønsted–Lowry bases in this equilibrium.

b) Identify the conjugate acid–base pairs in this equilibrium.

Solution

a) Brønsted–Lowry acids: $HCN(aq)$ and $H_3O^+(aq)$.

Brønsted–Lowry bases: $CN^-(aq)$ and $H_2O(l)$.

b) $HCN(aq)/CN^-(aq)$ and $H_3O^+(aq)/H_2O(l)$.

Assessment tip

Any equilibrium involves two reactions, forward and reverse. In this forward reaction, hydrogen cyanide loses a proton to water, so $HCN(aq)$ acts as an acid and $H_2O(l)$ acts as a base. In the reverse reaction, the hydronium ion loses a proton to the cyanide ion, so $H_3O^+(aq)$ is the acid and $CN^-(aq)$ is the base.

Assessment tip

Remember that the species in a conjugate acid–base pair differ by *one* proton. For example, H_2SO_4 and SO_4^{2-} are *not* conjugates, as they differ by two protons.

Amphiprotic species, such as water, can both donate and accept protons:

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

$H_2O(l) + H^+(aq) \rightleftharpoons H_3O^+(aq)$

Amphoteric species can react with both acids and bases. All amphiprotic species are amphoteric, but not all amphoteric species are amphiprotic. For example, zinc oxide can react with both acids and bases, so it is amphoteric:

$ZnO(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2O(l)$

$ZnO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Zn(OH)_4]^{2-}(aq)$

At the same time, ZnO cannot donate a proton (as it has none), so it is not amphiprotic.

Typical amphiprotic species are amino acids (topic B.2) and acid salts, such as $NaHCO_3$ (topic D.4). Oxides and hydroxides of zinc, aluminium and transition metals are amphoteric (topic 3.2).

Example 8.1.2.

The hydrogenphosphate ion, HPO_4^{2-}, is amphiprotic. Outline what is meant by amphiprotic, giving the formulas of both species it forms when it behaves in this manner.

Solution

The ion HPO_4^{2-} is amphiprotic because it can both donate and accept a proton:

$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

$HPO_4^{2-}(aq) + H^+(aq) \rightleftharpoons H_2PO_4^-(aq)$

Alternative equations can involve H_3O^+, OH^- or any other acids and bases, for example:

$HPO_4^{2-}(aq) + OH^-(aq) \rightleftharpoons PO_4^{3-}(aq) + H_2O(l)$

$HPO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons H_2PO_4^-(aq) + H_2O(l)$

TOPIC 8.2 PROPERTIES OF ACIDS AND BASES

You should know:

- ✔ most acids participate in characteristic reactions with active metals, metal oxides, hydroxides, carbonates and hydrogencarbonates;
- ✔ neutralization reactions are exothermic and produce salts and water.

You should be able to:

- ✔ deduce and balance equations for typical reactions of acids;
- ✔ identify the acid and base required to make different salts;
- ✔ explain how to determine an unknown concentration by acid–base titration.

Neutralization reactions are utilized in acid–base titrations (topic 18.3) and used in medicine for relieving heartburn by antacids (topic D.4). Measurement of enthalpy changes is discussed in topic 5.1.

Neutralization reactions can be represented by molecular and ionic equations:

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \quad \Delta H^\ominus = -57.6\ kJ$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \quad \Delta H^\ominus = -57.6\ kJ$

The neutralization of any strong acid with any strong base has the same net ionic equation and releases the same amount of heat per mole of $H^+(aq)$ or $OH^-(aq)$ ions.

Example 8.2.1.

Potassium sulfate can be produced by a neutralization reaction. Identify the acid and base required for this reaction and formulate its molecular and net ionic equations.

Solution

Reactants: sulfuric acid, H_2SO_4, and potassium hydroxide, KOH.

Molecular equation: $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

Net ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Other neutralization reactions can involve ammonia, metal oxides, carbonates and hydrogencarbonates:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$$
$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)$$

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$
$$MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$$

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$
$$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$
$$HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

Most acids react with metals above hydrogen in the activity series (topic 9.1), producing hydrogen gas and metal salts:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$
$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

All the above reactions can be used to reveal the presence of acids in solutions (table 8.2.1). Bases in solutions can be discovered by the release of heat in reactions with acids. Acidic and basic solutions can also be distinguished by the use of acid–base indicators or a pH meter (topic 8.3).

▼ **Table 8.2.1.** Common tests for acids

Reagent type	Example	Observation
soluble base (alkali)	NaOH(aq) or NH_3(aq)	heat released
insoluble metal oxide, hydroxide or carbonate	CuO(s), $Mg(OH)_2$(s) or $CaCO_3$(s)	solid dissolves*
soluble metal carbonate or metal hydrogencarbonate	Na_2CO_3(aq) or $NaHCO_3$(aq)	bubbles of gas*
active metal	Mg(s) or Zn(s)	bubbles of gas, metal dissolves*

*Heat may also be released.

Assessment tip

It is important to distinguish between changes at the molecular level and their macroscopic effects. If you are asked to state an observable change in the reaction between an acid and a carbonate, the answer "carbon dioxide forms" will score no marks, as we cannot visually distinguish carbon dioxide from any other colourless gas. A correct answer must refer to the bubbles of gas produced or, in the case of an insoluble carbonate, to the dissolution of the solid.

TOPIC 8.3 THE pH SCALE

You should know:

- ✔ pH = –log[H^+] and [H^+] = 10^{-pH};
- ✔ a change of one pH unit represents a tenfold change in [H^+];
- ✔ pH values distinguish between acidic, neutral and alkaline solutions;
- ✔ the ionic product of water, $K_w = [H^+][OH^-]$, is a constant equal to 1.00×10^{-14} at 298 K.

You should be able to:

- ✔ solve problems involving [H^+], [OH^-] and pH;
- ✔ explain the use of a pH meter and universal indicator.

- The **ionic product of water, K_w**, is the equilibrium constant for the dissociation of water:

  $K_w = [H^+][OH^-]$
- The concentration of water is included in the value for K_w.
- The **pH** scale describes acidity as the **potential of hydrogen**:

  pH = –log[H^+]

Assessment tip

The *potential of hydroxide* is similar to pH: pOH = –log[OH^-]. From the expression for K_w, it follows that at 25°C, pH + pOH = 14. You can use this expression in any pH calculation, although problems involving pOH appear only in higher level topic 18.2.

Assessment tip

Remember that each mole of sulfuric acid produces two moles of H^+(aq) ions. Similarly, one mole of a strong diprotic base, such as barium hydroxide, $Ba(OH)_2$, produces two moles of OH^-(aq) ions. You should always write the dissociation equation for an electrolyte before calculating the pH of its solution.

Another common error is the use of [OH^-] instead of [H^+] in pH calculations. If you obtain a numerical answer that seems unlikely (e.g., a pH < 7 for a basic solution), check your calculations once more.

Water is a weak electrolyte. Its dissociation is characterized by the *ionic product of water*, K_w:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = [H^+][OH^-]$$

In dilute solutions at room temperature (25°C), $K_w = 1.00 \times 10^{-14}$. Therefore, it is sufficient to know either [H^+] or [OH^-] in a solution, as the concentration of the other ion can be found from the K_w expression.

The acidity and basicity of solutions (table 8.3.1) over a broad range of H^+ and OH^- concentrations can be characterized by a single value, known as the *potential of hydrogen*, or pH:

$$pH = -\log[H^+]$$

Note that pH values are unitless.

Solution	[H^+] and [OH^-]	pH
acidic	$[H^+] > [OH^-]$	< 7
neutral	$[H^+] = [OH^-]$	7
basic	$[H^+] < [OH^-]$	> 7

▲ **Table 8.3.1.** Acidic, neutral and basic aqueous solutions at 25°C

Example 8.3.1.

Calculate the pH values for 0.0100 mol dm^{-3} solutions of sulfuric acid, H_2SO_4, and sodium hydroxide, NaOH.

Solution

Sulfuric acid: $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

$[H^+] = 2 \times [H_2SO_4] = 2 \times 0.0100 = 0.0200$ mol dm^{-3}

pH = –log(0.0200) ≈ 1.699

Sodium hydroxide: $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

$[OH^-] = [NaOH] = 0.0100$ mol dm^{-3}

$[H^+] \times [OH^-] = 1.00 \times 10^{-14}$

$$[H^+] = \frac{1.00 \times 10^{-14}}{0.0100} = 1.00 \times 10^{-12} \text{ mol dm}^{-3}$$

pH = –log(1.00×10^{-12}) = 12.000

The pH of a solution can be measured with a digital pH probe or estimated using universal indicator, which gradually changes colour across the whole pH range.

For a solution with known pH, the concentration of $H^+(aq)$ ions in mol dm^{-3} can be found by using the formula $[H^+] = 10^{-pH}$.

Example 8.3.2.

A solution of potassium hydroxide has a pH of 11.70. Calculate the concentration, in mol dm^{-3}, of potassium hydroxide in this solution.

Solution

$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$

$[H^+] = 10^{-11.70} \approx 2.0 \times 10^{-12}$ mol dm^{-3}

$$[OH^-] = \frac{1.00 \times 10^{-14}}{2.0 \times 10^{-12}} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$c(KOH) = [OH^-] = 5.0 \times 10^{-3}$ mol dm^{-3}

Assessment tip

The progress of an acid–base titration can be monitored with a pH probe connected to a data logger or computer. Alternatively, the equivalence point of the titration can be determined using an acid–base indicator (topic 18.3). You should be familiar with these techniques and be able to describe the purpose and practical details of typical titration experiments.

TOPIC 8.4 STRONG AND WEAK ACIDS AND BASES

You should know:

- ✔ strong and weak acids and bases differ in the extent of their ionization in aqueous solutions;
- ✔ a strong acid is a good proton donor and has a weak conjugate base;
- ✔ a strong base is a good proton acceptor and has a weak conjugate acid.

You should be able to:

- ✔ distinguish between strong and weak acids and bases in terms of the rates of their typical reactions and the electrical conductivities of their solutions.

Strong acids, such as hydrogen chloride, HCl, dissociate completely in aqueous solutions while weak acids, such as ethanoic acid, CH_3COOH, dissociate reversibly:

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

In addition to HCl, strong acids include sulfuric acid, H_2SO_4, nitric acid, HNO_3, perchloric acid, $HClO_4$, chloric acid, $HClO_3$, hydrogen bromide, HBr, and hydrogen iodide, HI. Almost all other acids are weak.

Strong bases include all hydroxides of Group 1 metals (Li to Cs) and some hydroxides of group 2 metals (Ca to Ba). All other bases are weak.

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

With the exception of sulfuric acid, all polyprotic acids are weak and dissociate stepwise. The second and following protons dissociate less than the first proton because the acid anion exerts a stronger electrostatic attraction for the next leaving $H^+(aq)$ cation.

Assessment tip

Strong acids and bases dissociate irreversibly, which is shown by the straight arrow (→) in equations. The dissociation schemes of weak acids and bases must include the equilibrium sign (⇌).

Assessment tip

The terms "strong" and "weak" refer to the nature of acids and bases but **not** to their concentrations. A solution of a strong acid can be dilute, while a solution of a weak acid can be concentrated. Colloquial expressions, such as "strong solution" or "weak solution", must never be used in examination answers.

Assessment tip

When the strengths of acids and bases are compared, the solutions used for pH, conductivity or reaction rate measurements must have equal concentrations. Many students lose marks by forgetting to mention this fact in examinations.

Enthalpies of neutralization and reaction rates are discussed in topics 5.1 and 6.1, respectively. The reactions of acids with active metals, oxides, carbonates and hydrogencarbonates are discussed in topics 8.2, 8.5 and D.4.

Example 8.4.1.

Deduce the scheme of the successive dissociation of phosphoric acid, H_3PO_4.

Solution

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

Note that equilibrium signs are used in all equations, as phosphoric acid is a weak acid.

Relative strengths of acids and bases can be determined experimentally by comparing the properties of their solutions of equal concentration. A solution of a strong acid will have a lower pH than a solution of a weak acid; a solution of a strong base will have a higher pH than a solution of a weak base. Both strong acids and strong bases have higher standard enthalpies of neutralization and produce solutions with higher electrical conductivities than weak acids and bases. Strong acids react with active metals, oxides, carbonates and hydrogencarbonates faster than weak acids.

Assessment tip

The electrical conductivities of solutions can be compared using a beaker with a pair of electrodes that form a series circuit with a battery and a light bulb. The bulb will glow brighter when the beaker contains a solution with more ions. For precise measurements, the bulb can be replaced with a digital ammeter. You should be able to describe the setting of a conductivity experiment and interpret its results.

TOPIC 8.5 ACID DEPOSITION

You should know:

- ✔ rain is naturally acidic and has a pH of approximately 5.6 because of dissolved CO_2, while acid deposition has a pH below 5.0;
- ✔ acid deposition is caused by oxides of nitrogen and sulfur that dissolve in water to form HNO_3, HNO_2, H_2SO_4 and H_2SO_3;
- ✔ acid deposition has natural and anthropogenic causes, and damages soil, forests and watercourses as well as buildings.

You should be able to:

- ✔ deduce and balance the equations for the combustion of sulfur and nitrogen and the subsequent formation of acids;
- ✔ distinguish between the pre-combustion and post-combustion methods of reducing emissions of sulfur oxides;
- ✔ deduce the equations for the reactions of acid deposition with reactive metals and carbonates.

Assessment tip

Remember that carbon dioxide is *not* responsible for acid deposition, as it cannot reduce the pH of rainwater below 5.0.

Rainwater is naturally acidic and has a pH of approximately 5.6 from the following processes:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Acid deposition commonly occurs in the form of acid rain, which has a significantly lower pH than normal rainwater (typically < 5.0). Acid rain forms when oxides of nitrogen and sulfur (table 8.5.1) react with rainwater:

$$2NO_2(g) + H_2O(l) \rightleftharpoons HNO_2(aq) + HNO_3(aq)$$

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

The acids produced in these reactions dissociate and form $H^+(aq)$ ions, which decrease the pH of rainwater.

Large quantities of sulfur dioxide are formed as a by-product of the combustion of fossil fuels (topic C.2).

Oxide	Source	
	Natural	**Anthropogenic**
NO	lightning strikes, biological processes	reaction of nitrogen with oxygen at high temperature in car or jet engines: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
NO_2	oxidation of NO in the atmosphere: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	
SO_2	volcanic eruptions, forest fires, biological processes	combustion of fossil fuels containing sulfur impurities: $S(s) + O_2(g) \rightarrow SO_2(g)$
SO_3	oxidation of SO_2 in the atmosphere: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	

▲ **Table 8.5.1.** Sources of oxides of nitrogen and sulfur

Acid rain can damage some stone, concrete and mortar in buildings, and works of art made of marble or limestone. The main component of these materials is calcium carbonate, $CaCO_3$, which reacts with acids in the rainwater, for example:

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$$

Other negative effects of acid deposition include damage to aquatic environments (such as lakes, rivers and wetlands), deforestation, reduced productivity of soil and corrosion of metals.

The emissions of sulfur oxides from power plants can be reduced by physical and chemical treatment of the fuels (pre-combustion) or their combustion products (post-combustion). Common pre-combustion methods include flotation (physical removal of elementary sulfur from coal) and hydrodesulfurization (chemical removal of sulfur from natural gas and oil). Post-combustion methods include alkaline scrubbing (chemical removal of sulfur and nitrogen oxides by their reactions with bases and water) and the use of catalytic converters in cars. Another technique, lime-injection fluidized bed combustion, permits capture of oxides of sulfur immediately after they are released by combustion of solid fuels.

Catalytic converters use palladium, platinum and other precious metals as heterogeneous catalysts (topic A.3).

Example 8.5.1.

Sulfur dioxide is a major cause of acid rain. Explain, using chemical equations, how lime, CaO, and limestone, $CaCO_3$, can be used to reduce sulfur dioxide emissions from coal power plants.

Solution

Coal contains traces of elementary sulfur, which forms sulfur dioxide upon combustion:

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

Both lime and limestone react with sulfur dioxide:

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$$

$$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g)$$

Calcium sulfite is non-volatile, so no sulfur is released into the atmosphere.

Note that the last two reactions can occur either during the combustion (when lime and limestone are added to coal) or after the combustion (when the combustion products are bubbled through a mixture of lime, limestone and water). In the second case, lime is converted first into calcium hydroxide, which reacts with sulfur dioxide:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

$$Ca(OH)_2(aq) + SO_2(g) \rightarrow CaSO_3(s) + H_2O(l)$$

Sulfur can be removed from combustion products with calcium oxide (lime). Lime is obtained by heating calcium carbonate to drive off carbon dioxide, which is released into the atmosphere. Thus, a solution to one problem—acid deposition—contributes to another—global warming.

SAMPLE STUDENT ANSWER

Outline, using an ionic equation, what is observed when magnesium powder is added to a solution of ammonium chloride. [2]

This answer could have achieved 1/2 marks:

Hydrogen is released:

$2NH_4^+ + Mg \rightarrow Mg^{2+} + 2NH_3 + H_2$

▼ Not accepted, as "hydrogen" is not an observable change—"gas" or "bubbles" would score the first mark

▲ Correct equation

SAMPLE STUDENT ANSWER

Suggest why the enthalpy change of neutralization of CH_3COOH is less negative than that of HCl. [2]

This answer could have achieved 1/2 marks:

Because CH_3COOH is a weaker acid than HCl, so it dissociates only partially, while HCl dissociates completely.

▲ Correct statement about the acid strength

▼ This is a two-mark question, so a further explanation is required; for example, "some of the energy released by neutralization is used to fully ionize CH_3COOH" would score the second mark

Practice problems for Topic 8

Problem 1

What occurs when solid calcium carbonate reacts with aqueous nitric acid?

A. Bubbles of nitrogen dioxide form.

B. Bubbles of carbon dioxide form.

C. Bubbles of hydrogen form.

D. Bubbles of both carbon dioxide and nitrogen dioxide form.

Problem 2

What is the ratio of $[H^+]$ in aqueous ammonia of pH 10 to $[H^+]$ in water at 298 K?

A. 4 : 7

B. 10 : 7

C. 1 : 10^3

D. 1 : 10^{10}

Problem 3

The hydrogencarbonate ion, HCO_3^-, participates in the following equilibria:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Identify **one** conjugate acid–base pair and **two** amphiprotic species in these reactions.

Problem 4

Barium hydroxide, $Ba(OH)_2$, is a strong base. State the equation for the dissociation of barium hydroxide and calculate the pH of its 2.00×10^{-3} mol dm^{-3} solution.

Problem 5

Acid deposition is responsible for accelerated corrosion of active metals. State the molecular and net ionic equations for the reaction of sulfuric acid from rainwater with zinc metal.

9

REDOX PROCESSES

TOPIC 9.1 OXIDATION AND REDUCTION

You should know:

- ✔ oxidation and reduction can be defined in terms of oxygen gain/hydrogen loss, electron transfer or change in oxidation state;
- ✔ transition metals and most main-group non-metals can have variable oxidation states;
- ✔ the activity series ranks metals according to the ease with which they undergo oxidation;
- ✔ the Winkler method uses biochemical oxygen demand (BOD) as a measure of the degree of pollution in a water sample.

You should be able to:

- ✔ deduce the oxidation state of an atom in an ion or compound;
- ✔ deduce the name of a transition metal compound from its formula;
- ✔ identify oxidized species, reduced species and oxidizing and reducing agents in redox reactions;
- ✔ deduce redox reactions using half-equations in acidic or neutral solutions;
- ✔ deduce the feasibility of a redox reaction from the activity series or reaction data;
- ✔ solve redox titration problems.

Redox (reduction–oxidation) reactions play a fundamental role in many chemical and biochemical processes.

Oxidation and reduction can be defined in several ways (table 9.1.1).

▼ Table 9.1.1. Definitions of oxidation and reduction

In terms of…	Oxidation	Reduction
oxygen/hydrogen gain/loss	gain of oxygen or loss of hydrogen	gain of hydrogen or loss of oxygen
oxidation state	increase in oxidation state	decrease in oxidation state
electron transfer	loss of electrons	gain of electrons

In a redox reaction, one species is oxidized by reacting with another, which is reduced. The species that is reduced is therefore an *oxidizing agent*, and the *reducing agent* is the species that is oxidized.

$$\underset{\substack{\text{oxidizing}\\\text{agent}}}{Cl_2(g)} + \underset{\substack{\text{reducing}\\\text{agent}}}{2I^-(aq)} \rightarrow \underset{\substack{\text{reduced}\\\text{(gained electrons)}}}{2Cl^-(aq)} + \underset{\substack{\text{oxidized}\\\text{(lost electrons)}}}{I_2(aq)}$$

- **Oxidation state**, also known as **oxidation number**, is the hypothetical charge that an atom would have if all its polar covalent bonds were ionic.
- An **oxidizing agent** increases the oxidation state of another species while being reduced itself.
- A **reducing agent** decreases the oxidation state of another species while being oxidized itself.

One example of a key redox process in the core syllabus is the oxidation of alcohols in topic 10.2.

Oxidation state

The rules for assigning oxidation states are as follows:

- The oxidation state of any atom in an elementary substance is 0.
- Group 1 metals always have a +1 oxidation state in ions and compounds.
- Group 2 elements always have a +2 oxidation state in ions and compounds.

- Aluminium, a member of group 3, has an oxidation state of +3 in most of its compounds.
- The oxidation state of hydrogen is +1 when hydrogen is bonded to a non-metal (e.g., in HCl), and −1 when it is bonded to a metal (e.g., in NaH).
- The oxidation state of oxygen is usually −2. The main exception are peroxides (species with an –O–O– linkage), in which the oxidation state of oxygen is −1.
- The oxidation state of fluorine is −1 in all its compounds. For the other group 17 elements (halogens), the oxidation state is usually −1 in binary compounds (HI, NaCl, KBr) but can be positive in oxides, oxoanions and oxoacids (e.g., chlorine in $HClO_4$ has a +7 oxidation state).
- In a neutral molecule the sum of the oxidation states of all the atoms is zero.
- In a polyatomic ion the sum of the oxidation states of all the atoms equals the overall charge on the ion.

Note that transition metals and main group non-metals can have variable oxidation states. These states are specified by Roman numerals. For example, $FeCl_3$ and SO_2 are called iron(III) chloride and sulfur(IV) oxide, respectively. There are also non-systematic names for oxoanions of main group non-metals, such as hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-).

Assessment tip

When writing oxidation states, the charge precedes the number. For example, the oxidation state of magnesium in $MgCO_3$ is +2, not 2+. This is a common error seen in answers to exam questions.

The common oxidation states of transition metals are listed in section 14 of the data booklet.

Some oxoanions and their non-systematic names are listed in topic 4.1.

Section 5 of the data booklet gives the names of the elements in the periodic table.

Example 9.1.1.

Deduce the names of the transition metal compounds CuO and $Co(NO_3)_3$.

Solution

To deduce the names of transition metal complexes you first need to work out the oxidation state of the transition metal. Let x be the oxidation state:

CuO: $x + (-2) = 0$, so $x = +2$.

$Co(NO_3)_3$: $x + 3 \times (-1) = 0$, so $x = +3$

The names are therefore copper(II) oxide and cobalt(III) nitrate.

Assessment tip

The answer "copper oxide" would not get any credit, as it could apply to both Cu_2O (copper(I) oxide) and CuO (copper(II) oxide).

The activity series

The activity series ranks metals in order of the ease with which they undergo oxidation, and enables us to predict whether redox reactions will occur. More reactive elements will displace less reactive elements from their compounds, for example:

$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$

The activity series is given in section 25 of the data booklet.

Half-equations

A half-equation is an equation that includes electrons and describes either the oxidation or reduction process for the overall redox reaction. For example, the reaction of iron metal with copper(II) sulfate (see above) can be represented by the following two half-equations:

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ oxidation
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ reduction

Example 9.1.2.

a) Deduce the balanced redox equation in an acidic solution for the reaction of copper metal, Cu(s), with nitrate ions, $NO_3^-(aq)$, to give copper(II) ions, $Cu^{2+}(aq)$, and nitrogen dioxide, $NO_2(g)$.

b) Identify the oxidizing and reducing agents.

Solution

a)

Step 1: Deduce the oxidation states for all atoms present in each species.

Cu(s): 0 (since copper is an elementary substance)

$NO_3^-(aq)$: −2 for oxygen; $x + 3 \times (-2) = -1$, so $x = +5$ for nitrogen

$Cu^{2+}(aq)$: +2

$NO_2(g)$: −2 for oxygen; $x + 2 \times (-2) = 0$, so $x = +4$ for nitrogen

Step 2: Deduce which species is oxidized and which species is reduced.

N is reduced from +5 to +4 (decrease in oxidation state)

Cu is oxidized from 0 to +2 (increase in oxidation state)

There is no change in the oxidation state for oxygen.

Step 3: Formulate half-equations for the oxidation and reduction processes:

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Reduction: $NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

Note that $H^+(aq)$ ions and water are used to balance half-equations in acidic solutions.

Step 4: Balance the half-equations so that the number of electrons lost equals the number of electrons gained:

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Reduction: $2NO_3^-(aq) + 4H^+(aq) + 2e^- \rightarrow 2NO_2(g) + 2H_2O(l)$

Step 5: Add the half-equations to give the overall equation:

$$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$$

b) Oxidizing agent (undergoes reduction): nitrate ions, $NO_3^-(aq)$
Reducing agent (undergoes oxidation): copper metal, Cu(s)

Assessment tip

Note that the oxidizing agent is the nitrate ion, $NO_3^-(aq)$. No marks would be awarded for the answers "nitrogen" or "N".

Redox titrations

Titrations involving redox reactions require the same types of calculations as acid–base titrations, starting from the balanced equation. If you do not know the equation, you can work it out using the method based on half-equations above.

Acid–base titrations are discussed in topics 1.3 and 18.3.

The half-equations for some reagents typically used in redox titrations are given below.

manganate(VII) ions (oxidizing agent):

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

dichromate(VI) ions (oxidizing agent):

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

thiosulfate ions (reducing agent): $2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$

Assessment tip

Manganate(VII) ions, MnO_4^-, are also known as permanganate ions.

- **Biochemical oxygen demand (BOD)** is the amount of oxygen required to oxidize organic matter in a sample of water at a specified temperature over a period of five days.
- The **Winkler method** measures the BOD of water by redox titration.

The *Winkler method* uses thiosulfate ions in a redox reaction to measure the amount of dissolved oxygen in water (see practice problem 2). Since oxygen in water is used by microorganisms to break down (oxidize) waterborne organic pollutants, the *biochemical oxygen demand (BOD)* acts as a measure of the degree of pollution in a water sample. A high concentration of dissolved oxygen implies a low BOD, which means low pollution levels. The more pollutants are present, the more bacteria thrive and use oxygen, so the higher the demand becomes.

TOPIC 9.2 ELECTROCHEMICAL CELLS

You should know:

- ✔ in electrochemical cells, reduction always occurs at the cathode and oxidation at the anode;
- ✔ in voltaic cells, chemical energy released by spontaneous reactions is converted to electrical energy;
- ✔ in electrolytic cells, electrical energy is converted to chemical energy by driving non-spontaneous reactions.

You should be able to:

- ✔ construct and annotate voltaic and electrolytic cells;
- ✔ explain how a redox reaction is used to produce electricity in a voltaic cell and how current is conducted in an electrolytic cell;
- ✔ distinguish between electron flow and ion flow in an electrochemical cell;
- ✔ write a one-line cell diagram notation for a voltaic cell;
- ✔ deduce the products of the electrolysis of a molten salt.

There are two types of electrochemical cells—voltaic cells, which convert chemical energy to electrical energy (in a spontaneous process), and electrolytic cells, which convert electrical energy to chemical energy (in a non-spontaneous process).

Voltaic cells

In voltaic (galvanic) cells, the two parts of a redox reaction – the oxidation and reduction processes – occur in two separate half-cells, each containing an electrode and an electrolyte solution. The electrodes are linked together by a wire, and the solutions by a salt bridge (through which ions move) to complete the circuit. This separation prevents the spontaneous reaction from occurring in one half-cell and instead forces the electrons to travel along the wire. There may be a voltmeter or a light bulb in the circuit if the cell supplies electrical energy. Commercial batteries are voltaic cells.

In all electrochemical cells, reduction occurs at the cathode, and oxidation at the anode. In voltaic cells, a spontaneous redox reaction occurs, so in the half-cell where reduction occurs, the species that is reduced withdraws electrons from the electrode; in other words, the cathode is positive, and the anode is negative (figure 9.2.1).

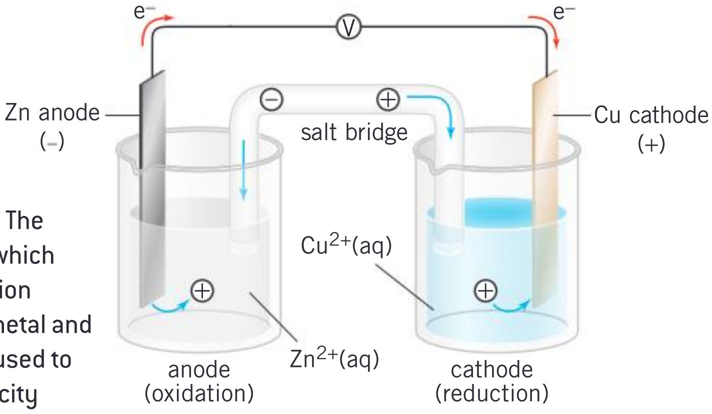


Figure 9.2.1. The Daniell cell, in which the redox reaction between zinc metal and copper ions is used to produce electricity

Cell diagram notation provides a quick way to represent a voltaic cell in a single line. The salt bridge is represented by two vertical lines, ||, and each phase boundary by a single vertical line, |. By convention, the cathode is always written on the right-hand side. For example, the cell diagram for the Daniell cell in figure 9.2.1 is written as follows:

$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

In fuel cells, a fuel that would normally be combusted in air is instead oxidized in a voltaic cell, so that a large proportion of the energy is released in the form of electricity rather than heat. One example is the hydrogen–oxygen fuel cell, in an acidic electrolyte:

Oxidation: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Overall: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Assessment tip

The command term “annotate” is often used in examination questions. It means that you should add appropriate labels to a diagram or graph. In drawing electrochemical cells, make sure that you label all relevant parts on the diagram, including the anode, the cathode and the direction of electron flow.

Fuel cells are discussed in more detail in option C.6.

Electrolytic cells

Electrolytic cells use an external source of electrical energy to drive non-spontaneous redox reactions. In electrolytic cells the cathode is negative and the anode is positive.

Electrolysis can be used to extract metals from their salts (example 9.2.1).

Example 9.2.1.

Lead can be produced by the electrolysis of molten lead(II) bromide, $PbBr_2$.

a) Explain how molten lead bromide conducts electric current.

b) Identify the electrodes at which oxidation and reduction occur during the electrolysis.

c) State a half-equation for the reaction occurring at each electrode.

d) Deduce the overall cell reaction.

e) Outline what you would observe during the electrolysis.

f) Suggest why this experiment might not be suitable for a school laboratory.

Solution

a) Molten lead bromide, $PbBr_2$, contains ions that are free to move *only* in the molten state. The Pb^{2+} ions are positive so will move towards the negative electrode (the cathode, in an electrolytic cell). The Br^- ions are negative so will move towards the positive electrode (the anode).

b) Reduction in any electrochemical cell takes place at the cathode and oxidation at the anode.

c) Reduction: $Pb^{2+} + 2e^- \rightarrow Pb(l)$

Oxidation: $2Br^- \rightarrow Br_2(g) + 2e^-$

d) Overall cell reaction: $PbBr_2(l) \rightarrow Pb(l) + Br_2(g)$

e) A silvery-grey molten metal, Pb(l), will form at the cathode, and a brown gas will form at the anode, $Br_2(g)$. The characteristic odour of bromine gas will be noticeable.

f) The reaction should be done in a fume cupboard as bromine is both corrosive and toxic. Lead(II) bromide is also toxic.

SAMPLE STUDENT ANSWER

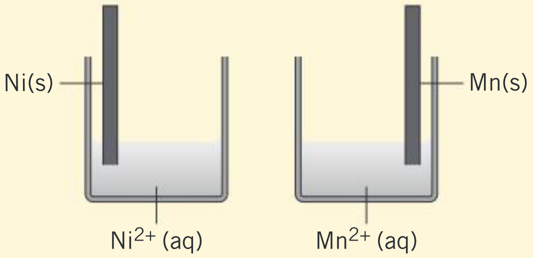
The activity series lists the metals in order of reactivity.

Mn	↑	**most reactive**
Ni		
Ag		**least reactive**

a) Identify the strongest reducing agent in the given list. [1]

b) A voltaic cell is made up of a $Mn^{2+}|Mn$ half-cell and a $Ni^{2+}|$ Ni half-cell. Deduce the equation for the cell reaction. [1]

c) The voltaic cell stated in part (b) is partially shown below. Draw and label the connections needed to show the direction of electron movement and ion flow between the two half-cells. [2]



This answer could have achieved 2/4 marks:

(a) Ag

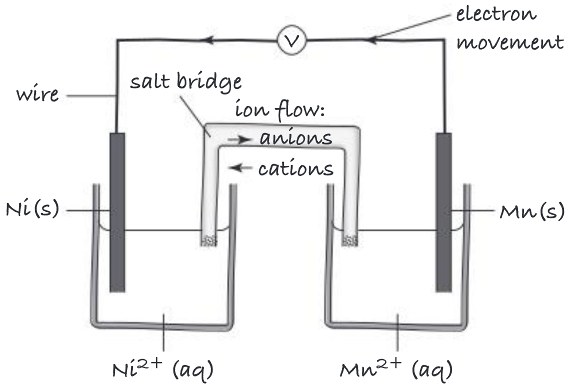
Mn is oxidized most easily here, and therefore is the strongest reducing agent

(b) $Ni(s) + Mn^{2+}(aq) \rightleftharpoons Mn(s) + Ni^{2+}(aq)$

This equation is the wrong way round and the arrow should not be reversible—as Mn is above Ni in the activity series, Mn will undergo oxidation and Ni^{2+} will be reduced:

$Mn(s) + Ni^{2+}(aq) \rightarrow Ni(s) + Mn^{2+}(aq)$

(c)



A perfect answer, with all the key parts of the voltaic cell labelled correctly

Practice problems for Topic 9

Problem 1

Deduce the names of the following compounds: MnO_2, $Fe(OH)_2$, $Cr_2(SO_4)_3$.

Problem 2

The Winkler method uses redox reactions to determine the concentration of oxygen present in water. A 0.100 dm^3 water sample was taken from a river and analysed using this method. The reactions taking place are summarized as follows:

Step 1:

$2Mn^{2+}(aq) + 4OH^-(aq) + O_2(aq) \rightarrow 2MnO_2(s) + 2H_2O(l)$

Step 2:

$MnO_2(s) + 2I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O(l)$

Step 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

a) Identify the oxidizing and reducing agents in each step.

b) 0.00150 mol of $I^-(aq)$ formed in step 3. Calculate the amount, in mol, of oxygen, $O_2(aq)$, dissolved in the water sample.

Problem 3

The following reactions occur spontaneously.

$Fe(s) + NiCl_2(aq) \rightarrow FeCl_2(aq) + Ni(s)$

$Zn(s) + FeCl_2(aq) \rightarrow ZnCl_2(aq) + Fe(s)$

$Ni(s) + PbCl_2(aq) \rightarrow NiCl_2(aq) + Pb(s)$

What is the **increasing** order of the reactivity of the metals?

A. Fe < Ni < Zn < Pb
B. Pb < Ni < Fe < Zn
C. Ni < Zn < Pb < Fe
D. Zn < Fe < Ni < Pb

Problem 4

Zinc can be produced by the electrolysis of molten zinc chloride, $ZnCl_2$.

a) Explain how molten zinc chloride conducts electric current.

b) Identify the electrodes at which oxidation and reduction occur during the electrolysis.

c) State a half-equation for the reaction occurring at each electrode.

d) Deduce the overall cell reaction.

e) Outline what you would observe during the electrolysis.

10 ORGANIC CHEMISTRY

TOPIC 10.1 FUNDAMENTALS OF ORGANIC CHEMISTRY

You should know:

- ✔ functional groups are the reactive parts of molecules;
- ✔ compounds in a homologous series have the same general formula but differ from each other by one or more CH_2 groups;
- ✔ structural formulas can be full or condensed;
- ✔ structural isomers have the same molecular formula but different arrangements of atoms;
- ✔ saturated compounds contain single bonds only while unsaturated compounds contain double and/or triple bonds;
- ✔ benzene is an unsaturated, aromatic hydrocarbon.

You should be able to:

- ✔ explain the trends in boiling points within a homologous series;
- ✔ distinguish between empirical, molecular and structural formulas;
- ✔ construct 3D models of organic molecules;
- ✔ identify different functional groups and classes of organic compounds;
- ✔ apply IUPAC rules for naming straight-chain and branched molecules;
- ✔ identify primary, secondary and tertiary carbon and nitrogen atoms;
- ✔ discuss the structure of benzene using physical and chemical evidence.

Organic compounds are all substances containing carbon atoms except elementary carbon, its oxides, carbonic acid, carbonates, carbides and cyanides. Topic 10: Organic chemistry covers the classification, nomenclature, structures and properties of organic compounds.

Empirical and molecular formulas are discussed in topic 1.2.

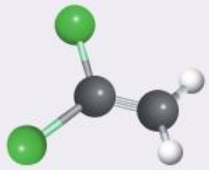
- An **empirical formula** shows the simplest integer ratio of atoms in a chemical substance.
- A **molecular formula** shows the exact number of atoms of each kind in the molecule.
- A **full structural formula** shows all atoms and all covalent bonds in the molecule.
- A **condensed structural formula** shows all atoms but omits single covalent bonds, with all monovalent substituents grouped together. Double and triple bonds are shown optionally.

Depicting organic compounds

Carbon is a group 14 non-metal with four electrons in its outer energy level. In all organic compounds, carbon is tetravalent. The elemental composition of organic compounds is represented by *empirical* and *molecular formulas*, while the bonding order of atoms is shown by *structural formulas*. Three-dimensional shapes of molecules are visualized by 3D models.

Example 10.1.1.

1,1-Dichloroethene, shown on the right, was widely used in the 1990s for making cling film and other food packaging.



a) State the molecular and empirical formulas for 1,1-dichloroethene.

b) Draw the skeletal, full and condensed structural formulas for this compound.

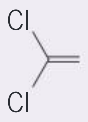
Solution

a) Molecular formula — Empirical formula

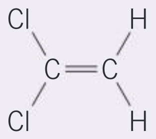
$C_2H_2Cl_2$ — CHCl

Note that the molecular formula shows the actual number of each atom in the molecule, while the empirical formula does not.

b) Skeletal formula



Full structural formula



Condensed formula

$Cl_2C{=}CH_2$

or

Cl_2CCH_2

Note that the double bond in a condensed formula is optional, so there are two possible answers.

Classifying organic compounds

Organic compounds are divided into classes according to functional groups or unsaturations in their molecules (tables 10.1.1–10.1.3). Double and triple carbon–carbon bonds, aromatic (benzene) rings and halogen atoms can also be treated as functional groups.

Alkanes have no functional groups.

n	Alkane (C_nH_{2n+2})		Alkyl substituent (C_nH_{2n+1})	
	Name	**Formula**	**Name**	**Formula**
1	methane	CH_4	methyl	$-CH_3$
2	ethane	CH_3CH_3	ethyl	$-CH_2CH_3$ or $-C_2H_5$
3	propane	$CH_3CH_2CH_3$	propyl	$-CH_2CH_2CH_3$
			isopropyl	$-CH(CH_3)_2$
4	butane	$CH_3(CH_2)_2CH_3$	butyl	$-CH_2(CH_2)_2CH_3$
5	pentane	$CH_3(CH_2)_3CH_3$	pentyl	$-CH_2(CH_2)_3CH_3$
6	hexane	$CH_3(CH_2)_4CH_3$	hexyl	$-CH_2(CH_2)_4CH_3$

▲ Table 10.1.1. Alkanes and alkyl substituents

n	Alkene (C_nH_{2n})		Alkyne (C_nH_{2n-2})	
	Name	**Formula**	**Name**	**Formula**
2	ethene	$H_2C{=}CH_2$	ethyne	$HC{\equiv}CH$
3	propene	$H_2C{=}CHCH_3$	propyne	$HC{\equiv}CCH_3$
4	but-1-ene	$H_2C{=}CHCH_2CH_3$	but-1-yne	$HC{\equiv}CCH_2CH_3$
5	pent-1-ene	$H_2C{=}CH(CH_2)_2CH_3$	pent-1-yne	$HC{\equiv}C(CH_2)_2CH_3$
6	hex-1-ene	$H_2C{=}CH(CH_2)_3CH_3$	hex-1-yne	$HC{\equiv}C(CH_2)_3CH_3$

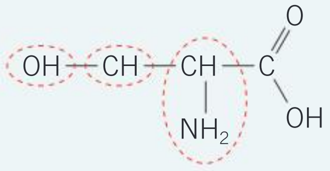
▲ Table 10.1.2. Alkenes and alkynes

- A **skeletal formula** shows all covalent bonds as lines but omits carbon atoms and any hydrogen atoms attached to carbon atoms.
- **Semi-condensed formulas** are intermediate between full and condensed. In such formulas, the carbon and hydrogen atoms are omitted in rings but shown in side chains, with monovalent substituents grouped together.

Examples of semi-condensed structural formulas are given in sections 35 and 37 of the data booklet.

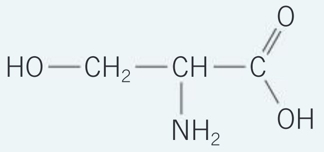
Assessment tip

Missing hydrogen atoms and incorrectly drawn bonds in structural formulas are the two most common errors in organic chemistry in examinations. Double-check all formulas you write: make sure that each carbon atom forms four covalent bonds, and each covalent bond connects to the correct atom.



✗ incorrect

The semi-condensed formula above will score no marks, as one hydrogen atom is missing, one covalent bond points at a hydrogen atom of the OH group (instead of oxygen) and another covalent bond points between two pairs of atoms (instead of C and N).



✓ correct

▼ Table 10.1.3. Common functional groups in decreasing order of priority

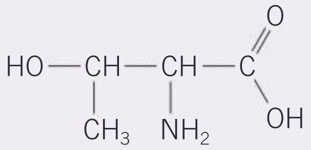
Class name	Functional group				Example	
	Name	**Formula**	**Prefix**	**Suffix**	**Formula**	**Name**
carboxylic acid	carboxyl	$-COOH$	—*	-oic acid	CH_3COOH	ethanoic acid
ester	ester	$-COOR$	—*	-oate	CH_3COOCH_3	methyl ethanoate
amide	amido	$-CONH_2$**	—*	-amide	CH_3CONH_2	ethanamide
nitrile	cyano	$-C{\equiv}N$	cyano-	-nitrile	CH_3CN	methanenitrile
aldehyde	carbonyl	$-CHO$	oxo-	-al	CH_3CHO	ethanal
ketone		$-C(O)-$		-one	$CH_3C(O)CH_3$	propanone
alcohol	hydroxyl	$-OH$	hydroxy-	-ol	CH_3CH_2OH	ethanol
amine	amino	$-NH_2$**	amino-	-amine	$CH_3CH_2NH_2$	ethanamine
ether	ether	$-OR$	R-oxy-	—	$CH_3CH_2OCH_3$	methoxyethane

Hydrocarbon substituents are denoted as R.
*Not required for the IB Chemistry Diploma Programme.
**Substitution of hydrogen atoms in this group by R does not affect the class or group name.

Common substituents not listed in tables 10.1.1 and 10.1.3 include fluoro ($-F$), chloro ($-Cl$), bromo ($-Br$), iodo ($-I$) and phenyl ($-C_6H_5$) groups. These substituents form prefixes only.

Example 10.1.2.

Threonine, a component of proteins, has the following structure:



a) Identify the class name of threonine.

b) State the names of **three** functional groups that are present in the molecule.

Solution

a) Class name: carboxylic acid.

Note that the senior group (the one highest in table 10.1.3) determines the class name. The answer "amino acid" would also be accepted here.

b) Three functional groups: carboxyl ($-COOH$), amino ($-NH_2$) and hydroxyl ($-OH$).

Assessment tip

Note that "methyl" is not a functional group, so is not a correct answer to (b). "Carbonyl" will not be accepted either, as the C=O fragment in this compound is a part of a more complex group, $-COOH$. The answers "carboxylic acid", "amine" and "alcohol" are incorrect, as they are class names, not group names (see table 10.1.3).

Compounds of each class form a homologous series with a specific general formula, such as C_nH_{2n+2} for alkanes. Homologues have similar structures that differ by one or more CH_2 groups. Their chemical properties are also similar, while their melting and boiling points gradually increase with the chain length as London (dispersion) forces between molecules increase.

In compounds with similar molecular masses from different classes, the melting and boiling points generally increase in the following order: hydrocarbon < aldehyde ≈ ketone ≈ ester ≈ ether < alcohol < carboxylic acid. The differences are a result of different intermolecular forces (only London in hydrocarbons, dipole–dipole too in aldehydes, ketones, esters and ethers, and hydrogen bonding too in alcohols and acids).

Isomers

Structural isomers have the same molecular formula but different structural formulas. Isomers can belong to the same or different classes of organic compounds and thus might differ in both chemical and physical properties.

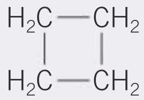
Intermolecular forces are discussed in topic 4.4.

Example 10.1.3.

Butane, cyclobutane and but-1-ene are members of different homologous series.

a) Draw the structures of **one** isomer of butane and **one** homologue of but-1-ene.

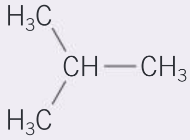
b) Cyclobutane has the following structure:



State, with a reason, the relationship between cyclobutane and but-1-ene.

Solution

a) One isomer of butane: One homologue of but-1-ene



$H_2C{=}CH_2$

Any other straight-chain alkene would also be a valid homologue of but-1-ene. Note that a homologue can have more or fewer CH_2 groups than the original compound.

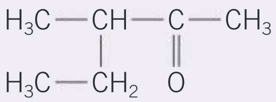
b) They are structural isomers because they have the same molecular formula, C_4H_8.

Naming organic compounds

Each organic compound has a unique IUPAC name, which is constructed systematically. The stem of an IUPAC name specifies the length and saturation of the primary chain. Functional groups are ranked as shown in table 10.1.3, with the most senior group forming the suffix in the IUPAC name. Subordinate functional groups and substituents form prefixes, which are listed alphabetically. The principal chain is numbered from one end to the other to give the lowest possible number to the senior functional group or, if it is absent, to the first substituent.

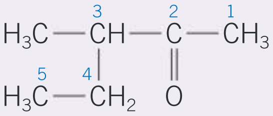
Example 10.1.4.

Deduce the IUPAC name of the following compound.



Solution

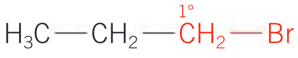
This compound is a ketone (table 10.1.3), so the suffix in the IUPAC name will be "-one". The longest chain is saturated and consists of five carbon atoms, so the stem will be "pentan" (see table 10.1.1). Now we need to number this chain from the end closest to the functional group (C=O):



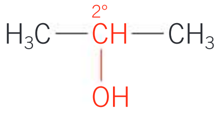
The position of the functional group in the chain must be specified by the number (*locant*) before the last suffix ("-2-one"). There is also a substituent (methyl) at position 3, which will form the prefix "3-methyl". Now we can assemble the full IUPAC name (prefix + stem + suffix):

"3-methyl" + "pentan" + "-2-one" = 3-methylpentan-2-one

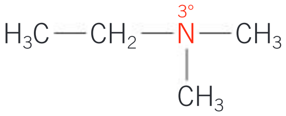
Halogenoalkanes and alcohols can be classified as *primary* (1°), *secondary* (2°) and *tertiary* (3°) according to the number of carbon atoms bonded directly to the carbon with a halogen or hydroxyl group. Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom:



primary halogenoalkane



secondary alcohol



tertiary amine

Example 10.1.5.

Which compound contains a secondary carbon atom?

A. CH_3CH_2OH

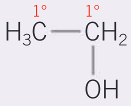
B. $(CH_3)_3COH$

C. $(CH_3)_2CHCH(OH)CH_3$

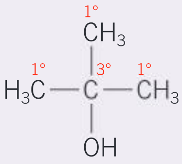
D. $(CH_3)_2CHCH_2OH$

Solution

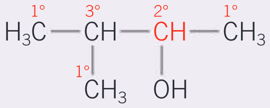
It is a good idea to draw the structural formulas of all four compounds:



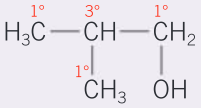
A



B



C

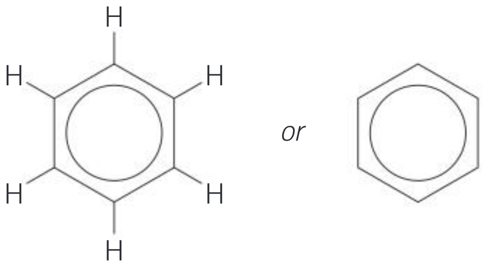


D

The correct answer is **C**, as only this compound contains a carbon atom that is bonded to two other carbon atoms. Note that **A** and **D** are primary alcohols, **C** is a secondary alcohol, and **B** is a tertiary alcohol.

Aromatic compounds

Benzene (C_6H_6) is the simplest arene, or aromatic hydrocarbon. Each carbon atom in benzene forms three localized bonds with its neighbours and donates its fourth outer electron to a common π-electron cloud that surrounds all carbon atoms in the aromatic ring. This increases the order of each carbon–carbon bond from 1 to 1.5. Therefore, the structure of benzene is commonly represented by a six-membered ring with a circle inside:



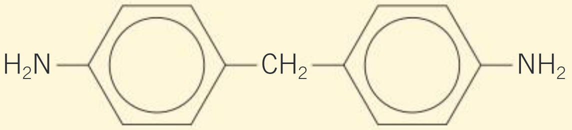
The equivalence of carbon–carbon bonds in benzene is supported by physical and chemical evidence (table 10.1.4). The reactions of alkenes and aromatic compounds are introduced in topic 10.2.

Technique	**Type of data**	**Observation**
X-ray crystallography	carbon–carbon bond length C–C–C bond angle	identical for all six bonds identical for all six atoms
^{1}H NMR spectroscopy	signals of CH groups in alkenes	one singlet
IR spectroscopy	absorptions of C=C bonds in alkenes	absent
analytical chemistry	bromine test	negative
synthetic chemistry	addition reactions substitution reactions number of disubstituted isomers	uncommon proceed readily three

▲ **Table 10.1.4.** Evidence for the structure of benzene

SAMPLE STUDENT ANSWER

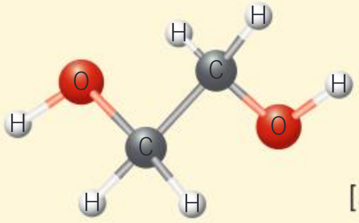
a) One important industrial use of phosgene is in the production of polyurethanes. Phosgene is reacted with diamine X, derived from phenylamine.



Classify diamine X as a primary, secondary or tertiary amine. [1]

b) The other monomer used in the production of polyurethane is compound Z, shown on the right.

State the name, applying IUPAC rules, of compound Z and the class of compounds to which it belongs. [2]



This answer could have achieved 2/3 marks:

a) Primary.

b) Name: ethane-1,2-diol.

Class: diol.

▲ Correct, as each NH_2 group in X is bonded to only one carbon atom

▲ Correct IUPAC name

▼ "diol" is the part of the IUPAC name that refers to two hydroxyl groups in Z; the class name of Z is "alcohol"

TOPIC 10.2 FUNCTIONAL GROUP CHEMISTRY

You should know:

- ✔ alkanes have low reactivity and undergo radical substitution reactions;
- ✔ alkenes are more reactive than alkanes and undergo addition reactions;
- ✔ bromine water is used to distinguish between alkanes and alkenes;
- ✔ alcohols undergo nucleophilic substitution reactions with acids (also called esterification or condensation) and some undergo oxidation reactions;
- ✔ halogenoalkanes are more reactive than alkanes, and undergo nucleophilic substitution reactions;
- ✔ addition polymers are made from monomers and form the basis of the plastics industry;
- ✔ benzene does not readily undergo addition reactions but does undergo electrophilic substitution reactions.

You should be able to:

- ✔ write equations for the complete and incomplete combustion of hydrocarbons and alcohols;
- ✔ explain the radical substitution reactions of alkanes with halogens;
- ✔ write equations for the reactions of alkenes with hydrogen, halogens, hydrogen halides and water;
- ✔ outline the addition polymerization of alkenes;
- ✔ describe the relationship between monomers, polymers and repeating units;
- ✔ write equations for the oxidation of primary and secondary alcohols;
- ✔ explain the use of distillation and refluxing for the isolation of aldehydes and carboxylic acids from the oxidation of alcohols;
- ✔ write equations for the condensation reactions of alcohols with carboxylic acids;
- ✔ write equations for the substitution reactions of halogenoalkanes with sodium hydroxide.

Combustion

All organic compounds undergo complete combustion, producing carbon dioxide and water. Amines, amides and nitriles also produce molecular nitrogen. Incomplete combustion can produce carbon monoxide or elementary carbon (soot) instead of carbon dioxide.

Example 10.2.1.

Formulate the equations for complete and incomplete combustion of propene.

Solution

Complete combustion:

$$2C_3H_6(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Incomplete combustion:

$$C_3H_6(g) + 3O_2(g) \rightarrow 3CO(g) + 3H_2O(l)$$

or

$$2C_3H_6(g) + 3O_2(g) \rightarrow 6C(s) + 6H_2O(l)$$

- A **radical**, formerly known as **free radical**, is a reactive species (atom, molecule or ion) with an unpaired valence electron.
- In a **substitution reaction** one atom or group in a molecule is replaced by another.

Alkanes: Radical substitution

Alkanes undergo *radical substitution* (S_R) reactions with halogens. These reactions are catalysed by ultraviolet (UV) light and involve initiation, propagation and termination steps.

The reaction products, halogenoalkanes, react with dilute aqueous solutions of alkalis to produce alcohols.

Example 10.2.2.

Halogenation of methane can occur at low temperatures.

a) Formulate the equation for the reaction of one mole of methane with one mole of chlorine.

b) Outline the mechanism of this reaction.

c) The organic product of this reaction can be converted into an alcohol in one step. Suggest a suitable reagent and deduce the equation for this process.

Solution

a) $CH_4(g) + Cl_2(g) \xrightarrow{hv} CH_3Cl(g) + HCl(g)$

Note that the symbol "*hv*" over the reaction arrow refers to UV light, which is required to initiate the reaction. "Sunlight" is an acceptable alternative to "UV light".

b) Initiation:

$Cl_2(g) \xrightarrow{hv} 2Cl\bullet(g)$

Chain propagation:

$CH_4(g) + Cl\bullet(g) \rightarrow H_3C\bullet(g) + HCl(g)$
$H_3C\bullet(g) + Cl_2(g) \rightarrow CH_3Cl(g) + Cl\bullet(g)$

Chain termination:

$H_3C\bullet(g) + Cl\bullet(g) \rightarrow CH_3Cl(g)$
$2Cl\bullet(g) \rightarrow Cl_2(g)$
$2H_3C\bullet(g) \rightarrow C_2H_6(g)$

Note that the combination of two alkyl radicals produces a new alkane (in this case, ethane) with twice as many carbon atoms as that in the original molecule. Halogenation of ethane under similar conditions would produce butane.

c) Reagent for conversion into an alcohol:

A dilute aqueous solution of sodium hydroxide (or any other strong base).

Equation:

$CH_3Cl(g) + NaOH(aq) \rightarrow CH_3OH(aq) + NaCl(aq)$

or

$CH_3Cl(g) + OH^-(aq) \rightarrow CH_3OH(aq) + Cl^-(aq)$

Alkenes: Electrophilic addition

Alkenes undergo *electrophilic addition* (A_E) reactions with halogens even in the absence of UV light, for example:

$H_2C{=}CH_2(g) + Br_2(aq) \longrightarrow BrCH_2CH_2Br(l)$

orange-brown colourless

The bromine test (decolorization of aqueous bromine) is used for distinguishing alkenes and alkanes. Other A_E reactions of alkenes include hydrogenation, hydrohalogenation and hydration:

$H_2C{=}CH_2(g) + H_2(g) \xrightarrow{Ni} CH_3CH_3(g)$

$H_2C{=}CH_2(g) + HBr(aq) \longrightarrow CH_3CH_2Br(l)$

$H_2C{=}CH_2(g) + H_2O(l) \xrightarrow{H^+} CH_3CH_2OH(aq)$

Hydrogenation of alkenes is catalysed by transition metals (such as Ni or Pt) and requires high temperature and pressure. Hydrohalogenation does not require a catalyst. Hydration proceeds in the presence of concentrated inorganic acids, such as H_3PO_4 or H_2SO_4.

Addition polymerization of alkenes (the *monomers*) is catalysed by radicals or salts of transition metals and proceeds at high temperatures, producing *macromolecules* with many *repeating units*. The structure of a *polymer* can be written as a condensed formula, which must include square brackets around the repeating unit, continuation bonds (which must cross the brackets) and the degree of polymerization (*n*):

ethene (monomer) polyethene (polymer)

The use of fossil fuels and chlorinated solvents has ethical, economic and environmental implications (see the links below).

Alkanes are major components of fossil fuels (topic C.2), which produce carbon dioxide upon combustion and thus contribute to global warming (topic C.5). Methane itself is a common greenhouse gas (topic C.5). Chlorinated organic compounds are ozone-depleting agents (topic 14.1).

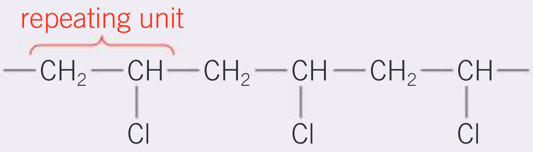
- An **electrophile** is an electron-deficient species that is attracted to an electron-rich centre, such as a negatively charged carbon atom or a carbon–carbon double bond.
- A **nucleophile** is an electron-rich species containing a lone electron pair that it donates to an electrophile.

- A **polymer**, or **macromolecule**, is a large molecule composed of many **repeating units** connected to one another by covalent bonds.
- **Addition polymerization** produces macromolecules from unsaturated **monomers** with no by-products.

Example 10.2.3.

Chloroethene (C_2H_3Cl), also known as vinyl chloride, is used as a monomer in the production of polyvinylchloride (PVC). Draw a section of PVC with three repeating units.

Solution



$$-\overbrace{CH_2-CH}^{\text{repeating unit}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

Note that the continuation bonds are required for the mark.

Other reactions of alkenes and their mechanisms are discussed in topic 20.1. Polymers and polymer-based materials are discussed in topic A.5.

Arenes: Electrophilic substitution

Typical reactions of benzene and other arenes, or aromatic compounds, include *electrophilic substitution* (S_E), such as halogenation and nitration:

$$C_6H_6(l) + Br_2(org) \xrightarrow{FeBr_3} C_6H_5Br(l) + HBr(org)$$

$$C_6H_6(l) + HNO_3(conc.) \xrightarrow{H_2SO_4} C_6H_5NO_2(l) + H_2O(l)$$

The halogenation of benzene is catalysed by Lewis acids and requires anhydrous conditions (hence the state symbol “org”, which means an organic solvent). The nitration proceeds in the presence of concentrated sulfuric acid.

Lewis acids are discussed in topic 18.1. The mechanism of substitution in benzene and other aromatic compounds is discussed in topic 20.1.

Alcohols: Oxidation and nucleophilic substitution

Alcohols undergo oxidation and condensation (nucleophilic substitution) reactions.

Primary alcohols are oxidized by acidified potassium dichromate stepwise, producing first aldehydes and then carboxylic acids:

$$CH_3CH_2OH(aq) \xrightarrow{[O]} CH_3CHO(aq) \xrightarrow{[O]} CH_3COOH(aq)$$

The aldehyde can be isolated by *distillation* using excess alcohol. The acid is obtained by heating the reaction mixture *under reflux* and using excess oxidizing agent.

- **Distillation** is the evaporation of a volatile substance with subsequent condensation of its vapour and collection of the resulting liquid.
- **Heating under reflux** involves condensation of vapour and its return to the reaction mixture. This technique permits volatile substances to be heated with other reactants at their boiling point for long periods.

Secondary alcohols are oxidized to ketones, which do not undergo further oxidation:

$$(CH_3)_2CHOH(aq) \xrightarrow{[O]} (CH_3)_2C{=}O$$

In all cases, the reaction mixture changes colour from orange to green as the dichromate oxidising agent is reduced:

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + 14H^+(aq) + 6e^- \rightarrow \underset{\text{green}}{2Cr^{3+}(aq)} + 7H_2O(l)$$

A **condensation reaction** involves two or more reactants that combine together to form a larger molecule (main product) and release a small molecule (by-product). In the case of **esterification**, the main product is an ester.

Tertiary alcohols are resistant to oxidation, so they can be distinguished from primary and secondary alcohols by the dichromate test, as explained in the exam question below.

Condensation reactions of alcohols with carboxylic acids (*esterification* reactions) are catalysed by concentrated inorganic acids, such as H_2SO_4, HCl or H_3PO_4, and proceed reversibly:

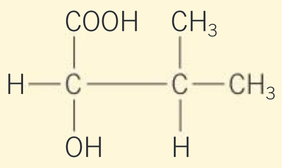
$$CH_3CH_2OH(l) + CH_3COOH(l) \xrightleftharpoons{H^+} CH_3COOCH_2CH_3(l) + H_2O(l)$$

Condensation reactions, also known as nucleophilic substitution reactions (S_N), are very common in organic chemistry and biochemistry. The types and mechanisms of these reactions are discussed in topics 20.1, A.9, B.2 and B.3.

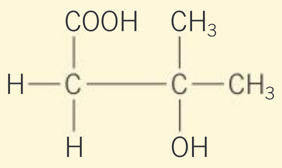
The equilibrium can be shifted to the right by distilling off the ester or water (whichever boils lower) from the reaction mixture.

SAMPLE STUDENT ANSWER

The structural formulas of two organic compounds are shown below.


$H-C(COOH)(OH)-C(CH_3)(H)-CH_3$

A


$H-C(COOH)(H)-C(CH_3)(OH)-CH_3$

B

a) Deduce the type of chemical reaction and the reagents used to distinguish between these compounds. [2]

b) State the observation expected for each reaction, giving your reasons. [2]

This answer could have achieved 2/4 marks:

a) They can be distinguished by the oxidation reaction using potassium dichromate.

b) Compound A will oxidize, so the orange solution of potassium dichromate will turn green. Compound B will not oxidize, so the solution will stay orange.

▲ Correct reaction type

▼ The second reagent (acid) is missing—"acidified potassium dichromate" would score the mark

▲ Correct observations for both compounds

▼ No reasons given—the marks could be scored by stating that **A** contains a secondary OH group while **B** contains a tertiary OH group

Biodiesel and other biofuels (topic C.4) are produced by transesterification of fatty acids. Their use raises ethical and environmental issues, such as those of the "food vs fuel" debate, deforestation and sustainability.

Practice problems for Topic 10

Problem 1

How many halogenoalkanes are structural isomers of C_4H_9Br?

A. 2 **B.** 3 **C.** 4 **D.** 5

Problem 2

Two organic compounds, 3-methylpent-2-ene (M_r 84.18) and 2-methylpropanoic acid (M_r 88.12), have similar molecular masses but very different boiling points.

a) Draw the structural formulas of these compounds.

b) Explain the difference in their boiling points.

Problem 3

Alkenes undergo hydration reactions in the presence of catalysts.

a) Formulate the equation for the reaction of but-2-ene with water.

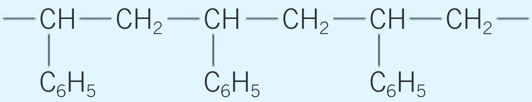
b) State the reaction type and the catalyst required.

c) Deduce the IUPAC name of the reaction product.

d) Suggest a chemical test that can be used to distinguish between the reaction product and 2-methylpropan-2-ol, stating the expected result for each compound.

Problem 4

Polystyrene is a polymer with the following structure:


$-CH(C_6H_5)-CH_2-CH(C_6H_5)-CH_2-CH(C_6H_5)-CH_2-$

a) Deduce the structural formula for the monomer of polystyrene.

b) State, with a reason, whether this monomer is a homologue of benzene or not.

Problem 5

Compound **A** can be converted to compound **B**, which has a lower molecular mass, by heating it under reflux with acidified potassium dichromate. Identify one functional group present in **A** and one functional group present in **B**.

11 MEASUREMENT AND DATA PROCESSING

TOPIC 11.1 UNCERTAINTIES AND ERRORS IN MEASUREMENT AND RESULTS

You should know:

- ✔ non-numerical observations are qualitative, while measurements are quantitative and are always affected by random errors/uncertainties and by human limitations;
- ✔ the impact of random errors/uncertainties on a final result can be propagated/estimated;
- ✔ systematic errors from experimental design and procedure cause a deviation in a particular direction;
- ✔ repeat trials and measurements reduce random errors but not systematic errors.

You should be able to:

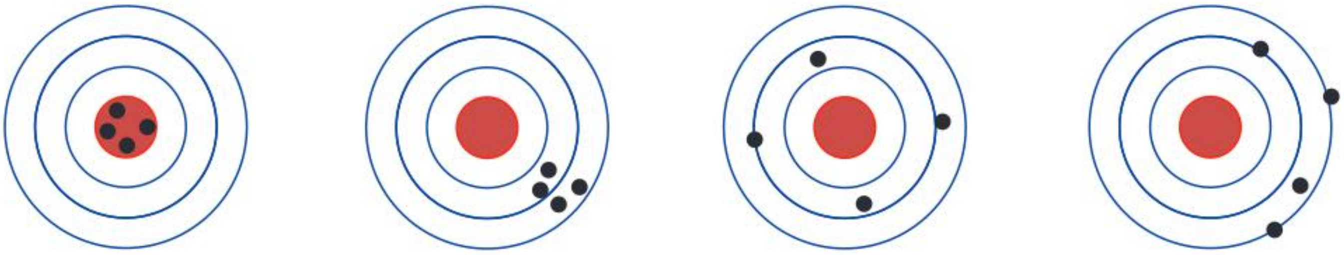
- ✔ record uncertainties in all measurements as a range (±) to an appropriate precision;
- ✔ discuss ways to reduce uncertainties and systematic errors in an experiment;
- ✔ estimate whether a particular source of error is likely to have a major or minor effect on the final result;
- ✔ determine the relative uncertainty ($\Delta A/A$) and the percentage relative uncertainty [$(\Delta A/A) \times 100\%$];
- ✔ deduce the propagation of uncertainties in processed data;
- ✔ distinguish between accuracy and precision in evaluating results.

- **Precision** is the closeness of agreement between repeated measurements under stated conditions.
- **Accuracy** is the closeness of the agreement between the result of a measurement and the true value of the measured quantity.

Precision and accuracy

Qualitative analysis relies on non-numerical information obtained from observations. It identifies or classifies substances on the basis of their properties, such as their reactions. *Quantitative analysis* uses numerical data from measurements, which are always associated with random errors and uncertainties. Each measurement has a limit of *precision* and of *accuracy* (figure 11.1.1).

The precision of a measurement is reflected in the number of significant figures used.



high precision and high accuracy

high precision and low accuracy

low precision and high accuracy

low precision and low accuracy

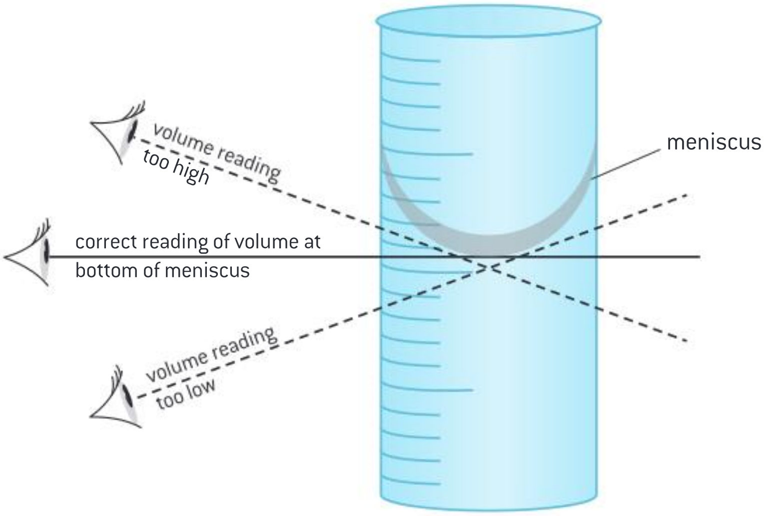
▲ **Figure 11.1.1.** Precision and accuracy demonstrated on a target

Errors and uncertainties

Systematic errors affect the accuracy of measurements. They result from flaws in the experimental design or instrumentation. They can be reduced by changing the equipment, materials or experimental procedure.

Random errors affect the precision of measurements. They are due to uncontrolled variables in an experiment, and cannot be eliminated; however, they can be reduced by averaging over repeat trials.

Examples of causes of systematic errors	Examples of causes of random errors
• leaking gas syringes • faulty calibration of a pH meter • poor insulation around a calorimeter • evaporation of volatile liquids on heating a sample • parallax error in reading a graduated cylinder (figure 11.1.2).	• estimation of a quantity that lies between the marked graduations of an instrument (e.g. a burette) • fluctuations in instrument readings due to changes in the surroundings (e.g. temperature variations, airflow, changes in pressure) • human reaction time.



▲ **Figure 11.1.2.** Parallax errors in reading the position of a meniscus in a measuring cylinder

Experimental results should be reported in the form ($A \pm \Delta A$) unit, where A is the measurement and ΔA is the *absolute uncertainty*. Uncertainty can also be expressed as *relative uncertainty*, in proportion to the measurement.

The degree of uncertainty in a measurement can be propagated – that is, the effect it will have on the final result can be estimated by following the uncertainty through the calculations.

- When adding or subtracting measurements, the **absolute** uncertainty is calculated from $\sqrt{\sum(\Delta A)^2}$.
- When multiplying or dividing measurements, the **relative** uncertainty is calculated from $\sqrt{\sum\left(\frac{\Delta A}{A}\right)^2}$.

You may also need to calculate the percentage error to compare your result with a known reference value.

$$\text{Percentage error} = \frac{|\text{literature value} - \text{experimental value}|}{\text{literature value}} \times 100\%$$

Assessment tip

Read questions carefully to check whether an answer with a specific number of significant figures or decimal places is required.

- For multiplication or division, the result should be expressed based on the measurement with the smallest number of significant figures.
- For addition or subtraction, the result should be expressed based on the measurement with the smallest number of decimal places.

The uncertainties and errors associated with measurement and results must be considered as part of your internal assessment (IA).

Seven international organizations, including IUPAC, collaborated on the *Guide to the Expression of Uncertainty in Measurement* published by the International Standards Organization (ISO) in 1995. This guidance has been translated into several languages and adopted in most countries.

- **Absolute uncertainty (ΔA)** is the margin of uncertainty associated with an experimental result.
- **Relative uncertainty** $= \frac{\Delta A}{A}$,

and percentage relative uncertainty $= \frac{\Delta A}{A} \times 100\%$

Maths skills

The symbol "Σ" represents the sum of two or more values. The two vertical lines, |XX|, represent the modulus and imply that any negative value is considered positive.

Example 11.1.1.

Using a graduated pipette, (8.35 ± 0.05) cm^3 of a solution was transferred into a tared flask and its mass was recorded using an analytical balance, giving a reading of (15.329 ± 0.001) g.

a) Calculate the density of the solution, in g cm^{-3}, and the relative uncertainty of this value.

b) State your answer to part (a) in units of kg m^{-3}, and express it in scientific notation correct to two significant figures.

Solution

a) $\rho = \frac{m}{V} = \frac{15.329}{8.35} \approx 1.84 \text{ g cm}^{-3}$

Propagation of uncertainties: division is involved, so the net relative uncertainty is:

$$\sqrt{\left(\frac{0.05}{8.35}\right)^2 + \left(\frac{0.001}{15.329}\right)^2} \approx 0.006, \text{ or } 0.6\%.$$

b) $\rho = \frac{1.84\ \cancel{\text{g}}}{1\ \cancel{\text{cm}^3}} \times \frac{1\text{ kg}}{10^3\ \cancel{\text{g}}} \times \frac{10^6\ \cancel{\text{cm}^3}}{1\text{ m}^3} = 1840 \text{ kg m}^{-3}$

$\approx 1.8 \times 10^3 \text{ kg m}^{-3}$ to 2 sf.

TOPIC 11.2 GRAPHICAL TECHNIQUES

You should know:

- ✔ graphs show the effect of an independent variable (plotted on the *x*-axis) on a dependent variable (plotted on the *y*-axis), and can be used to determine physical quantities;
- ✔ sketched graphs have labelled but unscaled axes, and are used to show trends, such as proportionality;
- ✔ drawn graphs have labelled and scaled axes, and are used in quantitative measurements.

You should be able to:

- ✔ draw and interpret appropriate graphs involving experimental data;
- ✔ produce and interpret lines and curves of "best-fit" from raw data;
- ✔ calculate the slope (gradient) and intercept from a linear plot.

Graphical techniques have widespread applications, including gaseous volume, temperature and pressure graphs (topic 1.3); Maxwell–Boltzmann energy distribution, concentration–time and rate–concentration plots from chemical kinetics (topic 6.1 and 16.1); the Arrhenius plot to deduce the activation energy, E_a, of a reaction (topic 16.2) and titration curves from acid–base chemistry (topic 18.3).

Maths skills

Every drawn (not merely sketched) graph should include the following:

- title (always based on *y* against *x*)
- labelled *y*- and *x*-axes, with the dependent variable (the effect) plotted on the *y*-axis against the independent variable (the cause) plotted on the *x*-axis
- appropriate units (note: logarithmic quantities such as pH do not have units)
- appropriate scaling so that the graph fills the available page as much as possible.

In a sketched graph the units and scales are not necessary.

The slope (gradient), *m*, of a line connecting two points (x_1, y_1) and (x_2, y_2) can be deduced from the equation:

$$m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$$

The intercept, *b*, can be deduced in two ways (figure 11.2.1):

a) From the equation of a line, $y = mx + b$. If the slope, m, is known, one point on the line can be selected, (x_b, y_b), and then b can be deduced by rearranging the equation to give:

$$b = y_b - mx_b$$

b) Alternatively, if the scale of the x-axis includes $x = 0$, the line can be *extrapolated* back to the y-axis to find b.

Mathematical or statistical relationships between variables can often be discovered most easily by plotting a graph. Any *dependence* between two sets of data becomes visible when data points fall into a pattern such as a line. Because of measurement uncertainties, the relationship may not be perfect, but any *correlation* can be measured in terms of the *correlation coefficient*, *r*.

Maths skills

A proportion is a mathematical comparison between two numbers. The mathematical symbol for proportionality is $\propto$. When two variables, y and x, are *directly proportional* to each other, then $y \propto x$, or $y = kx$, where k is a constant. When two variables, y and x, are *inversely proportional* to each other, then $y \propto 1/x$, so $y = k/x$.

Example 11.2.1.

The concentration of a protein in solution can be determined by a colorimetric method as explained in example B.7.4 in option B.

a) The Beer–Lambert law states that $A = \varepsilon lc$, where A is the absorbance of the protein solution, ε is the extinction coefficient (in $\text{mol}^{-1}\ \text{dm}^2$), l is the absorption path length (in dm) and c is the protein concentration (in mol dm^{-3}). Comment if the calibration curve shown in example B.7.4, on page 182, obeys the Beer–Lambert law.

b) Calculate the percentage error of the extinction coefficient calculated in example B.7.4, correct to one decimal place, given that the literature value for ε is $2.23 \times 10^3\ \text{mol}^{-1}\ \text{dm}^2$.

c) The correlation coefficient (r) for the absorbance (A) and protein concentration (c) was found to be 0.993. Suggest what this value tells us about the experimental data.

Solution

a) The Beer–Lambert plot of A against c is a straight line that crosses the origin. The best-fit plot obtained is also a straight line that can be extrapolated to the origin. Therefore, the Beer–Lambert law is obeyed.

b) Percentage error $= \dfrac{2.35 \times 10^3 - 2.23 \times 10^3}{2.23 \times 10^3} \times 100\% \approx 5.4\%$

c) The value of $r = 0.993$ suggests that the model matches the results, as over 99% of variance is accounted for. The positive sign of r implies a positive correlation.

Assessment tip

Questions in paper 3 can include material from the core syllabus. Graphs are common in paper 3, particularly in section A, but also appear in many of the options.

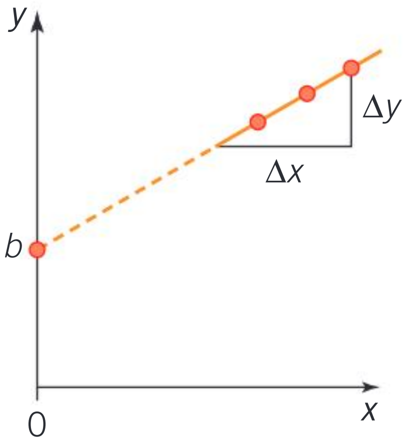


Figure 11.2.1. Calculating a gradient and extrapolating a line to the intercept

- **Extrapolation** is the extension of a line on a graph beyond the range of measurements.
- **Interpolation** involves using known data points or values to estimate values at other unknown points within the range of measurements.

- **Dependence** is any statistical relationship between two variables.
- **Correlation** is the extent to which two variables vary with each other; for a positive correlation, the two variables increase or decrease together, and with a negative correlation, one variable increases when the second decreases, or vice versa.
- The **correlation coefficient**, r, shows the strength of the relationship between two variables. It ranges from -1 to $+1$; ±1 means all data points lie on a straight line, with either a positive or negative correlation. If $r = 0$, there is no correlation.
- When two variables are **directly proportional** to each other, increasing (or decreasing) one by some multiple will cause the other variable to increase (or decrease) by the same multiple.
- When two variables are **inversely proportional** to each other, increasing (or decreasing) one by some multiple will cause the other variable to decrease (or increase) by the same multiple.

TOPIC 11.3 SPECTROSCOPIC IDENTIFICATION OF ORGANIC COMPOUNDS

You should know:

- ✔ the degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine the number of rings or multiple bonds in a molecule from its molecular formula;
- ✔ mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and infrared spectroscopy (IR) can help to identify compounds and to determine their structure.

You should be able to:

- ✔ determine the IHD from a structural or molecular formula;
- ✔ deduce information about molecular structure from percentage composition data, MS, ^{1}H NMR or IR.

Spectroscopy is the study of physical systems through detection of electromagnetic radiation that they interact with or produce, and *spectrometry* is the measurement of such radiation. These techniques are powerful analytical tools for identifying organic compounds.

Index of hydrogen deficiency (IHD)

The degree of unsaturation or *index of hydrogen deficiency (IHD)* can be used to determine the total number of rings and multiple bonds in a molecule. For the generic molecular formula $C_cH_hN_nO_oX_x$, where X is a halogen atom (F, Cl, Br or I):

$$IHD = 0.5(2c + 2 - h - x + n)$$

Determination of the empirical formula from percentage composition or other experimental data and determination of the molecular formula from the empirical formula and experimental data is covered in topic 1.2.

Assessment tip

Each benzene ring increases the IHD of a molecule by four units.

Example 11.3.1.

Deduce the IHD of:

a) the opioid fentanyl, $C_{22}H_{28}N_2O$

b) paracetamol (acetaminophen), the structure of which is given in section 37 of the data booklet.

Solution

a) For $C_{22}H_{28}N_2O$, IHD = 0.5(44 + 2 − 28 + 2) = 10

b) Paracetamol has one C=O, one ring and three double bonds (in its Kekulé structure), so IHD = 5

The absorption of quanta of energy in the form of photons is similar to the process behind the line spectra (topic 2.2). Photons of visible and UV light have similar energy to that of electron transitions. Bond vibrations are far less energetic, so they fall into the energy range of longer wavelength IR photons.

Infrared spectroscopy (IR)

The energy of photons of IR radiation is in the same range as the energy of the vibrations (stretches and bends) of bonds in molecules. When an IR photon has exactly the same energy as a particular vibration of a covalent bond, it can be absorbed by that bond, provided that the vibration will change the molecular dipole moment.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR)

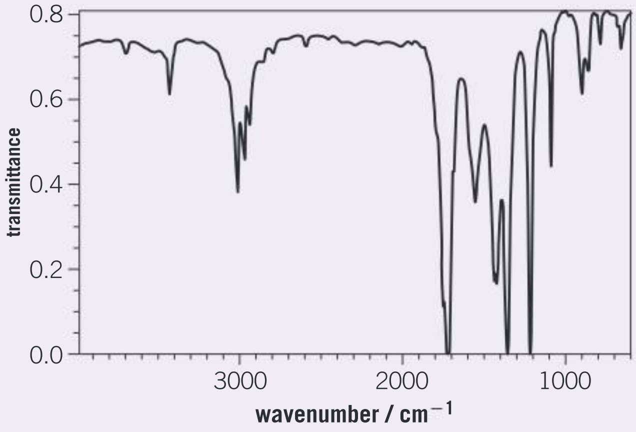
The nuclei of hydrogen atoms can exist in two spin states, "up" and "down", and behave as tiny magnets. When not in a magnetic field, the two states have equal energies. However, a magnetic field causes the spins to align with or against the field. The energy difference between the two states is equivalent to the energy of radio waves. The precise energy difference for a given proton depends on its chemical environment. Accordingly, radiofrequency spectroscopy for an organic compound in a strong magnetic field yields a ^{1}H NMR spectrum, in which the number of signals shows the number of different chemical environments of hydrogen atoms in a molecule. Each type of hydrogen environment produces a signal in a certain frequency range, which can be used to identify the different groups containing hydrogen. In addition, the relative numbers of hydrogen atoms in each environment can be deduced from the relative areas under the peaks (signals), which are calculated automatically by the NMR spectrometer and displayed as an integration trace.

Assessment tip

Chemical shifts of typical hydrogen environments are listed in section 27 of the data booklet.

Example 11.3.2.

a) The IR spectrum of propanone, $CH_3C(O)CH_3$, is shown below.



Identify the bonds causing the absorptions at ~3000 cm^{-1} and ~1715 cm^{-1} using section 26 of the data booklet.

b) Predict the number of signals in the ^{1}H NMR spectrum of propanone.

Solution

a) 3000 cm^{-1}: C–H bond

1715 cm^{-1}: C=O bond

Note that both absorptions are strong.

b) One, since the propanone molecule is symmetrical and all six protons are in the same chemical environment.

Mass spectrometry (MS)

Mass spectra of organic compounds show peaks corresponding to charged fragments of the original molecules. The intense peak with the highest m/z ratio, the molecular ion peak, corresponds to the relative molecular mass of the compound.

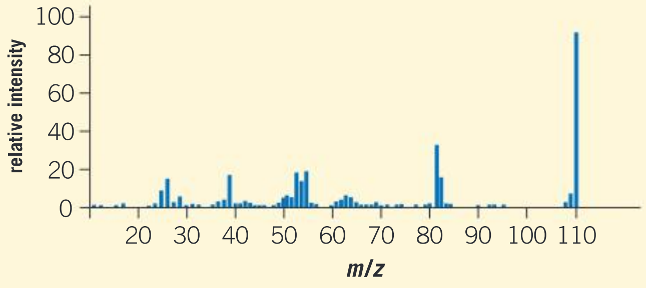
Mass spectrometry is described in topic 2.1. Section 28 of the data booklet contains a table showing a selection of mass spectral fragments.

Assessment tip

It is important to include the positive charge on ions detected by MS when identifying different fragments. For example, for ethanol, CH_3CH_2OH ($M_r = 46$), the peak appearing at $m/z = 29$ is produced by the ion $CH_3CH_2^+$, $(M_r - 17)^+$.

SAMPLE STUDENT ANSWER

Identify the species responsible for the peak at $m/z = 110$ in the mass spectrum of hydroquinone, $C_6H_4(OH)_2$. [1]



This answer could have achieved 0/1 marks:

$C_6H_4(OH)_2$

▼ The student has identified the m/z peak as the molecular ion peak, corresponding to M_r for hydroquinone, but the positive charge is missing: $C_6H_4(OH)_2^+$

Practice problems for Topic 11

Problem 1

Which of the following is an example of a random error?

A. Using an acid–base indicator that changes colour within a pH range beyond the equivalence point of the titration

B. Variation in pressure readings due to air fluctuations that occur as students open and close the door to the laboratory

C. Faulty calibration of a pH meter

D. Reading the final titre volume in a burette of a solution of potassium permanganate from the bottom of the meniscus instead of from the top

Problem 2

The pH of a sample of blood was measured to be 7.40. Calculate the hydronium ion concentration, $[H_3O^+]$, in mol dm^{-3}, in the blood and express your answer to the correct number of significant figures.

Problem 3

Charles's law, one of the gas laws, states that the volume, V, occupied by a fixed amount of gas, n, is directly proportional to its absolute temperature, T, if the pressure, p, remains constant. State how you would express this law mathematically and suggest the type of linear graph you would sketch to illustrate this relationship.

Problem 4

The Arrhenius equation can be represented as a linear equation of the form $y = mx + b$:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

What is the slope, m, and the intercept, b, from this linear equation?

	m	b
A	$-E_a/R$	A
B	$-E_a/R$	$\ln A$
C	$\ln A$	$-E_a/RT$
D	$-E_a/RT$	$\ln A$

Problem 5

Deduce the index of hydrogen deficiency (IHD) for:

a) morphine, the structure of which is given in section 37 of the data booklet

b) clenbuterol, the molecular formula of which is $C_{12}H_{18}Cl_2N_2O$.

Problem 6

Compound X contains carbon, hydrogen and oxygen. Laboratory combustion analysis of X determined the following mass percent composition: C 54.5% and H 9.2%. The molecular ion peak in the MS of X occurred at $m/z = 44$. The IR spectrum of X shows two strong absorptions at wavenumbers 1725 cm^{-1} and 2976 cm^{-1}. On the basis of this information:

a) deduce the empirical and molecular formula of X

b) deduce the index of hydrogen deficiency (IHD) for X

c) deduce the molecular structure of X

d) suggest which ion can produce the peak at $m/z = 29$ in the mass spectrum of X

e) predict the following in the ^{1}H NMR spectrum of X:

  (i) number of signals

  (ii) approximate chemical shift (δ) values, in ppm, using section 27 of the data booklet.

12 ATOMIC STRUCTURE (AHL)

TOPIC 12.1 ELECTRONS IN ATOMS

You should know:

- ✔ in a line emission spectrum, the limit of convergence at higher frequency corresponds to the first ionization energy, IE_1;
- ✔ trends in IE_1 across periods account for the existence of the electron energy levels (n) and sublevels (s, p, d and f) in atoms;
- ✔ successive ionization energy values provide information about electron configurations.

You should be able to:

- ✔ solve problems using the equation $E = h\nu$;
- ✔ calculate the value of IE_1 from the convergence limit of a line spectrum;
- ✔ deduce the group to which an element belongs from its successive IE data;
- ✔ explain the trends and discontinuities in IE_1 across a period.

Line emission spectra provide experimental evidence for the existence of atomic energy levels. The lines in these spectra converge at higher energies. The frequency of the radiation at the limit of convergence can be used to determine IE_1.

The line emission spectrum of hydrogen is described in topic 2.2. The definition and periodic trends of ionization energy are discussed in topic 3.2.

Example 12.1.1.

a) A beam of infrared radiation emitted from a chemical oxygen–iodine laser (COIL) has a wavelength $\lambda = 1.315\ \mu\text{m}$. Determine the energy, in J, per photon of this radiation.

b) Calculate the first ionization energy, IE_1, in kJ mol⁻¹, for hydrogen, given that the frequency at which convergence occurs in the Lyman series (the series of spectral lines for electrons returning to the $n = 1$ level) is $\nu = 3.288 \times 10^{15}$ Hz.

Solution

a) In this question you have to consider the prefix for the unit of λ.

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{1.315 \times 10^{-6}\ \text{m}}$$

$$= 1.51 \times 10^{-19}\ \text{J}$$

b) $IE_1 = h\nu = 6.63 \times 10^{-34}\ \text{J s} \times 3.288 \times 10^{15}\ \text{Hz} = 2.18 \times 10^{-18}\ \text{J}$

The question requires IE_1 to be expressed in kJ mol⁻¹, so dimensional analysis should be applied:

$$IE_1 = 2.18 \times 10^{-18}\ \text{J} \times \frac{1\ \text{kJ}}{10^{3}\ \text{J}} \times 6.02 \times 10^{23}\ \text{mol}^{-1} = 1.31 \times 10^{3}\ \text{kJ mol}^{-1}$$

Assessment tip

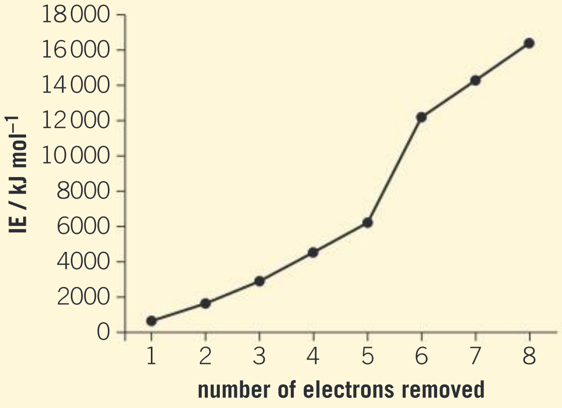
Take care when handling units in numerical questions. Use SI units and make sure that you understand the meaning of decimal prefixes (e.g., μ, m, k). You should also ensure that your final answer is expressed in the units required by the question.

Relevant information for the questions in example 12.1.1 can be found in sections 1 and 2 of the data booklet.

Successive ionization energies increase as electrons are removed from an increasingly positive species. However, this increase is not a smooth progressive trend. A large jump in value between IE_x and $IE_{(x+1)}$ means that the $(x + 1)$th electron has been removed from a lower energy level/sublevel or a half-filled sublevel.

SAMPLE STUDENT ANSWER

Eight successive ionization energies of vanadium are shown in the graph below.



a) State the sublevels from which each of the first four electrons are lost. [1]

b) Outline why there is an increase in ionization energy from electron 3 to electron 5. [1]

c) Explain why there is a large increase in the ionization energy between electrons 5 and 6. [3]

This answer could have achieved 5/5 marks:

a) first: 4s, second: 4s, third: 3d, fourth: 3d

▲ Correct: the condensed electron configuration for V is [Ar]$3d^3 4s^2$, and electrons are first removed from the sublevel with the highest value of *n* (*n* = 4)

b) Electrons 3 to 5 are removed from the same 3d sublevel. However, they are being removed from an increasingly positive ion, so more energy is required to remove successive electrons as the electrostatic forces of attraction become stronger.

▲ The key point here is that the electrons are in the same 3d sublevel, but that as more electrons are removed the pull of the positive ion holds the remaining electrons more tightly

c) Electron 6 is removed from a different sublevel than electron 5, 3p instead of 3d. The 3p sublevel is closer to the nucleus, resulting in a higher electrostatic force of attraction between 3p electrons and the nucleus.

▲ Correct and comprehensive answer that scores all three marks

Practice problems for Topic 12

Problem 1

The first five ionization energies for an unknown element are 787, 1577, 3232, 4356 and 16 091 kJ mol^{-1}, respectively.

In which group of the periodic table would the unknown element be found?

A. 1 **B.** 3 **C.** 14 **D.** 15

Problem 2

a) Explain the convergence of lines in the hydrogen emission spectrum.

b) State what can be determined from the frequency of the convergence limit.

Problem 3

Sketch a graph of the first seven successive ionization energies of chromium.

13 THE PERIODIC TABLE—THE TRANSITION METALS (AHL)

TOPIC 13.1 FIRST-ROW d-BLOCK ELEMENTS

You should know:

- ✔ the characteristic properties of transition elements include formation of complex ions, variable oxidation states, existence of coloured compounds and ions, magnetic properties and ability to catalyse reactions;
- ✔ transition elements have an oxidation state of +2 when the s-electrons are removed;
- ✔ Zn is not a transition element as it does not form ions with incomplete d orbitals.

You should be able to:

- ✔ explain the ability of transition elements to have variable oxidation states from successive ionization energies;
- ✔ explain the nature of the coordinate bond within a complex ion;
- ✔ deduce the total charge of a complex, from the formula of the ion and ligands;
- ✔ explain magnetic properties of transition metals in terms of unpaired electrons.

Transition elements (groups 3–11) have incomplete d sublevels in their atoms or cations. Zinc and other group 12 elements belong to the d-block but are not classified as transition elements because they have complete d sublevels in all their compounds.

In period 3, there are two exceptions to the [Ar]$3d^x4s^2$ electron configuration, namely chromium, Cr: [Ar]$3d^54s^1$, and copper, Cu: [Ar]$3d^{10}4s^1$. Partially or completely filled sublevels vary slightly in energy, causing this deviation from the expected pattern. However, when ions of first-row d-block elements are formed, electrons are always removed from the 4s level before the 3d level. Across the period, first ionization energy (IE_1) values increase gradually, because the increasing numbers of 3d electrons shield the $4s^2$ electrons from the nucleus.

Many of the characteristic properties of transition elements depend on the existence of the incomplete d sublevel, including their variable oxidation states, their ability to form complex ions with ligands, their coloured compounds and ions, their magnetic properties and their ability to catalyse reactions. For example, variable oxidation states are possible because successive *IE* values increase by relatively small amounts.

Transition metal ions form complexes with *ligands*, which donate electrons into empty d orbitals to form *coordinate bonds*. Ligands may be *monodentate* or *polydentate* (chelate). The central atoms in the resultant complexes often have *coordination number* 6 and are thus octahedral in geometry (figure 13.1.1). Other configurations are possible, for example tetrahedral or square planar complexes, in both of which the central atom has a coordination number of four. In a coordination complex, the central atom or ion acts as a Lewis acid (electron-pair acceptor) while the ligands act as Lewis bases (electron-pair donors).

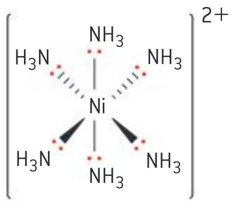
Assessment tip

The electron configuration of ions never rearranges to form a half-filled or fully filled d sublevel (e.g., the electron configuration of Fe^{2+} is [Ar]$3d^6$, not [Ar]$3d^54s^1$).

Representations of electron configurations are covered in topic 2.2. Ionization energies are discussed in topics 3.2 and 12.1. Redox reactions are considered in topic 9.1, and the difference between homogeneous catalysis and heterogeneous catalysis is outlined in option A.3.

Common oxidation states of the first-row transition metal ions are listed in section 14 of the data booklet.

Ligands are ions or molecules with a lone pair of electrons able to form coordinate bonds with the metal cation.



▲ **Figure 13.1.1.** Octahedral geometry in the complex of Ni^{2+} with monodentate ammonia ligands, $[Ni(NH_3)_6]^{2+}$

Assessment tip

VSEPR theory cannot be used to deduce the geometries of transition metal complexes if they involve ions with an incomplete d sublevel.

- A **coordinate bond** is a covalent bond in which both electrons in the shared pair originate from the same atom.
- A **monodentate** ligand can form only one bond with the metal ion, whereas a **polydentate** (chelate) ligand has two or more donor atoms that can form coordinate bonds with the ion.
- **Coordination number** is the number of coordinate bonds formed by the metal ion with its ligands in a complex.

Coordinate bonds were introduced in topic 4.3.

- **Paramagnetic** materials are attracted by an external magnetic field and develop an induced magnetic field in the direction of the applied field.
- **Diamagnetic** materials are repelled by an external magnetic field and develop an induced magnetic field in the direction opposite to the applied field.

The hydrogenation of alkenes is covered in topic 10.2 and the Haber process in topic 7.1.

Example 13.1.1.

Consider the transition metal complex $[Co(NH_3)_5Br]SO_4$.

a) Deduce the charge of the transition metal complex.

b) Deduce the oxidation state of cobalt in the complex.

c) State the condensed electron configuration of cobalt in this oxidation state.

d) Predict the geometry of the complex.

Solution

a) The complex is cationic, as the sulfate counteranion (which lies outside the complex in the lattice) carries a 2– charge. Hence, the charge on the cationic complex is 2+.

b) The oxidation state (x) of cobalt in the complex can be deduced from the charges on the ligands and the sulfate anion:
$x + (5 \times 0) + (-1) + (-2) = 0$, so $x = +3$.

c) Co: $[Ar]3d^7 4s^2$, so Co^{3+}: $[Ar]3d^6$.

d) In this compound, the cationic complex is $[Co(NH_3)_5Br]^{2+}$. The central cobalt(III) is coordinate-bonded to six monodentate ligands. Hence, the complex is likely to be octahedral.

The magnetic properties of transition metals and their complexes can be influenced by the oxidation state of the metal, its coordination number, and the geometry of the complex. *Paramagnetic* complexes contain unpaired electrons, which are able to behave as tiny magnets and are attracted by an external magnetic field. *Diamagnetic* complexes do not contain unpaired electrons and are repelled by an external magnetic field.

Example 13.1.2.

Deduce whether zinc metal is paramagnetic or diamagnetic.

Solution

The orbital diagram for zinc can be represented as:

As the 3d level has no unpaired electrons, atomic zinc is diamagnetic.

Transition metals are often used as catalysts, for example nickel in the hydrogenation of alkenes, iron in the Haber process or platinum, palladium and rhodium in catalytic converters.

TOPIC 13.2 COLOURED COMPLEXES

You should know:

✔ complexes of d-block elements are coloured because light is absorbed when electrons are promoted between the split d orbitals;

✔ the colour absorbed is complementary to the colour observed.

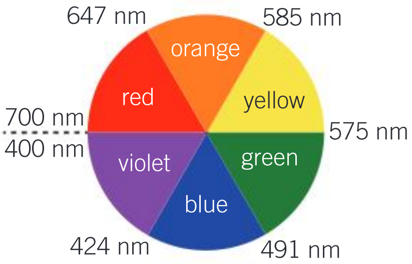
You should be able to:

✔ explain the effects of the identity of the metal ion, the oxidation state of the metal and the nature of the ligand on the colour of transition metal ion complexes;

✔ explain the effect of different ligands on the splitting of the d orbitals in an octahedral crystal field and the observed colour of the transition metal complex.

The five 3d orbitals all have the same energy when surrounded by a symmetrical electrical field. However, when a transition metal ion forms an octahedral complex with ligands, the d sublevel is split into two sets of orbitals with different energies. This difference in energy corresponds to the energy of a photon of visible light. The precise difference varies depending on the metal and the ligands. Thus, many transition metal complexes are coloured: they absorb certain wavelengths from white light, transmitting the complementary colour (figure 13.2.1).

The colour wheel in section 17 of the data booklet can be used to deduce the complementary colour observed for a complex.



▲ **Figure 13.2.1.** The colour wheel, with approximate wavelengths

A more detailed explanation is provided by crystal field theory (CFT). This describes how the d orbitals of a transition metal in an octahedral crystal field split into two sets of energy levels, with three degenerate orbitals at lower energy (t_{2g}) and two degenerate orbitals at higher energy (e_g). The energy separation between these two sets of orbitals is termed the *crystal field splitting energy*, Δ. The size of the energy separation, Δ, and therefore the colour of a transition metal complex depends on four factors:

- identity of the metal ion
- oxidation state of the metal ion (for a given metal, Δ increases as the oxidation state increases)
- nature of the ligands (ligands have different charge densities)
- geometry of the complex ion (for example, a tetrahedral complex has a smaller Δ than an octahedral complex with the same ligands).

Ligands can be arranged by increasing Δ in the spectrochemical series:

$$I^- < Br^- < S^{2-} < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < CN^- \approx CO$$

$$\text{small } \Delta \xrightarrow{\hspace{6cm}} \text{large } \Delta$$

The spectrochemical series is given in section 15 of the data booklet.

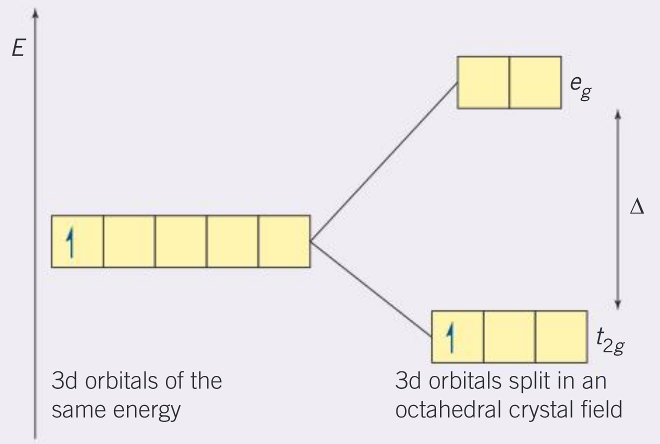
Example 13.2.1.

a) Sketch the energy-level diagram showing the splitting of the d orbitals in an octahedral crystal field for the complex $[Ti(H_2O)_6]Cl_3$.

b) Explain why $[Ti(H_2O)_6]Cl_3$ has a red-violet colour.

Solution

a) The oxidation state of titanium in this complex is +3. The condensed electron configuration of elemental Ti is $[Ar]3d^24s^2$, so for Ti^{3+} it is $[Ar]3d^1$. In an octahedral crystal field the five orbitals in the 3d sublevel split as follows:



b) In $[Ti(H_2O)_6]^{3+}$, the 3d orbitals split in an octahedral crystal field. When white light passes through a solution of the complex, the single electron in the lower-energy t_{2g} set of orbitals absorbs energy and moves to the higher-energy e_g set of orbitals. This d-to-d electron transition absorbs a photon of yellow-green light, so light of the complementary colour, red-violet, is transmitted.

SAMPLE STUDENT ANSWER

Explain why iron forms many different coloured ions. [3]

This answer could have achieved 1/3 marks:

Due to its oxidation states, Fe(II) is green whereas Fe(III) is yellow.

▲ Iron as a transition metal has more than one oxidation state

▼ Marks would have been awarded for a statement that colour depends upon the energy difference between the split d orbitals

▼ and that different ligands will have different charge densities; or different geometries of the complex ions affect the colour

Assessment tip

Deduce is a higher-order command term and means that a conclusion must be reached from the information given. You should include in your answer the reasoning behind your conclusion.

Practice problems for Topic 13

Problem 1

Consider the transition metal compound $K_3[Cr(CN)_6]$.

a) Deduce the charge of the complex.

b) Deduce the oxidation state of chromium in the complex.

c) Predict the geometry of the complex.

d) Describe the bonding in the complex.

e) Deduce whether atomic chromium is paramagnetic or diamagnetic.

Problem 2

a) State and explain the type of reaction that occurs between Ni^{2+} and H_2O to form $[Ni(H_2O)_6]^{2+}$ in terms of acid–base theories.

b) State the name of the type of bonding between Ni^{2+} and H_2O in $[Ni(H_2O)_6]^{2+}$.

c) Draw the structure of the cationic complex $[Ni(H_2O)_6]^{2+}$.

d) Sketch the energy-level diagram showing the splitting of the d orbitals in an octahedral crystal field for the complex $[Ni(H_2O)_6]Cl_2$.

e) Predict whether $[Ni(H_2O)_6]Cl_2$ is paramagnetic or diamagnetic.

14 CHEMICAL BONDING AND STRUCTURE (AHL)

TOPIC 14.1 FURTHER ASPECTS OF COVALENT BONDING AND STRUCTURE

You should know:

- ✔ sigma (σ) bonds are formed by the head-on overlap of atomic orbitals;
- ✔ pi (π) bonds are formed by the sideways overlap of atomic orbitals;
- ✔ the preferred Lewis (electron dot) structure among various possibilities has atoms with formal charge values closest to zero;
- ✔ exceptions to the octet rule include some species having fewer than four electron pairs (incomplete octets) or up to six electron pairs (expanded octets);
- ✔ delocalization involves electrons shared between more than two atoms in a molecule or ion;
- ✔ a molecule or ion with delocalized electrons can be represented by two or more resonance structures.

You should be able to:

- ✔ predict whether σ or π bonds are formed from the linear combination of atomic orbitals;
- ✔ deduce the Lewis structures of molecules or ions with up to six electron pairs on each atom;
- ✔ apply formal charge to deduce the preferred Lewis structure;
- ✔ deduce the electron domain and molecular geometries of molecules and ions with up to six electron domains and their associated bond angles;
- ✔ explain the wavelength of light needed to dissociate oxygen and ozone;
- ✔ describe the mechanism of ozone depletion when catalysed by CFCs and NO_x.

Formal charge

When more than one Lewis (electron dot) structure is possible, the *formal charge* (FC) of each atom can be calculated as follows.

$$\text{FC} = (\text{number of valence electrons}) - \frac{1}{2}(\text{number of bonding electrons}) - (\text{number of non-bonding electrons})$$

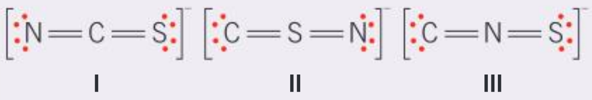
The most likely Lewis structure is the one with:

- FC difference ($\Delta\text{FC} = \text{FC}_{\text{max}} - \text{FC}_{\text{min}}$) closest to 0
- the negative charges located on the most electronegative atoms.

Note that once the 3d orbitals and above become available for bonding, molecules or ions can have up to six electron pairs on each atom.

Example 14.1.1.

The thiocyanate anion, $(SCN)^-$, can be represented by the following Lewis (electron dot) structures:



a) Deduce the formal charge on each of the atoms in **I, II** and **III**.

b) Predict which is the preferred Lewis structure out of **I, II** and **III**.

Solution

a)

	N	C	S
I	$FC = 5-\frac{4}{2}-4=-1$	$FC = 4-\frac{8}{2}-0=0$	$FC = 6-\frac{4}{2}-4=0$
II	$FC = 5-\frac{4}{2}-4=-1$	$FC = 4-\frac{4}{2}-4=-2$	$FC = 6-\frac{8}{2}-0=+2$
III	$FC = 5-\frac{8}{2}-0=+1$	$FC = 4-\frac{4}{2}-4=-2$	$FC = 6-\frac{4}{2}-4=0$

b) For **I**, $\Delta FC = 0-(-1) = 1$;

For **II**, $\Delta FC = +2-(-2) = 4$;

For **III**, $\Delta FC = +1-(-2) = 3$.

As ΔFC is closest to zero for **I**, this is the preferred Lewis structure for the thiocyanate anion out of **I, II** and **III**.

Assessment tip

Ensure you know the difference in meaning between the terms oxidation state, formal charge, ionic charge, partial charge and total charge.

VSEPR theory for five and six electron domains

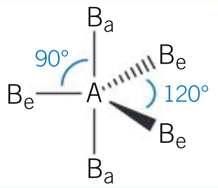
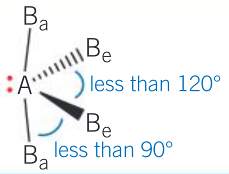
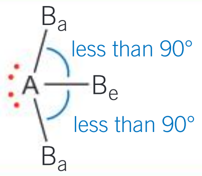
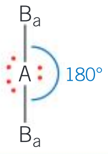
VSEPR theory can be extended to deduce the electron domain and molecular geometries of structures with five and six electron domains. However, it cannot be used to deduce the shapes of transition metal complexes that involve incomplete d sublevels.

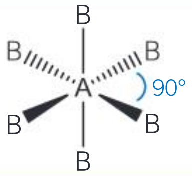
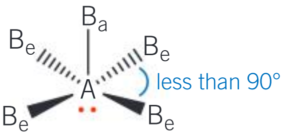
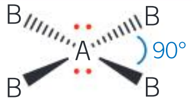
VSEPR theory involving molecules and ions with up to four electron domains was introduced in topic 4.3.

In geometries involving five electron domains, the lone pairs (represented by E) in the systems AB_4E (four bonding pairs and one lone pair), AB_3E_2 and AB_2E_3 always occupy the equatorial positions and not the axial positions. This is linked to the order of repulsion of electron pairs:

lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair.

▼ **Table 14.1.1.** Molecular geometries based on five and six electron domains

Electron domain geometry	Molecular geometry	Example molecule
trigonal bipyramidal (five domains)	trigonal bipyramidal (AB_5) 	PF_5
	see-saw (AB_4E) 	SF_4
	T-shaped (AB_3E_2) 	ClF_3
	linear (AB_2E_3) 	I_3^-

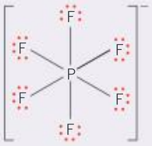
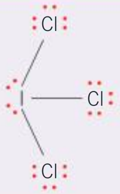
Electron domain geometry	Molecular geometry		Example molecule
octahedral (six domains)	octahedral (AB_6)		SF_6
	square pyramidal (AB_5E)		BrF_5
	square planar (AB_4E_2)		XeF_4

B_a = axial substituent, B_e = equatorial substituent

Example 14.1.2.

Apply the VSEPR theory to deduce the shapes of $[PF_6]^-$ and ICl_3. For each species, draw the Lewis (electron dot) structure, identify the electron domain geometry, state the name of the molecular geometry and predict the approximate value of the bond angle(s).

Solution

Species	Lewis (electron dot) structure	Electron domain geometry	Molecular geometry	Approximate value of bond angle(s) / °
$[PF_6]^-$		octahedral	octahedral	90° and 180°
ICl_3		trigonal bipyramidal	T-shaped	less than 90° (for Cl_e–I–Cl_a) and less than 180° (for Cl_a–I–Cl_a)

Cl_a = axial substituent, Cl_e = equatorial substituent

$[PF_6]^-$: Number of valence electrons is 5 + 6 + 1 (charge) = 12; number of electron domains is $\frac{12}{2} = 6$, so the electron domain geometry is octahedral.

ICl_3: Number of valence electrons is 7 + 3 = 10; number of electron domains is $\frac{10}{2} = 5$, so the electron domain geometry is trigonal bipyramidal.

For $[PF_6]^-$, there are six bonding pairs of electrons (AB_6 system) so the molecular geometry is also octahedral. For ICl_3, there are only three bonding pairs of electrons, so there are two lone pairs (AB_3E_2 system). The two lone pairs occupy equatorial positions. The molecular geometry is therefore T-shaped.

In $[PF_6]^-$, the bond angles have the ideal values for an octahedral molecular geometry, namely, 90° and 180°, but in ICl_3, Cl_e–I–Cl_a will be less than 90° (lone pairs occupy more space than bonding pairs).

Assessment tip

When drawing the Lewis structure of a cation or an anion, such as $[PF_6]^-$, include the square brackets and the respective charge. Remember to complete octets on the terminal atoms in a Lewis structure (except hydrogen, which has only two electrons associated with the bonding pair). You will not receive full marks otherwise, as a Lewis structure should show all the electrons present. Note also that each pair of electrons could be represented by dots (••), crosses (××) or a line (–).

- **Sigma (σ) bonds** form when atomic orbitals overlap head-on and share electron density directly between the nuclei of the two atoms that the bond connects.
- **Pi (π) bonds** form when one atomic orbital from each atom overlaps sideways with the other, resulting in electron density above and below the line between the nuclei of the bonding atoms.

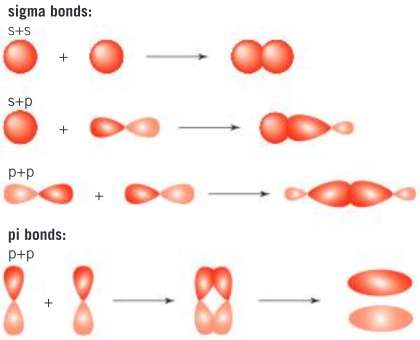


Figure 14.1.1. Formation of σ bonds and π bonds from s and p orbitals

- In **resonance**, two or more Lewis structures (resonance structures) can represent a particular molecule or ion that cannot be described fully with a single Lewis structure (a resonance hybrid).
- **Delocalization** is a quantum mechanical concept that describes π bonding in a conjugated system, in which electrons are "smeared out" or "shared" between more than two atoms.

Bond order = (total number of bonding pairs/total number of double bond positions)

The relationship between colour, wavelength, frequency and energy across the electromagnetic spectrum is discussed in topic 2.2.

Sigma and pi bonding

Sigma (σ) bonds are single covalent bonds formed when atomic orbitals overlap head-on (figure 14.1.1).

A double bond comprises a σ bond together with a *pi (π) bond*, in which one atomic orbital from each atom overlaps sideways with the other. A triple bond comprises a σ bond and two π bonds.

Delocalization and resonance

Some molecules or ions cannot be adequately depicted by a single Lewis structure. Such species can be represented by two or more contributing *resonance structures* (example 14.1.3). The "moving" bond in the *resonance hybrid* can also be represented as a dotted line, signifying *delocalization*. Delocalized electrons are shared between more than two atoms in a molecule or ion, as opposed to being localized between a pair of atoms.

Example 14.1.3.

a) Draw the resonance structures for the nitrite ion and ozone.

b) Comment on the nitrogen–oxygen bond lengths in the nitrite ion.

c) Explain why the dissociation of oxygen, $O_2(g)$, requires light of a shorter wavelength ($\lambda = 241$ nm) than the dissociation of ozone, $O_3(g)$ ($\lambda = 331$ nm).

Solution

a) Two resonance structures can be drawn for each species:

b) In the nitrite ion, the π bond is not localized between the nitrogen and oxygen atoms, so each nitrogen-to-oxygen link has a fractional *bond order*.

$$\text{bond order} = \frac{\text{total number of bonding pairs}}{\text{total number of positions}} = \frac{3}{2} = 1.5$$

Therefore, each nitrogen-to-oxygen bond in nitrite is intermediate in length between an N=O bond and an N–O bond.

Note that each covalent bond in ozone also has a bond order of 1.5.

c) The oxygen atoms in $O_2(g)$ are linked by a double bond (order of 2), which is stronger than the delocalized bonds of ozone (order of 1.5). The dissociation of a stronger bond requires more energy, which can only be provided by photons with a shorter wavelength (higher frequency).

Ozone, $O_3(g)$, contains relatively weak delocalized bonds (the average bond enthalpy for the oxygen-to-oxygen bond in ozone is 362 kJ mol^{-1}, whereas the bond enthalpy for O=O, given in section 11 of the data booklet, is 498 kJ mol^{-1}). These relatively weak bonds in ozone are easily broken by nitrogen oxides, $NO_x(g)$, or chlorine radicals, $Cl\bullet(g)$, produced from chlorofluorocarbons (CFCs). In all cases, the decomposition of ozone proceeds as a chain reaction in which the nitrogen oxide or chlorine radical acts as a homogeneous catalyst, for example:

$$O_3(g) + Cl\bullet(g) \rightarrow O_2(g) + ClO\bullet(g)$$

$$O_3(g) + ClO\bullet(g) \rightarrow 2O_2(g) + Cl\bullet(g)$$

Chain reactions are introduced in topic 10.2.

SAMPLE STUDENT ANSWER

There is concern about damage done to the ozone layer in the stratosphere by jet-propelled aircraft.

a) Formulate two equations to show how nitrogen(II) oxide, NO, catalyses the destruction of ozone. [2]

b) Suggest why the loss of ozone is an international environmental concern. [2]

This answer could have achieved 2/4 marks:

a) $\bullet NO(g) + O_3(g) \rightarrow \bullet NO_2(g) + O_2(g)$

$NO_2(g) + O_3(g) \rightarrow NO(g) + O_2(g)$

b) Ozone absorbs harmful UV radiation from the Sun. As ozone is destroyed, more UV rays reach the Earth and lead to global warming. Ozone absorbs IR energy reflected from the Earth and therefore helps retain heat in the atmosphere.

▲ Correct equation and consistent use of the dot notation representing a radical

▼ The second mark is not awarded as the equation is not balanced and the use of the dot notation is inconsistent

▲ Loss of ozone allows UV radiation to penetrate the atmosphere/reach the Earth

▼ The second mark could have been earned by describing how UV radiation causes skin cancer or causes tissue damage

TOPIC 14.2 HYBRIDIZATION

You should know:

- ✔ hybrid orbitals form when different types of atomic orbitals on the same atom mix with one another.

You should be able to:

- ✔ explain the formation of hybrid orbitals in methane (sp^3), ethene (sp^2) and ethyne (sp);
- ✔ identify and explain the relationships between Lewis structures, electron domains, molecular geometries and types of hybridization.

A covalent bond is formed when atomic orbitals of two adjacent atoms overlap and merge into a molecular orbital containing two shared electrons. The outer shell of a carbon atom has one 2s and three 2p orbitals that contain a total of four electrons. In methane, $CH_4(g)$, the different atomic orbitals on carbon *hybridize* to form four identical atomic orbitals, each with the same energy and with 25% s character and 75% p character. These hybrid sp^3 orbitals can then form molecular orbitals with hydrogen atoms.

Similarly, in ethene, $H_2C=CH_2$, each carbon atom starts bonding with three hybrid sp^2 orbitals and one p orbital; the p orbitals overlap to form the π bond in the C=C bond. In ethyne, HC≡CH, each carbon atom starts bonding with two hybrid sp orbitals and two p orbitals.

Hybridization is the mixing of atomic orbitals on the same atom to form the same number of new, hybrid orbitals that all have the same mean energy as the contributing atomic orbitals.

Number of electron domains	Hybrid orbitals
2	sp
3	sp^2
4	sp^3

▲ **Table 14.2.1.** Hybridization in main-group elements

Assessment tip

Remember that each multiple (double or triple) bond and each lone pair of electrons is counted as one electron domain.

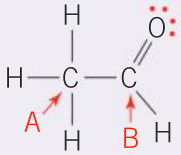
The type of hybridization in main-group elements can be deduced from the number of their electron domains (table 14.2.1).

Example 14.2.1.

Deduce the type of hybridization (sp, sp^2 or sp^3) of each carbon atom in ethanal.

Solution

You first need to deduce the Lewis structure of ethanal:



Carbon **A** has four electron domains (four bonding pairs), so its hybridization is sp^3. Carbon **B** has three electron domains (from one double bond and two single bonds), so its hybridization is sp^2.

Practice problems for Topic 14

Problem 1

Which statements about σ and π bonds are correct?

I σ bonds can result from the overlap of two s atomic orbitals.

II σ bonds can result from the overlap of an s atomic orbital and a p_x atomic orbital.

III π bonds can result from the sideways overlap of a p_y atomic orbital and a p_z atomic orbital.

A. I and II only

B. I and III only

C. II and III only

D. I, II and III

Problem 2

Consider the following statements.

I All carbon–oxygen bond lengths are equal in CO_2.

II All carbon–oxygen bond lengths are equal in CH_3COOH.

III All carbon–oxygen bond lengths are equal in CO_3^{2-}.

Which statements are correct?

A. I and II only

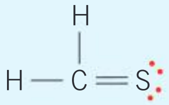
B. I and III only

C. II and III only

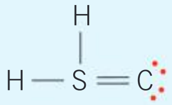
D. I, II and III

Problem 3

Considering formal charges, deduce which of the following two Lewis structures, **A** or **B**, is preferred.



A



B

Problem 4

Apply the VSEPR theory to deduce the shapes of $[IBr_4]^-$ and $[IF_4]^+$. For each ion, draw the Lewis (electron dot) structure, identify the electron domain geometry, state the name of the molecular geometry and predict the approximate value of the bond angle(s).

Problem 5

In which substance does a carbon atom have sp^2 hybridization?

A. cyclopropane

B. carbon dioxide

C. (*Z*)-3-bromopent-2-ene

D. ethanol

15 ENERGETICS/ THERMOCHEMISTRY (AHL)

TOPIC 15.1 ENERGY CYCLES

You should know:

- ✔ representative equations (e.g., $M^+(g) \rightarrow M^+(aq)$) can be used for enthalpy/energy of hydration, ionization, atomization, electron affinity, lattice and solution;
- ✔ enthalpies of solution, hydration and lattice are related in an energy cycle.

You should be able to:

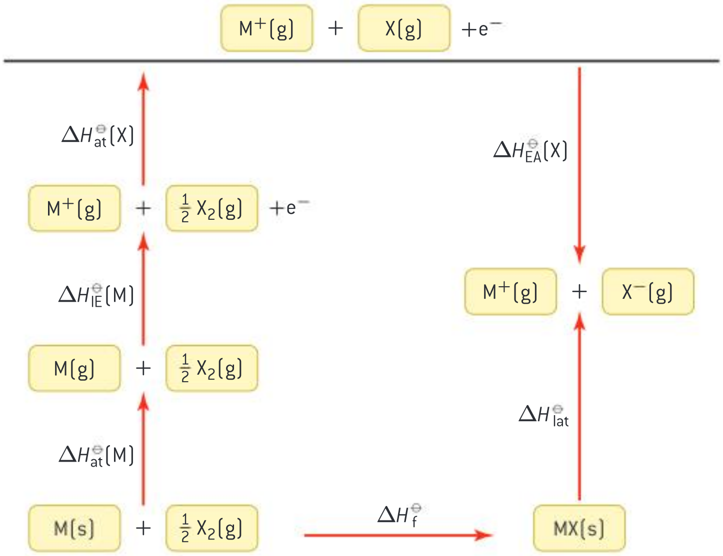
- ✔ construct Born–Haber cycles for group 1 and 2 oxides and chlorides;
- ✔ construct energy cycles from hydration, solution and lattice enthalpies;
- ✔ calculate enthalpy changes from Born–Haber or dissolution energy cycles;
- ✔ outline how size and charge of ions affect lattice and hydration enthalpies.

Born–Haber cycles

The energy change in a single-step reaction is equivalent to the sum of the energy changes for all steps in a multi-step reaction with the same reactants and products. For example, most *lattice enthalpies* are determined indirectly from *Born–Haber cycles*, which apply Hess's Law to ionic compounds. A typical Born–Haber cycle (figure 15.1.1) involves:

- the standard enthalpy of formation of the ionic compound, $\Delta H_f^\ominus$
- the ionization energy of the metal, $\Delta H_{IE}^\ominus$
- the electron affinity of the non-metal, $\Delta H_{EA}^\ominus$
- the standard enthalpy of atomization of a constituent element, $\Delta H_{at}^\ominus$
- the standard lattice enthalpy of the ionic compound, $\Delta H_{lat}^\ominus$.

- A **Born–Haber cycle** is a hypothetical series of steps representing the formation of an ionic compound.
- **Lattice enthalpy,** $\Delta H_{lat}^\ominus$, is the standard enthalpy change when 1 mol of gaseous ions is formed from the solid lattice and separated to an infinite distance from each other. $M_aX_b(s) \rightarrow aM^{b+}(g) + bX^{a-}(g)$



▲ **Figure 15.1.1.** A generalized Born–Haber cycle

Example 15.1.1.

a) Formulate an equation for the standard enthalpy change of formation of sodium chloride.

b) Construct a Born–Haber cycle for sodium chloride.

c) Calculate the lattice enthalpy for sodium chloride, in kJ mol^{-1}, using appropriate values from the data booklet and the following additional information:

$$\Delta H_f^{\ominus}(\text{NaCl}) = -411 \text{ kJ mol}^{-1}$$

$$\text{Na(s)} \rightarrow \text{Na(g)} \quad \Delta H_{sub}^{\ominus}(\text{Na}) = +108 \text{ kJ mol}^{-1}$$

Solution

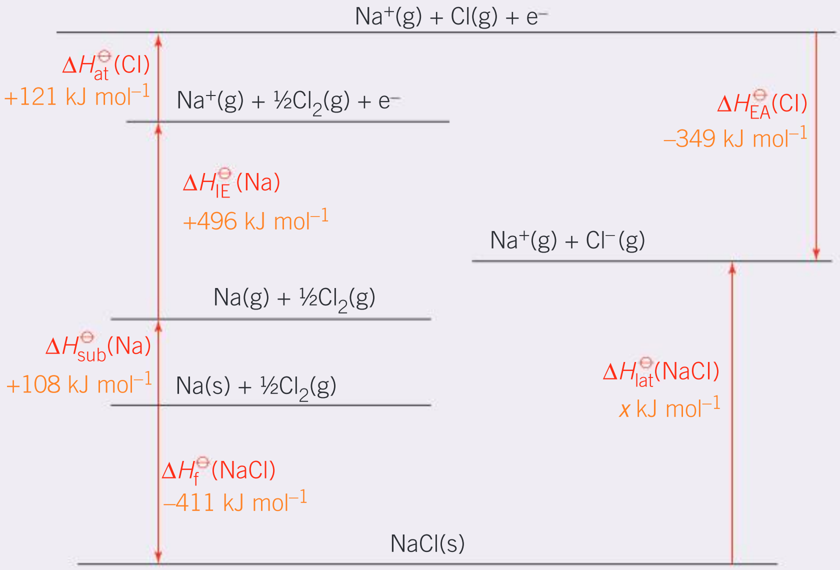
a) $\text{Na(s)} + \frac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{NaCl(s)}$

Assessment tip

When writing a thermochemical equation, remember to include the state symbols.

Remember that to find $\Delta H_{at}^{\ominus}$(Cl), you need to divide the bond dissociation enthalpy of the Cl–Cl bond by two (section 11 of the data booklet).

b)



▲ **Figure 15.1.2.** The Born–Haber cycle for sodium chloride

Ionization energies, electron affinities and bond enthalpies for Born–Haber cycles can be obtained from sections 8 and 11 of the data booklet.

c) To determine the lattice enthalpy for sodium chloride, the pathway in figure 15.1.2 should be followed, taking care to use the correct signs for the various enthalpy changes when finding the sum:

$$\begin{aligned}\Delta H_{lat}^{\ominus}(\text{NaCl}) &= -\Delta H_f^{\ominus}(\text{NaCl}) + \Delta H_{sub}^{\ominus}(\text{Na}) + \Delta H_{IE}^{\ominus}(\text{Na}) + \Delta H_{at}^{\ominus}(\text{Cl}) + \\ &\quad \Delta H_{EA}^{\ominus}(\text{Cl}) \\ &= -(-411) + 108 + 496 + 121 + (-349) = +787 \text{ kJ mol}^{-1}\end{aligned}$$

Lattice enthalpy and solution enthalpies

Lattice enthalpy, $\Delta H_{lat}^{\ominus}$, increases with increasing ionic charge and decreases with increasing ionic radius. Highly charged ions, and ions that are small and pack closely together, experience stronger electrostatic attraction.

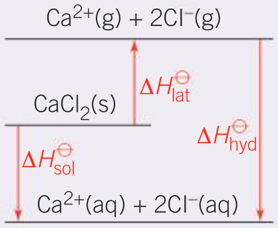
Lattice enthalpies calculated from Born–Haber cycles may differ from experimental lattice enthalpy values, suggesting that an ionic compound may have partial covalent character.

Atomic radii, ionic radii and ionization energies are discussed in topic 3.2, and bond enthalpies are considered in topic 5.3.

Lattice enthalpies can be determined from dissolution energy cycles, along with the *enthalpy change of solution* and the *enthalpy of hydration* (or solvation). The magnitude of the enthalpy of hydration increases with ionic charge, and decreases as the ionic radius increases.

Example 15.1.2.

Calculate the enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, for calcium chloride using the following enthalpy cycle:



▲ **Figure 15.1.3.** Solution enthalpy cycle for $CaCl_2$

Solution

$\Delta H^{\ominus}_{lat}(CaCl_2(s)) = +2271$ kJ mol^{-1} (section 18 of the data booklet)
$\Delta H^{\ominus}_{hyd}(CaCl_2) = -1616 + 2 \times (-359) = -2334$ kJ mol^{-1} (section 20)
$\Delta H^{\ominus}_{sol} = \Delta H^{\ominus}_{lat} + \Delta H^{\ominus}_{hyd} = +2271 + (-2334) = -63$ kJ mol^{-1}

- The **standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$**, is the change in enthalpy when 1 mol of a substance in its standard state is dissolved in a large excess of a pure solvent.
- The **enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$**, for an ion is the enthalpy change when 1 mol of the gaseous ion is added to water to form a dilute solution.

Assessment tip

When there is more than one of an ion in the formula unit, for example, the two chloride ions here, remember to multiply the hydration enthalpy accordingly.

TOPIC 15.2 ENTROPY AND SPONTANEITY

You should know:

- ✔ entropy, S, refers to the distribution of available energy among particles—the more ways energy can be distributed, the greater the entropy;
- ✔ under the same conditions, entropy is highest in gases and lowest in solids;
- ✔ the Gibbs free energy change, ΔG, tells us about the spontaneity of a reaction, and relates enthalpy change, entropy change and absolute temperature.

You should be able to:

- ✔ predict whether a change will result in an increase or decrease in entropy by considering the states of reactants and products;
- ✔ calculate the standard entropy change, $\Delta S^{\ominus}$, from the equation:

  $$\Delta S^{\ominus} = \Sigma[S^{\ominus}(\text{products})] - \Sigma[S^{\ominus}(\text{reactants})];$$
- ✔ apply the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ to solving numerical problems and predicting the spontaneity of a reaction under standard state conditions.

In accordance with the *second law of thermodynamics*, a chemical or physical change is spontaneous if it leads to an increase in the total *entropy* (system plus surroundings).

The entropy of a system increases from the solid to the liquid to the gaseous state. A reaction may increase or decrease the entropy of the system if the states of reactants and products differ. The standard entropy change, $\Delta S^{\ominus}$, can be calculated from the equation:

$$\Delta S^{\ominus} = \Sigma[S^{\ominus}(\text{products})] - \Sigma[S^{\ominus}(\text{reactants})].$$

Whether a reaction will occur spontaneously depends on:

- the enthalpy change, ΔH (endo- or exothermic?)
- the entropy change, ΔS (increasing or decreasing?)
- the temperature, T (measured in kelvins).

- The **second law of thermodynamics** states that a spontaneous process always increases the total entropy of the universe at the expense of energy available to do useful work.
- **Entropy, S,** refers to the distribution of available energy among particles; the more ways energy can be distributed, the greater the entropy. It can be thought of as a measure of disorder.

Thermochemistry was first introduced in topic 5, and equilibrium was considered in topic 7.

The **change in Gibbs free energy, ΔG**, for a reaction indicates the spontaneity of a reaction, and is calculated from $\Delta G = \Delta H - T\Delta S$.

These factors are combined in the equation for the change in Gibbs free energy, ΔG:

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

If ΔG is negative, the reaction is spontaneous; if ΔG is positive, the reaction is non-spontaneous; if $\Delta G = 0$, the system is at equilibrium.

Example 15.2.1.

Predict the sign of ΔS for each of the following processes:

a) $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$

b) $H_2O(l) \rightarrow H_2O(s)$

c) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Solution

To answer this type of question you need to consider the states of the reactants and products.

a) On the reactant side there is a solid and a gas, but on the product side both species are gaseous. Gaseous species are more disordered than solid species, so ΔS is positive.

b) In this reaction liquid water is converted to ice. As solids are more ordered than liquids, ΔS is negative.

c) In this reaction all species are gaseous, but the number of species decreases from two to one. Therefore, the entropy decreases, so ΔS is negative.

Assessment tip

When carrying out calculations in thermodynamics:

- use the correct units for temperature – convert °C to K
- consider the stoichiometric coefficients of reagents in ΔH, ΔS and ΔG calculations;
- check that the units of ΔH and ΔS correspond (kJ mol^{-1} and kJ K^{-1} mol^{-1} or J mol^{-1} and J K^{-1} mol^{-1}).

SAMPLE STUDENT ANSWER

The reaction for the formation of liquid tetracarbonylnickel is shown below:

$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(l)$

a) Calculate the standard entropy change, $\Delta S^\ominus$, of the reaction in J K^{-1}, using the values given. [2]

	$S^\ominus$ / J K^{-1} mol^{-1}
Ni(s)	29.9
CO(g)	197.6
$Ni(CO)_4(l)$	313.4

b) Calculate the $\Delta H^\ominus$ value, in kJ, of the reaction. [1]

	$\Delta H_f^\ominus$ / kJ mol^{-1}
CO(g)	−110.5
$Ni(CO)_4(l)$	−633.0

c) Use your answers to (a) and (b) to determine the temperature, in °C, at which the decomposition of liquid tetracarbonylnickel to nickel and carbon monoxide becomes favourable.

(If you did not get answers to (a) and (b), use −500 J K^{-1} and −200 kJ respectively, but these are not the correct answers.) [3]

This answer could have achieved 3/6 marks:

a) $\Delta S^\ominus = \Sigma[S^\ominus(\text{products})] - \Sigma[S^\ominus(\text{reactants})]$

$= 313.4 - (29.9 + 4 \times 197.6) = -506.9\ \text{J K}^{-1}$

b) $\Delta H^\ominus = \Sigma[\Delta H^\ominus(\text{products})] - \Sigma[\Delta H^\ominus(\text{reactants})]$

$= -633.0 - 4 \times (-110.5) = -191.0\ \text{kJ}$

c) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus < 0$,

so $T < \Delta H^\ominus / \Delta S^\ominus$

$= -191.0/(-506.9) = 0.3768\ \text{K}$

▲ Correct answer

▲ The stoichiometric coefficients of all reagents have been taken into account

▲ Correct answer

▼ The student has not stated that $\Delta G^\ominus = 0$ at equilibrium (where the forward and reverse reactions are equally favourable);

▼ The units for $\Delta H^\ominus$ and $\Delta S^\ominus$ are inconsistent ($\Delta H^\ominus$ is in kJ and $\Delta S^\ominus$ is in J K^{-1}) so in fact $T = -191.0 \times 10^3/(-506.9) \approx 377\ \text{K}$

▼ The calculated temperature is expressed in K, and the question requires the final answer to be in °C, so the correct answer is $T = 377 - 273 = 104\,°\text{C}$

Practice problems for Topic 15

Problem 1

a) Formulate an equation for the standard enthalpy change of formation of calcium oxide.

b) Construct a Born–Haber cycle for calcium oxide.

c) Calculate the lattice enthalpy for calcium oxide, in kJ mol^{-1}, using appropriate values from the data booklet and the following additional information:

$\Delta H_f^\ominus(\text{CaO(s)}) = -635\ \text{kJ mol}^{-1}$

$\text{Ca(s)} \rightarrow \text{Ca(g)} \quad \Delta H_{sub}^\ominus(\text{Ca}) = +155\ \text{kJ mol}^{-1}$

$\Delta H_{IE2}^\ominus(\text{Ca}) = +1146\ \text{kJ mol}^{-1}$

Problem 2

List the ionic compounds MgO, SrO, KI and KF in order of decreasing lattice enthalpy.

Problem 3

Which process has the greatest increase in entropy at constant temperature?

A. $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$

B. $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)}$

C. $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(s)}$

D. $\text{CaO(s)} + \text{SO}_3\text{(g)} \rightarrow \text{CaSO}_4\text{(s)}$

Problem 4

Consider the following reaction:

$\text{CaO(s)} + \text{SO}_3\text{(g)} \rightarrow \text{CaSO}_4\text{(s)}$

a) Calculate the standard entropy change, $\Delta S^\ominus$, of the reaction in J K^{-1}, using the values given in the table.

	$S^\ominus$ / J K^{-1} mol^{-1}	$\Delta H_f^\ominus$ / kJ mol^{-1}
$\text{CaSO}_4\text{(s)}$	106.5	−1434.5
$\text{SO}_3\text{(g)}$	256.8	−395.7
CaO(s)	38.1	−634.9

b) (i) Calculate the standard enthalpy change, $\Delta H^\ominus$, of the reaction in kJ, using the values given in the table.

(ii) Deduce whether the reaction is exothermic or endothermic.

c) (i) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, of the reaction in kJ.

(ii) Comment on the spontaneity of the reaction.

16 CHEMICAL KINETICS (AHL)

TOPIC 16.1 RATE EXPRESSION AND REACTION MECHANISM

You should know:

- ✔ the rate equation expresses the reaction rate as a function of reactant concentrations;
- ✔ the reaction order is the sum of exponents in the rate equation;
- ✔ the value of the rate constant, k, depends on temperature, and the units of k are determined from the overall order of the reaction;
- ✔ the rate-determining step (RDS) is the slowest reaction step;
- ✔ a catalyst alters the reaction mechanism by introducing a new RDS with a lower activation energy;
- ✔ the molecularity of an elementary reaction is the number of reactant particles taking part in the reaction.

You should be able to:

- ✔ deduce rate equations from experimental data;
- ✔ solve problems involving rate equations;
- ✔ sketch, identify and analyse graphical representations for zero-, first- and second-order reactions;
- ✔ evaluate proposed reaction mechanisms using kinetic and stoichiometric data.

- The **rate equation**, also known as the **rate law**, links the reaction rate (v), the **rate constant** (k) and the reactant concentrations [A] and [B] as follows: $v = k[A]^n[B]^m$.
- The **reaction order** with respect to a particular reactant is the exponent of that reactant in the rate equation.
- The **overall reaction order** is the sum of all exponents in the rate equation.

The *rate equation*, also known as the *rate law*, is a mathematical expression that describes how the reaction rate depends on the concentrations of reactants. In the general case, the reaction and its rate equation are:

$$aA + bB \rightarrow xX + yY$$

$$v = k[A]^n[B]^m$$

In the above expression, k is the *rate constant*, [A] and [B] are the reactant concentrations, and n and m are the *reaction orders* with respect to each reactant. The *overall reaction order* is the sum of all exponents in the rate equation.

The rate constant and reaction orders can be determined experimentally by measuring the reaction rates at different concentrations of the reactants (example 16.1.1). As the name suggests, rate constants are not affected by concentration. However, they do vary with temperature (topic 16.2).

Assessment tip

Reaction orders can only be determined experimentally; they *cannot* be deduced from the reaction stoichiometry, as in many cases $n \neq a$ and $m \neq b$.

Fractional orders are known, but only whole-number orders (0, 1 or 2) will be assessed in IB examinations.

Example 16.1.1.

Nitrogen(II) oxide reacts with chlorine as follows:

$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

The following experimental data were obtained for this reaction at 260 K:

[NO] / mol dm^{-3}	$[Cl_2]$ / mol dm^{-3}	v / mol dm^{-3} min^{-1}
0.15	0.15	0.53
0.15	0.30	1.06
0.30	0.30	4.24

a) Deduce the reaction orders with respect to Cl_2 and NO.

b) State the rate expression and the overall reaction order.

c) Calculate the value of the rate constant at 260 K.

Solution

a) When $[Cl_2]$ doubles (increases from 0.15 to 0.30 mol dm^{-3}), the rate also doubles (increases from 0.53 to 1.06 mol dm^{-3} min^{-1}). Therefore, the reaction is first order with respect to Cl_2.

When [NO] doubles, the rate increases four times (from 1.06 to 4.24 mol dm^{-3} min^{-1}). Therefore, the reaction is second order with respect to NO.

b) Rate expression: $v = k[NO]^2[Cl_2]$.

Overall reaction order: 2 + 1 = 3. Note that the exponent of $[Cl_2]$ is 1, which is not written in the rate expression, but contributes to the overall reaction order.

c) The value of k does not depend on concentrations, so we can use data from any row of the table. The first row gives the following: $k = \dfrac{0.53 \text{ mol dm}^{-3} \text{ min}^{-1}}{(0.15 \text{ mol dm}^{-3})^2 \times 0.15 \text{ mol dm}^{-3}} \approx 1.6 \times 10^2 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$.

The reaction order can also be determined from rate–concentration and concentration–time graphs (figure 16.1.1). However, the concentration–time curves for the first- and second-order reactions look similar, so they cannot be distinguished from sketches. These reactions are often represented by the linear plots $\ln[A] = -kt + \ln[A]_0$ (first order) and $\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$ (second order), shown in figure 16.1.2.

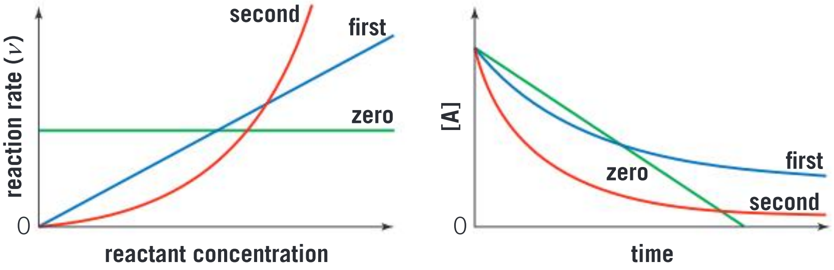


Figure 16.1.1. The rate–concentration and concentration–time graphs for zero-, first- and second-order reactions

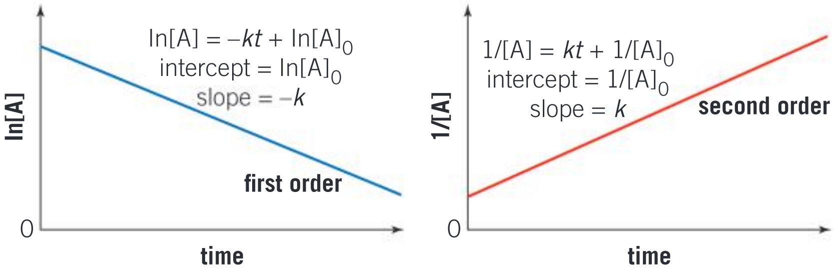


Figure 16.1.2. Linear plots for first-order (left) and second-order (right) reactions; [A] and $[A]_0$ are the actual and initial concentrations of reactant A, respectively, k is the rate constant and t is time

The **rate-determining step (RDS)** is the slowest step in a multi-step reaction mechanism. It controls the rate of the overall reaction.

Many reactions have a mechanism with more than one step, and each step has its own rate constant. The slowest step, known as the *rate-determining step (RDS)*, limits the overall reaction rate.

Mechanisms of organic reactions are discussed in topic 20.1.

Example 16.1.2.

The reaction from example 16.1.1 proceeds in two steps:

Step 1: $2NO(g) \rightleftharpoons N_2O_2(g)$

Step 2: $N_2O_2(g) + Cl_2(g) \rightarrow 2NOCl(g)$

Using the rate expression $v = k[NO]^2[Cl_2]$, identify the rate-determining step (RDS) in this reaction.

Solution

If step 1 were the slower step, the reaction rate would be independent of $[Cl_2]$, and the rate expression would be $v = k[NO]^2$. This contradicts the experimental data, so our hypothesis is incorrect, and the RDS is step 2. Indeed, if step 1 is fast, $[N_2O_2]$ is proportional to $[NO]^2$, so $v = k'[N_2O_2][Cl_2] = k[NO]^2[Cl_2]$.

Activation energy, catalysis and catalysts are introduced in topic 6.1. Activation energy is discussed in greater detail in topic 16.2 below, and catalysis in topic A.3.

- In an **elementary reaction** the reactants are transformed into products in a single step.
- The reaction **molecularity** is the number of reactant particles involved in an elementary reaction: **unimolecular** (one reactant particle), **bimolecular** (two), or **termolecular** (three).

Typically, the RDS has the highest activation energy, E_a, of all the reaction steps. A catalyst alters the reaction mechanism by introducing a new RDS with a new $E_a' < E_a$, thus increasing the overall reaction rate.

Elementary reactions proceed in one step. The number of reactant particles involved in that step is known as the reaction *molecularity*: *unimolecular* reactions involve a single reactant particle, *bimolecular* reactions involve two. *Termolecular* reactions are extremely rare, as the probability of three particles colliding at the same time is very low.

Individual steps in stepwise reactions can also be characterized by molecularity. For example, each step in the reaction from example 16.1.2 is a bimolecular process.

Assessment tip

Reaction molecularity must not be confused with reaction order. Molecularity can be deduced from the reaction mechanism but *not* from the reaction rate equation. In turn, the rate equation can be used for evaluating the reaction mechanism but not for proving it.

TOPIC 16.2 ACTIVATION ENERGY

You should know:

- ✔ the Arrhenius equation, $k = Ae^{-\frac{E_a}{RT}}$, shows the temperature dependence of the rate constant;
- ✔ a graph of ln k against $1/T$ is a linear plot with the gradient $-E_a/R$ and the intercept ln A;
- ✔ the pre-exponential factor, A, takes into account the symmetry and frequency of collisions of reacting particles.

You should be able to:

- ✔ solve problems involving the Arrhenius equation;
- ✔ analyse graphical representation of the Arrhenius equation in its linear form, $\ln k = -\frac{E_a}{RT} + \ln A$;
- ✔ describe the relationships between temperature and rate constant and between the pre-exponential factor and the complexity of colliding molecules;
- ✔ determine the activation energy and pre-exponential factor from experimental data.

The kinetic theory predicts that the rates of chemical reactions increase with temperature owing to higher frequency of successful collisions between reactant particles. This conclusion is expressed quantitatively by the *Arrhenius equation*, $k = Ae^{-\frac{E_a}{RT}}$, in which k is the reaction rate, E_a is the activation energy, R is the gas constant and T is temperature in kelvins. The pre-exponential factor A accounts for the frequency of collisions and the symmetry of reacting particles.

For simple and highly symmetrical reactant particles, such as individual atoms or diatomic molecules, A values are high, because collisions can lead to reaction of the particles at any mutual orientation. In contrast, reactions between large organic molecules occur only at specific orientation, so their rate constants have lower A values.

We can determine the activation energy of a reaction from the Arrhenius equation if we have k values (or their ratio) for the reaction at two different temperatures. The two Arrhenius equations for k_1 (at T_1) and k_2 (at T_2) can be combined as follows:

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The rearrangement of this equation gives the E_a value:

$$E_a = \frac{\ln\frac{k_1}{k_2} \times R}{\frac{1}{T_2} - \frac{1}{T_1}}$$

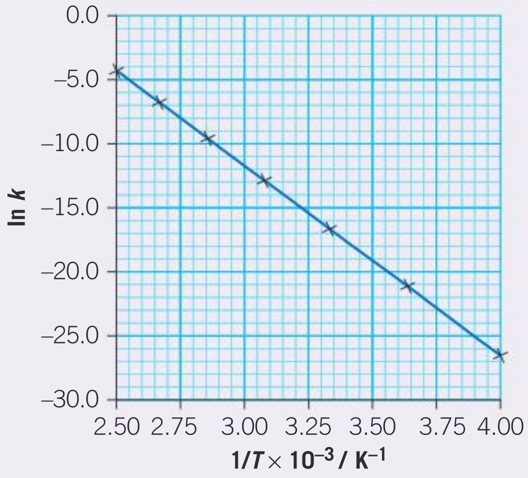
Alternatively, both the pre-exponential factor and the activation energy can be determined from the linear form of the Arrhenius equation, $\ln k = -\frac{E_a}{RT} + \ln A$, as shown in the example below.

Example 16.2.1.

The decomposition of organic peroxides produces highly reactive radicals, for example:

$CH_3C(O)OOC(O)CH_3 \rightarrow 2CH_3C(O)O\cdot$

The kinetic data for this reaction are shown in figure 16.2.1. Determine the activation energy, E_a, and the pre-exponential factor, A, for this reaction.



▲ **Figure 16.2.1.** Plot of ln k against $1/T$ for the decomposition of the organic peroxide $CH_3C(O)OOC(O)CH_3$

Collision theory is discussed in topic 6.1. The Arrhenius equation and the value of R are given in sections 1 and 2, respectively, of the data booklet.

Assessment tip

In all IB Chemistry problems, it is assumed that both A and E_a are independent of temperature.

The equation $\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is given in section 1 of the data booklet.

Assessment tip

If the concentrations of all reactants are kept constant, the reaction rate has the same temperature dependence as the rate constant: $\frac{v_1}{v_2} = \frac{k_1}{k_2}$.

Therefore, E_a can be determined from the reaction rates (instead of rate constants) at two different temperatures.

Assessment tip

The E_a values of many chemical reactions fall into a narrow range, so the rates of different reactions show similar temperature dependence. In most cases, the reaction rate approximately doubles when the temperature increases by 10 K (10°C).

Solution

The linear form of the Arrhenius equation, $\ln k = -\frac{E_a}{RT} + \ln A$, can be represented as $y = mx + b$, where $y = \ln k$, $m = -\frac{E_a}{R}$, $x = \frac{1}{T}$, and $b = \ln A$. The slope $(-\frac{E_a}{R})$ gives the activation energy while the intercept ($\ln A$) gives the pre-exponential factor.

To find the slope, we select any two points on the line: for example, (2.50, −4.3) and (4.00, −26.5):

$$-\frac{E_a}{R} = \frac{-26.5 - (-4.3)}{(4.00 - 2.50) \times 10^{-3}\,\text{K}^{-1}} = -1.48 \times 10^{4}\,\text{K}$$

Note that the units for $1/T$ on the plot are $10^{-3}\,\text{K}^{-1}$.

$E_a = -1.48 \times 10^4\,\text{K} \times (-8.31\,\text{J mol}^{-1}\,\text{K}^{-1}) \approx 1.23 \times 10^5\,\text{J mol}^{-1} = 123\,\text{kJ mol}^{-1}$

To find the intercept (when $1/T = 0$), we need to select any point on the line, for example, (2.50, −4.3), and solve the Arrhenius equation:

$$-4.3 = -\frac{1.23 \times 10^5\,\text{J mol}^{-1}}{8.31\,\text{J K}^{-1}\text{mol}^{-1}} \times 2.50 \times 10^{-3}\,\text{K}^{-1} + \ln A$$

$\ln A \approx -4.3 - (-37.0) = 32.7$

$A = e^{32.7} \approx 1.6 \times 10^{14}$

Note that the pre-exponential factor has a very large value.

SAMPLE STUDENT ANSWER

The reaction between hydrogen and nitrogen monoxide is thought to proceed by the mechanism shown below.

$2NO(g) \rightleftharpoons N_2O_2(g)$ fast equilibrium

$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ slow reaction

$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ fast reaction

a) State the equation for the overall reaction. [1]

b) Deduce the rate expression consistent with this mechanism. [1]

c) Explain how you would attempt to confirm this rate expression, giving the results you would expect. [3]

d) State, giving your reason, whether confirmation of the rate expression would prove that the mechanism given is correct. [1]

This answer could have achieved 2/6 marks:

a) $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

b) rate = $k[NO]^2[H_2]^2$

c) I would check how the rate changes when concentrations change. When [NO] doubles, the rate should quadruple, and so on.

d) If experimental data agree with the rate expression, the mechanism is correct.

▲ Correct equation, deduced by adding together the equations for all three steps

▼ The student has derived the exponents in the rate expression from the stoichiometric coefficients, which is wrong; instead, the slow RDS involves one $H_2(g)$ molecule and an $N_2O_2(g)$ molecule formed from two NO(g) molecules, so the correct expression is rate = $k[NO]^2[H_2]$

▼ The first statement is too vague, as the effect of each concentration change must be tested separately

▲ Correct prediction of the effect of [NO]

▼ The effect of $[H_2]$ is not predicted

▼ Like any scientific theory, the reaction mechanism can only be disproved, not proved; other mechanisms might give the same rate expression

Practice problems for Topic 16

Problem 1

The data below show the effect of reactant concentrations on the reaction rate at 25°C.

$F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g)$

Initial $[F_2]$ / mol dm^{-3}	Initial $[ClO_2]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} min^{-1}
0.10	0.010	1.2×10^{-3}
0.10	0.030	3.6×10^{-3}
0.15	0.010	1.8×10^{-3}

Which of the following is correct?

	Order with respect to $ClO_2(g)$	Overall reaction order
A.	1	1
B.	1	2
C.	2	2
D.	2	3

Problem 2

Consider the reaction between nitrogen dioxide and carbon monoxide.

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Experimental data show that the reaction is second order with respect to NO_2 and zero order with respect to CO.

a) State the rate expression for the reaction.

b) Deduce the units for the rate constant, *k*, in the reaction.

c) The following mechanism has been proposed for the reaction.

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

Identify the rate-determining step (RDS), giving your reason.

d) Sketch the relationship between the rate of reaction and the concentration of NO_2.

e) Outline the effect of a catalyst on the mechanism and RDS of this reaction.

Problem 3

The rate of a chemical reaction increases 7.8 times when the temperature rises from 25.0 to 45.0°C.

a) Calculate the activation energy, in kJ mol^{-1}, for the reaction (use sections 1 and 2 of the data booklet).

b) Describe how the pre-exponential factor for this reaction could be determined.

17 EQUILIBRIUM (AHL)

TOPIC 17.1 THE EQUILIBRIUM LAW

You should know:

- ✔ Le Châtelier's principle for changes in concentration can be explained by the equilibrium law;
- ✔ a system at equilibrium has maximum entropy and minimum Gibbs free energy;
- ✔ the position of equilibrium in a reversible reaction can be measured by the Gibbs free energy change and the equilibrium constant, which are related by the equation $\Delta G^{\ominus} = -RT \ln K$.

You should be able to:

- ✔ solve homogeneous equilibrium problems using the K_c expressions;
- ✔ calculate Gibbs free energy changes and K_c values using the equation $\Delta G^{\ominus} = -RT \ln K$.

The equilibrium law and Le Châtelier's principle are discussed in topic 7.1.

Equilibrium calculations

For reversible reactions, the position of equilibrium can be quantified by the equilibrium law. The K_c value depends only on temperature but not on other reaction conditions, such as pressure or concentrations. Therefore, it can be used to determine the composition of the reaction mixture at equilibrium.

Example 17.1.1.

Nitrogen dioxide, $NO_2(g)$, was cooled to +10°C in a sealed vessel until reached equilibrium with dinitrogen tetroxide, $N_2O_4(g)$:

$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = 11.5$

a) Deduce the K_c expression for this reaction.

b) Calculate the equilibrium concentration of $NO_2(g)$ if the equilibrium concentration of $N_2O_4(g)$ was 0.041 mol dm^{-3}.

c) Calculate the initial concentration of $NO_2(g)$.

Solution

a) $K_c = \dfrac{[N_2O_4]}{[NO_2]^2}$

b) $[NO_2]^2 = \dfrac{[N_2O_4]}{K_c} = \dfrac{0.041}{11.5} \approx 0.00357$

$[NO_2] = \sqrt{0.00357} \approx 0.060 \text{ mol dm}^{-3}$

c) According to the chemical equation, the formation of each mole of $N_2O_4(g)$ consumes two moles of $NO_2(g)$. Therefore:

$[NO_2]_{\text{initial}} = [NO_2] + 2 \times [N_2O_4] = 0.060 + 2 \times 0.041 = 0.142 \text{ mol dm}^{-3}$

Gibbs free energy change

The standard Gibbs free energy change (ΔG°) of a reaction and the equilibrium constant (K_c) can both be used to measure the position of the equilibrium, as shown in the sample exam question below. These two parameters are related by the equation:

$$\Delta G^\circ = -RT \ln K_c$$

The equilibrium state is characterized by the lowest possible G value and the highest possible entropy (S) value of the system (table 17.1.1). In other words, in this state the system is the most stable.

State of the system	***G***	***S***	Q_c
forward reaction favoured	above minimum	below maximum	$Q_c < K_c$
equilibrium	minimum	maximum	$Q_c = K_c$
reverse reaction favoured	above minimum	below maximum	$Q_c > K_c$

▲ **Table 17.1.1.** Thermodynamic functions, reaction quotient and equilibrium

SAMPLE STUDENT ANSWER

Phosgene, $COCl_2$, is usually produced by the reaction between carbon monoxide and chlorine according to the equation:

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

a) Deduce the equilibrium constant expression, K_c, for this reaction. [1]

b) At exactly 600°C the value of the equilibrium constant is 0.200. Calculate the standard Gibbs free energy change, ΔG°, for the reaction, in kJ, using sections 1 and 2 of the data booklet. State your answer to three significant figures. [3]

This answer could have achieved 2/4 marks:

a) $K_c = \dfrac{[COCl_2]}{[CO]+[Cl_2]}$

b) $T = 600 + 273 = 873\ K$

$\Delta G^\circ = -8.31 \times 873 \times \ln 0.200 \approx 1.17 \times 10^4\ kJ$

▼ A + sign appears in the denominator (this is a common error in K_c expressions)

▲ Correct conversion of temperature to kelvins

▼ The expression $\Delta G^\circ = -RT \ln K$ gives the ΔG° value in J, not kJ—the correct answer is 11.7 kJ

Assessment tip

In calculations, the K_c values are treated as unitless quantities. However, all equilibrium concentrations must still be expressed using appropriate units (typically, mol dm^{-3}).

Homogeneous equilibria involving weak acids and bases are discussed in topic 18.2.

Gibbs free energy, entropy and spontaneity are discussed in topic 15.2. The expression $\Delta G^\circ = -RT \ln K$ is given in section 1 of the data booklet. The reaction quotient, Q_c, is discussed in topic 7.1.

Practice problems for Topic 17

Problem 1

One mole of compound **X** was mixed with two moles of compound **Y** in a sealed 1.0 dm^3 vessel and heated up to a certain temperature. When equilibrium was reached, the vessel contained 0.25 moles of compound **Z**:

$2X(g) + Y(g) \rightleftharpoons Z(g)$

What is the K_c value at this temperature?

A. 0.25

B. 0.29

C. 0.57

D. 1.75

Problem 2

The ΔG° value for the following reaction at 650°C is −25.2 kJ.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

a) Calculate the K_c value for this reaction at 650°C.

b) Comment on the value of ΔG when the reaction quotient equals the equilibrium constant, $Q_c = K_c$.

18 ACIDS AND BASES (AHL)

TOPIC 18.1 LEWIS ACIDS AND BASES

You should know:

- ✔ a Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor;
- ✔ when a Lewis acid reacts with a Lewis base, a coordinate bond is formed.

You should be able to:

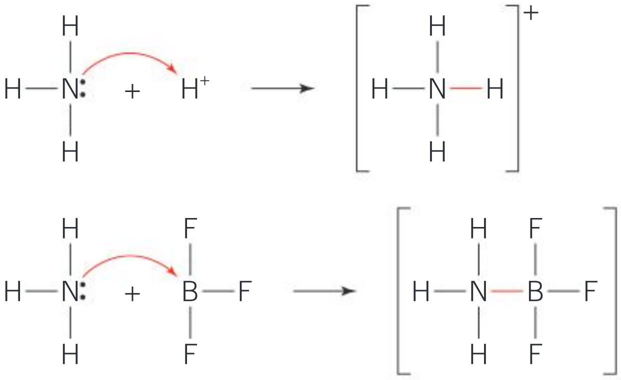
- ✔ identify inorganic and organic species that can act as Lewis acids and bases.

The Arrhenius and Brønsted–Lowry theories of acids and bases are described in topic 8.1.

Lewis theory does not falsify the Brønsted-Lowry theory but rather expands it to a broader range of acidic and basic species. The NH_3 in the first reaction is both a Lewis and a Brønsted–Lowry base, as it accepts a proton. In the second reaction NH_3 acts as a Lewis base but **not** as a Brønsted–Lowry base, as it does not accept a proton. Both H^+ and BF_3 are Lewis acids but **not** Brønsted–Lowry acids, as they do not donate protons to other species.

Coordinate bonds are common in transition metal complexes (topic 13), where the metal ion acts as a Lewis acid while ligands act as Lewis bases.

The acid–base concept can be extended beyond the Brønsted–Lowry theory to include reactions that do not involve proton transfer. According to the Lewis theory, any species that accepts an electron pair is an acid while any species that donates an electron pair is a base. In the following reactions, ammonia acts as a Lewis base while the hydrogen cation and boron trifluoride act as Lewis acids:



The *coordinate bonds* formed in these reactions are indistinguishable from "normal" covalent bonds, as they also involve shared electron pairs.

- A **coordinate bond**, formerly known as a **dative bond**, is a covalent bond formed from a lone electron pair of one atom and an empty electron orbital of another atom. In structural formulas, coordinate bonds are sometimes drawn as arrows.
- An **electrophile** is a species that is attracted to electrons. All Lewis acids are electrophiles.
- A **nucleophile** is a species that donates an electron pair to an electrophile. All Lewis bases are nucleophiles.

Example 18.1.1.

Suggest, with a reason, whether beryllium dihydride, methane and water can act as Lewis acids and/or bases.

Solution

BeH_2 is a Lewis acid because empty 2p orbitals in the beryllium atom can accept electron pairs. H_2O is a Lewis base because the oxygen atom can donate its lone electron pairs to other species. The carbon atom in CH_4 has neither empty orbitals nor lone electron pairs, so methane cannot act as a Lewis acid or base.

TOPIC 18.2 CALCULATIONS INVOLVING ACIDS AND BASES

You should know:

- ✔ weak acids and bases are characterized by their dissociation constants K_a and K_b, respectively;
- ✔ $pK_a = -\log K_a$ and $pK_b = -\log K_b$;
- ✔ for a conjugate acid–base pair in an aqueous solution at 25°C, $K_a \times K_b = 1.00 \times 10^{-14}$ and $pK_a + pK_b = 14$.

You should be able to:

- ✔ solve problems involving $[H^+]$, $[OH^-]$, pH, pOH, K_a, pK_a, K_b and pK_b;
- ✔ discuss the relative strengths of acids and bases using their K_a, pK_a, K_b and pK_b values.

Acid–base equilibria can be characterized quantitatively by the *acid dissociation constant* (K_a) and *base ionization constant* (K_b), which are defined as follows:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

weak acid conjugate base

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

weak base conjugate acid

The shorthand version of the first equation uses $H^+(aq)$ instead of $H_3O^+(aq)$:

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

weak acid conjugate base

In most practical situations we can assume that for a weak acid $[H^+] \approx [A^-] << [HA]$ and so $[H^+] \approx \sqrt{K_a \times [HA]}$. Similarly, for a weak base $[OH^-] \approx [BH^+] << [B]$ and so $[OH^-] \approx \sqrt{K_b \times [B]}$. These expressions can be used for calculating the concentrations of ions or pH and pOH values in solutions of weak acids and bases.

Acid–base equilibria and conjugate acid–base pairs are discussed in topics 8.1 and 8.4. The concept of pH is introduced in topic 8.3.

Assessment tip

Both variants of the K_a definition are equally acceptable in answers to IB Chemistry examinations. Note that water is not included in the K_a and K_b expressions, as its concentration in dilute solutions is assumed to be constant.

Assessment tip

The pH and pOH calculations can be simplified by using the logarithmic expressions $pH = 0.5(pK_a - \log [HA])$ and $pOH = 0.5(pK_b - \log [B])$. However, these expressions are not given in the data booklet, so you will need either to memorize or derive them, or use the traditional approach adopted in the IB Chemistry course.

Example 18.2.1.

Calculate the pH values for 0.0100 mol dm^{-3} solutions of ethanoic acid, CH_3COOH, and ethylamine, $C_2H_5NH_2$, at 25°C. Use section 21 of the data booklet.

Solution

Ethanoic acid (weak acid):

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

From the data booklet, $pK_a(CH_3COOH) = 4.76$, so $K_a = 10^{-4.76} \approx 1.7 \times 10^{-5}$

$[H^+] \approx \sqrt{1.7 \times 10^{-5} \times 0.0100} \approx 4.1 \times 10^{-4}$ mol dm^{-3}

$pH = -\log(4.1 \times 10^{-4}) \approx 3.38$

Ethylamine (weak base):

$C_2H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$

From the data booklet, $pK_b(C_2H_5NH_2) = 3.35$, so $K_b = 10^{-3.35} \approx 4.5 \times 10^{-4}$

$[OH^-] \approx \sqrt{4.47 \times 10^{-4} \times 0.0100} \approx 2.1 \times 10^{-3}$ mol dm^{-3}

$pOH = -\log(2.1 \times 10^{-3}) \approx 2.68$

$pH = 14 - pOH = 14 - 2.68 = 11.32$

Assessment tip

Relative strengths of weak acids and bases can be compared using their ionization constants. The stronger the acid, the higher its K_a value and the lower its pK_a value. Similarly, the stronger the base, the higher its K_b value and the lower its pK_b value. Stronger acids produce weaker conjugate bases, and stronger bases produce weaker conjugate acids.

The dissociation and ionization of weak acids, bases and water are endothermic processes, so their K_a, K_b and K_w values increase with temperature, while pK_a, pK_b and pK_w decrease. All pH and pOH calculations at temperatures other than 25°C (298 K) remain the same, except that the formulas $[H^+][OH^-] = 1.00 \times 10^{-14}$ and $pH + pOH = 14$ cannot be used. For example, at 35°C the K_w value is 2.09×10^{-14}, so in a dilute solution at that temperature $[H^+][OH^-] = 2.09 \times 10^{-14}$ and thus $pH + pOH = -\log(2.09 \times 10^{-14}) \approx 13.680$.

TOPIC 18.3 pH CURVES

You should know:

- ✔ the shape of a pH curve from a neutralization reaction depends on the strengths of the acid and base used in the titration;
- ✔ buffer solutions resist pH changes upon addition of small amounts of acids or bases;
- ✔ an acid–base indicator is a weak acid or a weak base that has a conjugate of a different colour;
- ✔ an acid–base indicator changes its colour over a pH interval $pK_a \pm 1$.

You should be able to:

- ✔ sketch typical pH curves and explain their features;
- ✔ identify an appropriate acid–base indicator for a titration;
- ✔ explain how buffer solutions can be prepared from acids, bases and salts;
- ✔ predict the pH of aqueous solutions of salts formed by strong and weak acids and bases.

Titration

In a typical *titration* experiment, a solution of an acid or base with unknown concentration is neutralized by a *standard* solution of a base or acid, respectively, which is added dropwise.

Acid–base titrations are discussed in topics 1.3 and 8.2.

The progress of the neutralization can be represented by a *titration curve*, which shows the pH of the reaction mixture as a function of the added volume of the standard solution.

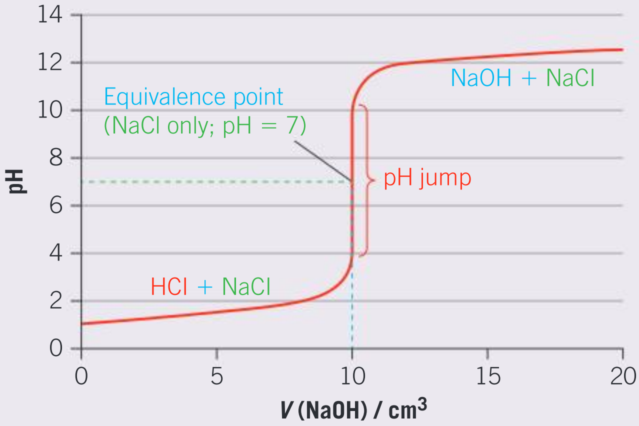
Example 18.3.1.

a) Sketch and annotate the pH curve for the titration of 10.0 cm^3 of 0.10 mol dm^{-3} HCl with 0.10 mol dm^{-3} NaOH.

b) Describe how the shape of the pH curve will differ if the solution of HCl(aq) from part (a) is added to the solution of NaOH(aq) of the same concentration.

Solution

a) At the beginning of the titration the solution of known volume contains only HCl(aq), so the curve begins at $pH = -\log(0.10) = 1.00$. Initially the curve is almost horizontal. Approaching the equivalence point at $V(NaOH) = 10.0\ cm^3$ the pH rises sharply to 7.0, where the mixture contains only NaCl(aq). Immediately after the equivalence point the curve continues to rise sharply. When a large excess of the titrant NaOH has been added, the curve flattens out and gradually comes close to the pH of the standard NaOH(aq) solution ($14 + \log(0.10) = 13.00$) (figure 18.3.1).



▲ **Figure 18.3.1.** The pH curve for titration of 10.0 cm^3 of 0.10 mol dm^{-3} HCl(aq) with 0.10 mol dm^{-3} NaOH(aq)

b) The new pH curve will be nearly a mirror image of that shown in figure 18.3.1. It will begin almost horizontally at $pH = 13.0$, fall sharply near the equivalence point ($V(HCl) = 10.0\ cm^3$, $pH = 7.0$) and then flatten out, gradually approaching $pH = 1.0$.

If either the acid or the base used in the titration experiment is weak, equivalence will be achieved at $pH \neq 7$. A salt of a weak acid and a strong base will produce a slightly basic solution ($pH > 7$), while a salt of a strong acid and a weak base will produce a slightly acidic solution ($pH < 7$). In both cases the "pH jump" around the equivalence point in the titration curve will be less pronounced, and the curve will have an

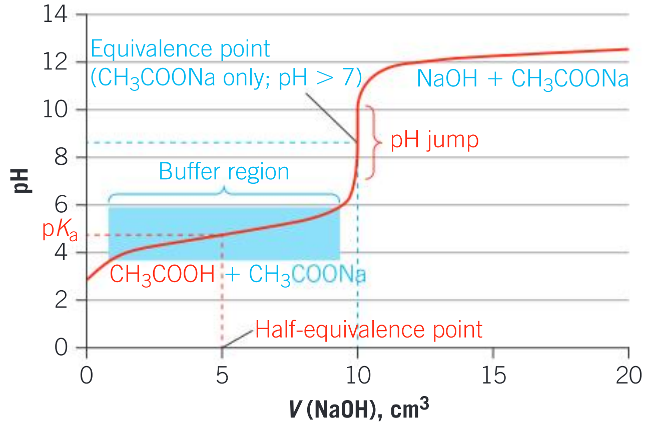
- A **standard solution** is a solution of a reagent (**titrant**), such as an acid or a base, with known concentration.
- **Titration** is a method of determining the unknown concentration of a substance (**analyte**) in a certain volume of its solution by gradual addition of a standard solution.
- A **titration curve** is a plot of the solution pH (or any other characteristic) against the added volume of the standard solution. For pH, it is also known as a **pH curve**.
- The **equivalence point** is the point at which the analyte is completely neutralized by the titrant.

A **buffer region** of a pH curve is produced when the reaction mixture contains a conjugate acid–base pair where both components of the pair are weak electrolytes. For example, the mixture in figure 18.3.2 with V(NaOH) between 1 and 9 cm^3 contains significant quantities of both a weak conjugate acid, $CH_3COOH(aq)$, and its conjugate base, $CH_3COO^-(aq)$, which is also weak.

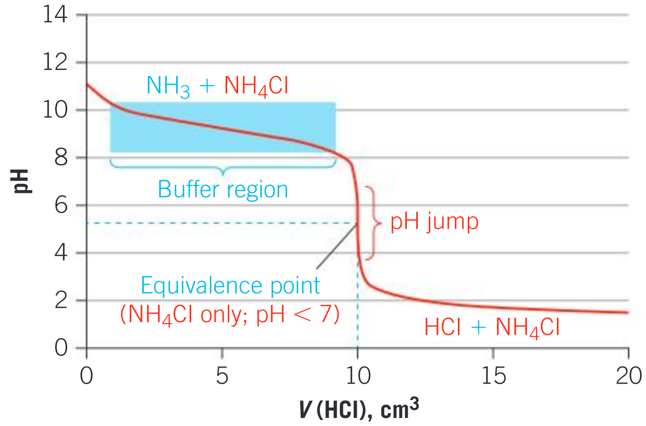
Assessment tip

The pH curves of titrations involving both a weak acid and a weak base have no characteristic "pH jump", and thus the equivalence point cannot be determined accurately. Such titrations can be carried out only with a digital pH probe (topic 8.3), as the use of acid–base indicators (see below) would cause unacceptably large experimental errors.

almost horizontal *buffer region* with pH ≈ pK_a (for a weak acid, figure 18.3.2) or pH ≈ 14 − pK_b (for a weak base, figure 18.3.3).



▲ **Figure 18.3.2.** The pH curve for the titration of 10.0 cm^3 of 0.10 mol dm^{-3} $CH_3COOH(aq)$ with 0.10 mol dm^{-3} NaOH(aq)



▲ **Figure 18.3.3.** The pH curve for the titration of 10.0 cm^3 of 0.10 mol dm^{-3} $NH_3(aq)$ with 0.10 mol dm^{-3} HCl(aq)

The pK_a of an unknown acid can be determined from the titration curve: at the moment when V(titrant) = 0.5 × V_{eq}(titrant), which is known as the *half-equivalence point*, pH = pK_a. Similarly, for a weak base at half-equivalence, pH = 14 − pK_b.

Acid–base buffers, or simply **buffer solutions** resist changes in pH upon addition of small amounts of strong acids and bases.

Buffer solutions

Acid–base buffers contain conjugate weak acid–base pairs and resist changes in pH upon addition of small amounts of strong acids and bases.

When a small amount of a strong acid is added to a buffer solution, it is neutralized by the weak conjugate base of the buffer system, producing the weak conjugate acid:

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

Similarly, a small amount of a strong base is neutralized by the weak conjugate acid of the buffer, producing the weak conjugate base:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

In both cases, the overall composition of the buffer solution (a conjugate acid–base pair) and thus its pH remain almost unchanged.

Assessment tip

It is essential to state that a buffer solution can neutralize only **small** quantities of strong acids and bases. If a large quantity of a strong acid or base is added, it will completely use up one component of the buffer system, and then significantly change the solution pH.

Buffer solutions can be prepared by partial neutralization of weak acids or bases, or by mixing weak acids or bases with their salts. However, the nature of the buffer system (a conjugate pair of a weak acid and a weak base) remains the same in all cases.

The calculation of pH in buffer solutions is only assessed in options B.7 and D.4.

Example 18.3.2.

Which of the following will form a buffer solution if combined in appropriate molar ratios?

A. HCl(aq) and NaCl(aq)

B. NaOH(aq) and HCOONa(aq)

C. NH_4Cl(aq) and HCl(aq)

D. HCl(aq) and NH_3(aq)

Solution

Mixture **A** has no weak electrolytes (except water), so it cannot produce a buffer solution at any reactant ratios. Mixture **B** contains a weak base, $HCOO^-$, but no weak acid, so it also cannot produce a buffer. Similarly, mixture **C** cannot produce a buffer, as it contains only a weak acid, NH_4^+, but no weak base. The correct answer is **D**, where the buffer will form if ammonia is used in excess:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l) \quad \text{(molecular equation)}$$

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) + H_2O(l) \quad \text{(net ionic equation)}$$

The final solution will contain a weak acid, NH_4^+(aq), and its weak conjugate base, NH_3(aq), so it will be able to neutralize both strong acids and strong bases.

Indicators

The equivalence point of a titration can be determined by a pH probe or, less accurately, by a suitable acid–base indicator. Common indicators are weak organic acids or bases that change colour when they accept or lose a proton:

$$HInd(aq) \rightleftharpoons H^+(aq) + Ind^-(aq)$$

Colour A Colour B

In a typical experiment, a small amount of an acid–base indicator is added to the analysed solution before the titration. When the equivalence point is reached, the pH of the solution changes sharply, and the position of the equilibrium described above shifts either to the left (if a base is titrated with an acid) or to the right (if an acid is titrated with a base). As a result, the colour of the analysed solution changes, showing that the neutralization is complete. The closer the pK_a of the indicator to the pH at equivalence, the more accurately the equivalence point can be detected (table 18.3.1).

Acid	Base	Example	pH at equivalence	Indicator
strong	strong	HCl + NaOH	= 7	any
weak	strong	CH_3COOH + NaOH	> 7	$pK_a > 7$
strong	weak	HCl + NH_3	< 7	$pK_a < 7$
weak	weak	CH_3COOH + NH_3	≈ 7	cannot be used

▲ **Table 18.3.1.** Typical acid–base titrations

Assessment tip

Note that universal indicator (topic 8.3) is *not* used in titrations, as it changes colour gradually over the whole pH range rather than producing a sharp colour change within a narrow pH interval.

Common acid–base indicators and their pK_a values are listed in section 22 of the data booklet.

Assessment tip

In addition to the pH probe and acid–base indicators, the equivalence point can be detected using a digital thermometer (as neutralization reactions are exothermic) or a conductivity probe.

SAMPLE STUDENT ANSWER

Hydrazine reacts with water in a similar way to ammonia. (The association of a molecule of hydrazine with a second H^+ is so small that it can be neglected.)

$N_2H_4(aq) + H_2O(l) \rightleftharpoons N_2H_5^+(aq) + OH^-(aq)$

pK_b(hydrazine) = 5.77

a) Calculate the pH of a 0.0100 mol dm^{-3} solution of hydrazine. [3]

b) Suggest a suitable indicator for the titration of hydrazine solution with dilute sulfuric acid using section 22 of the data booklet. [1]

This answer could have achieved 2/4 marks:

a) $K_b = 10^{-5.77} \approx 1.7 \times 10^{-6}$

$[H^+] = \sqrt{0.0100 \times 1.7 \times 10^{-6}} \approx 1.3 \times 10^{-4}$ mol dm^{-3}

$pH = -\log(1.3 \times 10^{-4}) \approx 3.89$

b) Methyl orange.

▲ First step correct

▼ The use of K_b in the formula gives $[OH^-]$, not $[H^+]$ (this is a very common error)

▼ Answer makes no sense: hydrazine is a base, so the pH of its solution must be greater than 7; correct answer is pOH = 3.89 and so pH = 14 – 3.9 = 10.1

▲ Correct; other suitable indicators with $pK_a < 7$ are bromophenol blue, bromocresol green and methyl red

Practice problems for Topic 18

Problem 1

Which 0.10 mol dm^{-3} solution will form an acid–base buffer when mixed with 10 cm^3 of 0.10 mol dm^{-3} $H_2SO_4(aq)$?

A. 10 cm^3 of $CH_3COOH(aq)$

B. 20 cm^3 of $Na_2SO_4(aq)$

C. 30 cm^3 of $NH_3(aq)$

D. 40 cm^3 of KOH

Problem 2

Nickel forms the transition metal complex $[Ni(NH_3)_6]SO_4$.

Describe, in terms of acid–base theories, the type of reaction that takes place between the nickel(II) ion and ammonia to form the complex ion.

Problem 3

a) Calculate the pH of 0.10 mol dm^{-3} $NH_3(aq)$. Use section 21 of the data booklet.

b) Sketch and annotate the pH curve for the titration of 0.10 mol dm^{-3} HCl(aq) with the solution in part (a).

c) Suggest a suitable acid–base indicator for the titration in part (b). Use section 22 of the data booklet.

d) Describe how the shape of the pH curve in part (b) will change if 0.010 mol dm^{-3} solutions of HCl(aq) and $NH_3(aq)$ are used instead of 0.10 mol dm^{-3} solutions.

e) Suggest, with a reason, whether the pH curve in part (b) or that shown in figure 18.3.3 is more suitable for determining the pK_b of ammonia.

f) Demonstrate how the pK_b of ammonia can be determined from the pH curve of your choice.

g) State **one** technique, other than a pH titration, that could be used to detect the equivalence point in part (b).

19 REDOX PROCESSES (AHL)

TOPIC 19.1 ELECTROCHEMICAL CELLS

You should know:

- ✔ voltaic cells produce a cell potential E_{cell}, sending electrons from the anode (negative electrode) to the cathode (positive electrode) through the external circuit;
- ✔ standard electrode potentials $E^{\ominus}$ are measured relative to the standard hydrogen electrode (SHE);
- ✔ $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$, so an electrochemical reaction is spontaneous when $E^{\ominus}_{cell} > 0$;
- ✔ when aqueous solutions are electrolysed, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode;
- ✔ the amount of substance produced at an electrode during electrolysis depends on the current, I, the duration of electrolysis, t, and the charge on the ion, z.

You should be able to:

- ✔ calculate the cell potential from standard electrode potentials;
- ✔ predict whether a reaction will occur spontaneously in a voltaic cell and determine the standard Gibbs free energy change value using standard electrode potentials;
- ✔ deduce the product formed at each electrode during the electrolysis of an aqueous solution;
- ✔ determine the relative amounts of products formed during electrochemical processes;
- ✔ explain what occurs during the process of electroplating.

Voltaic cells

If two different half-cells are connected, the resulting voltaic cell produces a *cell potential* (voltage), E_{cell}. The greater the difference between the half-cells, the greater the cell potential. The cell potential measured under standard state conditions is the *standard cell potential*, $E^{\ominus}_{cell}$.

Electrode potentials of individual half-cells depend on concentrations and temperature. *Standard electrode potentials* of half-cells are measured under standard state conditions with respect to the potential of the *standard hydrogen electrode* (SHE), which is set arbitrarily to zero. In cell diagram notation by convention the cathode is always written on the right-hand side. The standard cell potential is calculated from right-hand and left-hand electrodes (rhe and lhe, respectively) as follows:

$$E^{\ominus}_{cell} = E^{\ominus}_{rhe} - E^{\ominus}_{lhe}$$

For a spontaneous reaction, the cathode (rhe) must have a higher (more positive or less negative) standard electrode potential than the anode, so that electrons flow from the anode to the cathode and $E^{\ominus}_{cell}$ is positive. The standard cell potential is related to the standard Gibbs free energy change, $\Delta G^{\ominus}$, as follows:

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$

where n is the amount, in mol, of electrons transferred in the balanced equation, and F is Faraday's constant. When $E^{\ominus}_{cell}$ is positive, $\Delta G^{\ominus}$ is negative and the reaction is spontaneous, and vice versa.

The differences between voltaic and electrolytic cells are discussed in topic 9.2.

Assessment tip

Ensure that you know how to draw and annotate a voltaic cell. Remember that electrons flow through the wires (external circuit) and ions flow through the electrolyte. You should know the direction of electron flow and the direction of ion flow (both in solution and across the salt bridge).

Redox processes are discussed in topic 9.1.

Cell diagram notation is introduced in topic 9.2.

A list of standard electrode potentials at 298 K is given in section 24 of the data booklet.

- The **cell potential**, E_{cell}, is the actual potential difference between the cathode (positive electrode) and the anode (negative electrode) when the voltaic cell is operating.
- The **standard cell potential**, $E^{\ominus}_{cell}$, is measured under standard state conditions (1 mol dm^{-3} for reactants in solution and 100 kPa for gaseous reactants).
- The **standard hydrogen electrode (SHE)** consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ions and hydrogen gas at 100 kPa and 298 K.
- The **standard electrode potential**, $E^{\ominus}$, is the potential of the reduction half-equation under standard state conditions measured relative to the SHE. Solute concentration is 1 mol dm^{-3} for reactants in solution and 100 kPa for gaseous reactants. $E^{\ominus}$ values are usually reported for 298 K.

Example 19.1.1.

A voltaic cell consists of an $Fe(s)\,|\,Fe^{2+}(aq)$ half-cell and an $Ni(s)\,|\,Ni^{2+}(aq)$ half-cell.

a) Calculate the standard cell potential, $E^{\ominus}_{cell}$, in V.

b) Calculate the standard free Gibbs energy change, $\Delta G^{\ominus}$, in kJ, of the cell reaction.

Solution

a) Using section 24 of the data booklet:

$$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s) \qquad E^{\ominus} = -0.45\ V$$

$$Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s) \qquad E^{\ominus} = -0.26\ V$$

The $Ni(s)\,|\,Ni^{2+}(aq)$ half-cell has the higher (less negative) $E^{\ominus}$ value, so it will act as the cathode.

$$E^{\ominus}_{cell} = E^{\ominus}_{rhe} - E^{\ominus}_{lhe} = -0.26\ V - (-0.45\ V) = +0.19\ V$$

b) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -2 \times 96\,500\ C\ mol^{-1} \times 0.19\ V \approx -37\,000\ J = -37\ kJ$

Electrolytic cells

The electrolysis of aqueous solutions is often complicated by redox reactions involving water. Common products of such reactions are molecular hydrogen and oxygen.

Assessment tip

Make sure that you are confident about the electrolysis of water and of the following aqueous solutions:

- concentrated NaCl(aq)
- dilute NaCl(aq)
- $CuSO_4(aq)$.

Remember:

- the standard electrode potentials, $E^{\ominus}$, given in section 24 of the data booklet are essential in deciding on the products formed at the cathode and the anode
- use half-equations for the reactions at each electrode to find the overall cell reaction
- know what is physically observed at each electrode.

Gibbs free energy change, ΔG, is discussed in topic 15.2.

The equation $\Delta G^{\ominus} = -nFE^{\ominus}$ is given in the data booklet in section 1, and Faraday's constant = 96 500 C mol^{-1} is given in section 2.

The electrolysis of molten electrolytes is discussed in topic 9.2.

Example 19.1.2.

Deduce half-equations for the formation of the major products at the anode and cathode when the following solutions are electrolysed:

- concentrated aqueous sodium chloride
- dilute aqueous sodium chloride.

Solution

For an electrolytic cell, the cathode acts as the negative electrode and the anode as the positive electrode. As we are dealing with the electrolysis of an aqueous solution, water must be considered alongside the sodium and chloride ions.

At the anode, oxidation takes place. There are two species to consider: $Cl^-(aq)$ and $H_2O(l)$.

The two relevant half-equations are found in section 24 of the data booklet, where they are stated as reduction processes. For oxidation, we need to reverse the order, and the sign of $E^\ominus$, for each half-equation:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $\quad E^\ominus = -1.36\ V$

$H_2O(l) \rightarrow 0.5O_2(g) + 2H^+(aq) + 2e^-$ $\quad E^\ominus = -1.23\ V$

In general, the more positive (less negative) $E^\ominus$ value for the oxidation indicates the preferred reaction, suggesting that oxidation of water occurs. Indeed, in the case of *dilute* aqueous sodium chloride, the oxidation of water takes place, and oxygen gas is released at the anode.

However, in the case of *concentrated* aqueous sodium chloride, the oxidation of chloride ions proceeds faster than that of water, so chlorine gas is released at the anode instead of oxygen.

At the cathode, reduction occurs. The species to consider are $Na^+(aq)$ and $H_2O(l)$.

The half-equations are:

$Na^+(aq) + e^- \rightarrow Na(s)$ $\quad E^\ominus = -2.71\ V$

$H_2O(l) + e^- \rightarrow 0.5H_2(g) + OH^-(aq)$ $\quad E^\ominus = -0.83\ V$

Water has a much higher reduction potential than sodium cations, so hydrogen gas will be produced at the cathode regardless of the concentration of sodium chloride.

Pure water has very low electrical conductivity, which makes its electrolysis problematic. Its conductivity can be increased by addition of small quantities of sulfuric acid, H_2SO_4, or sodium hydroxide, NaOH, which do not participate in redox reactions. Reduction of water occurs at the cathode, where bubbles of hydrogen gas form, while oxygen gas is evolved at the anode. The ratio of $H_2(g)$ to $O_2(g)$ by volume is 2:1.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

Added electrolyte	**Redox reaction**	
	cathode	**anode**
H_2SO_4	$2H^+(aq) + 2e \longrightarrow H_2(g)$	$H_2O(l) \longrightarrow 0.5O_2(g) + 2H^+(aq) + 2e^-$
NaOH	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	$2OH^-(aq) \longrightarrow 0.5O_2(g) + H_2O(l) + 2e^-$

▲ **Table 19.1.1.** Electrolysis of water

Products of the electrolysis of aqueous copper(II) sulfate depend on the electrode material (table 19.1.2). When inert electrodes (platinum or graphite) are used, water is oxidized at the anode, because sulfate ions contain sulfur in its highest oxidation state, +6, and so cannot be oxidized any further. As a result, bubbles of oxygen form at the anode. However, the use of a copper anode produces $Cu^{2+}(aq)$ ions instead, as the oxidation potential of copper metal (−0.34 V) is less negative than that of water (−1.23 V).

Assessment tip

If asked about physical observations, you must state that bubbles of gas are produced at each electrode. Chlorine gas can be detected by its strong odour or using damp litmus paper, which will turn first red (owing to the formation of hydrochloric acid, HCl) and then white, as the litmus dye is bleached. Oxygen gas can be confirmed by its ability to relight a glowing splint. Hydrogen is highly flammable, so ignites on contact with a burning splint.

The formation of hydroxide ions in the solution can be detected by an acid–base indicator or a pH meter.

Note that in the list of standard electrode potentials in section 24 of the data booklet, the processes are all written as reductions, and each half-equation has an equilibrium sign. However, when writing half-equations for a reaction taking place at an electrode, you should write an oxidation process for the anode and a reduction process for the cathode. For half-equations at electrodes, an equilibrium sign is never used. Use of one may result in your response being penalized.

Assessment tip

Note that the redox half-equations involve $H^+(aq)$ ions in acidic solutions and $OH^-(aq)$ in basic solutions (table 19.1.1). In both cases, the pH of the solution increases near the cathode (where H^+ ions are consumed or OH^- ions are produced) and decreases near the anode (where H^+ ions are produced or OH^- ions are consumed).

Assessment tip

In the case of inert electrodes, the blue colour of the copper(II) sulfate solution fades over time, as $Cu^{2+}(aq)$ ions are gradually removed. At the same time, the pH of the solution decreases, as copper(II) sulfate is replaced with sulfuric acid:

$$CuSO_4(aq) + H_2O(l) \rightarrow Cu(s) + 0.5O_2(g) + H_2SO_4(aq)$$

When a copper anode is used, both the solution colour and pH remain unchanged, as $Cu^{2+}(aq)$ ions discharged at the cathode are replaced with the same ions formed at the anode. This process can be used to purify copper: the impure copper from the anode first passes into the solution and then deposits as red or brown specks of pure copper at the cathode.

Faraday's constant is given in the data booklet in section 2.

Electrode material	Redox reaction	
	cathode	anode
inert (platinum or graphite)	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$; $E^\ominus = +0.34$ V	$H_2O(l) \rightarrow 0.5O_2(g) + 2H^+(aq) + 2e^-$; $E^\ominus = -1.23$ V
active (copper)		$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$; $E^\ominus = -0.34$ V

▲ **Table 19.1.2.** Electrolysis of aqueous copper(II) sulfate

Active electrodes (such as copper) are used in *electroplating*, in which a thin layer of one metal is deposited on the surface of another metal. The object to be plated is used as the cathode. The metal for the plating is used as the anode and its cations are used as the electrolyte. For example, steel cutlery can be electroplated with silver, using a silver anode and sodium dicyanoargentate(I) solution, $Na[Ag(CN)_2]$.

The amount of substance produced at an electrode during electrolysis depends on the current, I, the duration of electrolysis, t, and the charge on the ion, z. The current and the duration yield the amount of electric charge, Q, passed through the electrolyte:

$$Q = It$$

The charge in coulombs is related to the amount of electrons passing through a wire by Faraday's constant, 96 500 C mol^{-1}.

Example 19.1.3.

Calculate the mass, in g, of copper produced at the cathode when a current of 1.7 A is passed through a solution of aqueous copper(II) sulfate for 3.8 hours.

Solution

$Q = It = 1.7 \text{ A} \times (3.8 \times 60 \times 60 \text{ s}) \approx 2.3 \times 10^4 \text{ C}$

$F \equiv 9.65 \times 10^4 \text{ C mol}^{-1}$, so 1 C equates to $\dfrac{1}{9.65 \times 10^4}$ mol of e^-

2.3×10^4 C is $\dfrac{2.3 \times 10^4}{9.65 \times 10^4} \approx 0.24$ mol of e^-

The reduction half-equation taking place at the cathode is:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

So 0.24 mol e^- will produce 0.12 mol Cu(s)

$m = n \times M = 0.12 \text{ mol} \times 63.55 \text{ g mol}^{-1} \approx 7.6$ g of copper deposited at the cathode.

SAMPLE STUDENT ANSWER

a) Corrosion of iron is similar to the processes that occur in a voltaic cell. The initial steps involve the following half-equations:

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$$

$$0.5O_2(g) + H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq)$$

Calculate $E^\ominus$, in V, for the spontaneous reaction using section 24 of the data booklet. [1]

b) Calculate the standard change in Gibbs free energy, $\Delta G^\ominus$, in kJ, which is released by the corrosion of 1 mole of iron. Use section 1 of the data booklet. [2]

This answer could have achieved 2/3 marks:

a) $E^\ominus_{cell} = E^\ominus_{rhe} - E^\ominus_{lhe} = -0.45\ V - (+0.40\ V) = -0.85\ V$

b) $\Delta G^\circ = -nFE^\ominus_{cell} = -2 \times (9.65 \times 10^4) \times (-0.85)$

$= 164050\ J \approx 164\ kJ.$

▼ The electrodes are reversed: the rhe (cathode) must have the more positive $E^\ominus$ value: $E^\ominus_{cell} = +0.40\ V - (-0.45\ V) = +0.85\ V$

▲ The method is correct, so the mark is awarded even though an incorrect value for $E^\ominus_{cell}$ has been carried over from (a)

▲ The correct answer is −164 kJ

Assessment tip

In examination questions always refer to the precise species as the oxidizing or reducing agent. If $Cu^{2+}(aq)$ is the species being reduced, it is incorrect to state that “copper” is the oxidizing agent.

However, when discussing oxidation states, refer to the atom; for example, copper has an oxidation state of +2 in the species $Cu^{2+}(aq)$.

Practice problems for Topic 19

Problem 1

a) Draw and annotate a diagram of a voltaic cell made from a $Cu(s)|Cu^{2+}(aq)$ half-cell connected to a $Pb(s)|Pb^{2+}(aq)$ half-cell. In your diagram identify the cathode, the anode, the direction of electron flow and the direction of ion flow.

b) State the cell diagram notation for the voltaic cell.

c) Deduce the half-equations for the reactions taking place at each electrode and the overall cell reaction.

d) State which species acts as the oxidizing agent.

e) Calculate the standard cell potential, $E^\ominus_{cell}$, in V.

Problem 2

During electrolysis of aqueous copper(II) sulfate with graphite electrodes, 5.34 g of copper metal was deposited at the cathode. Calculate the volume of oxygen gas, in m^3, measured under STP conditions, formed at the anode.

20 ORGANIC CHEMISTRY (AHL)

TOPIC 20.1 TYPES OF ORGANIC REACTIONS

You should know:

- ✔ nucleophilic substitution (S_N) can follow unimolecular (S_N1) or bimolecular (S_N2) mechanisms, with a carbocation intermediate and a concerted mechanism, respectively;
- ✔ S_N1 reactions are typical for tertiary halogenoalkanes in polar, protic solvents, while S_N2 reactions are typical for primary halogenoalkanes in polar, aprotic solvents;
- ✔ electrophilic addition (A_E) is typical for alkenes in reactions with halogens/interhalogens and hydrogen halides;
- ✔ an electrophile is an electron-deficient species that can accept an electron pair from a nucleophile;
- ✔ the direction of an A_E reaction involving unsymmetrical reagents can be predicted using Markovnikov's rule and explained in terms of the relative stability of carbocations;
- ✔ electrophilic substitution (S_E) reactions are typical for benzene and other aromatic compounds, which have delocalized π electrons around their rings;
- ✔ aldehydes, ketones and carboxylic acids can be reduced by lithium aluminium hydride and sodium borohydride to alcohols.

You should be able to:

- ✔ deduce the mechanisms of S_N1 and S_N2 reactions of halogenoalkanes with NaOH(aq);
- ✔ explain how the rate of an S_N reaction depends on the identity of the halogen, the type of the halogenoalkane (primary, secondary or tertiary) and the choice of solvent;
- ✔ outline the difference between protic and aprotic solvents;
- ✔ deduce the mechanisms of A_E reactions of alkenes with halogens/interhalogens and hydrogen halides;
- ✔ deduce the mechanism of the S_E reaction (nitration) of benzene with a mixture of concentrated nitric and sulfuric acids;
- ✔ deduce the equations for the reduction of carbonyl compounds (aldehydes, ketones and carboxylic acids) to alcohols using suitable reducing agents;
- ✔ state the equations for the two-stage conversion of nitrobenzene to phenylamine.

Nucleophilic substitution

Reactions of halogenoalkanes with dilute aqueous sodium hydroxide occur by *nucleophilic substitution* (S_N), where the *nucleophile* (hydroxide anion, OH^-(aq)) attacks the carbon atom that has a partial or full positive charge. As a result, a halide ion (the *leaving group*) is released, and an alcohol is formed.

Tertiary halogenoalkanes in *protic solvents* readily form tertiary carbocations, so they produce alcohols via the unimolecular S_N1 mechanism (figure 20.1.1).

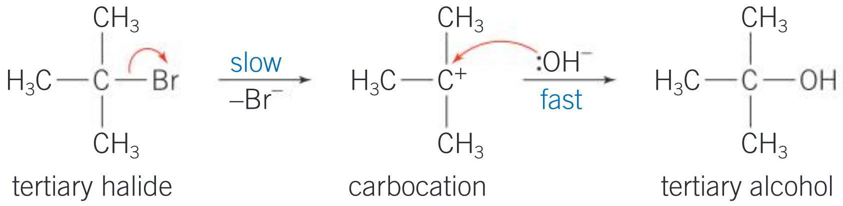


Figure 20.1.1. A typical S_N1 reaction mechanism (the curly arrows represent movement of an electron pair)

Assessment tip

To score the full mark, a diagram of an S_N1 mechanism must include the following elements:

- a curly arrow showing the halide ion leaving;
- the structure of the intermediate carbocation;
- a curly arrow from the lone electron pair in OH^- to C^+;
- the structure of the alcohol (main product) and the halide ion (by-product).

In contrast, primary carbocations are unstable, so primary halogenoalkanes undergo hydrolysis via the bimolecular S_N2 mechanism, which usually occurs in polar *aprotic solvents* and involves a concerted reaction with a transition state (figure 20.1.2). Secondary halogenoalkanes can participate in both S_N1 and S_N2 reactions, which often proceed in parallel to each other.

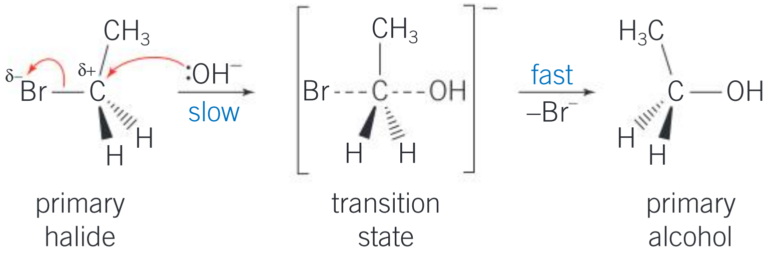


Figure 20.1.2. A typical S_N2 reaction mechanism

S_N1 reactions at chiral centres produce racemic mixtures of isomers (topic 20.3). In contrast, S_N2 reactions are stereospecific and proceed with an inversion of configuration of the carbon atom.

The slow (rate-determining) step in S_N1 reactions is the formation of the carbocation (figure 20.1.1). This step involves a single species, the halogenoalkane (RHal), so the reaction proceeds as a first-order process and is characterized by the rate equation $v = k[\text{RHal}]$. In contrast, the slow step in S_N2 reactions involves two species, RHal and OH^- (figure 20.1.2), so the reaction is second order and is characterized by the rate equation $v = k[\text{RHal}][\text{OH}^-]$.

- A **nucleophile**, such as water or a hydroxide anion, is a species that can donate a lone electron pair to a positively charged or electron-deficient carbon atom.
- An **electrophile**, such as $^+NO_2$ or a **carbocation** (a species with a full positive charge on a carbon atom), is a species that is attracted to electrons, such as in a negatively charged carbon atom or a carbon–carbon double bond.
- A **leaving group** is the ion or molecule that detaches from the substrate via a heterolytic bond fission.

The terms *primary* (1°), *secondary* (2°) and *tertiary* (3°) are introduced in topic 10.1. Condensation reactions of alcohols with carboxylic acids are described in topic 10.2. The reaction molecularity is discussed in topic 16.1.

- **Protic solvents**, such as water and alcohols, readily donate protons (H^+ ions) to nucleophiles or form hydrogen bonds with electron-rich species.
- **Aprotic solvents**, such as ethers, esters and ketones, cannot donate protons (H^+ ions) to other species.

Assessment tip

To score the full mark, a diagram of an S_N2 mechanism must include the same elements as for an S_N1 mechanism except that the transition state with a negative charge, square brackets and partial bonds must be shown instead of the carbocation.

Reaction order and rate equations are discussed in topic 16.1.

The reactivity of halogenoalkanes is summarized in table 20.1.1.

Table 20.1.1. Factors affecting the reactivity of halogenoalkanes (RHal)

Factor	Reactivity	Reason
nature of R	3° > 2° > 1°	stability of carbocation decreases
identity of Hal	RI > RBr > RCl >> RF*	strength of C–Hal bond increases; stability of leaving group decreases
nature of solvent	S_N1: protic > aprotic S_N2: aprotic > protic	protic solvents stabilize carbocations; aprotic solvents do not form H-bonds
charge of nucleophile	$OH^- > H_2O$	greater charge density in anion; greater attraction of anion to $C^+/C^{\delta+}$

*Fluoroalkanes are unreactive because the C–F bond energy is very high.

>> Assessment tip

To score the full mark, a diagram of an A_E mechanism must include the following elements:

- a curly arrow from the C=C bond to the electrophile;
- a curly arrow showing the halide ion leaving;
- the structure of the intermediate carbocation;
- a curly arrow from the lone pair in the halide ion to C^+;
- the structure of the final halogenoalkane.

Electrophilic addition

Electrophilic addition (A_E) reactions are typical for alkenes and other compounds with multiple carbon–carbon bonds. The substrate donates a pair of π electrons to a positively charged *electrophile* and forms a carbocation, which in turn reacts with a nucleophile and forms the final product (figure 20.1.3).

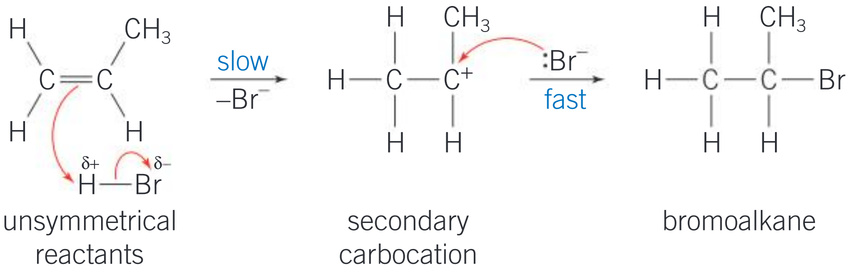


Figure 20.1.3. A typical A_E reaction mechanism

The electrophilic addition reactions of alkenes are introduced in topic 10.2.

Unsymmetrical alkenes can form two possible carbocations that differ in stability. The more stable cation (3° > 2° > 1°) is formed preferentially and gives the main reaction product.

Halogens and interhalogen compounds, such as IBr or ICl, react with alkenes in the same way as hydrogen halides. The less electronegative atom (I < Br < Cl) in interhalogen compounds has a partial positive charge and acts as the electrophile, binding to a carbon atom in the first step.

>> Assessment tip

Markovnikov's rule states that in reactions of unsymmetrical alkenes with hydrogen halides, the halogen atom forms a bond with the least hydrogenated carbon atom. Although this rule predicts the main products in some A_E reactions, it will not be accepted as an explanation in examinations because it does not **explain** why the reaction proceeds in a certain way. If the question requires an explanation, you must always refer to the relative stabilities of carbocations.

Example 20.1.1.

Explain, with reference to carbocations, how the main product and the by-product are formed when hex-1-ene reacts with hydrogen bromide.

Solution

When hex-1-ene accepts a proton, two possible carbocations can form:

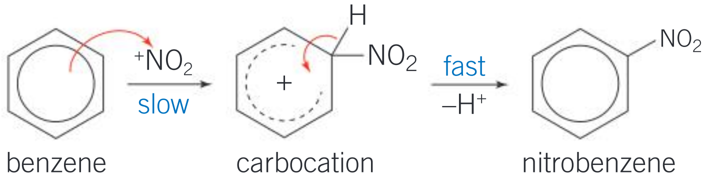
$$C_4H_9{-}CH{=}CH_2 \xrightarrow[-Br^-]{+HBr} C_4H_9{-}\overset{+}{C}H{-}CH_3 \text{ or } C_4H_9{-}CH_2{-}\overset{+}{C}H_2$$

secondary cation primary cation

The more stable secondary carbocations react with most of the bromide ions and give the main product, C_4H_9–CHBr–CH_3 (2-bromohexane), while the less stable primary carbocations form the by-product, C_4H_9–CH_2–CH_2Br (1-bromohexane).

Electrophilic substitution

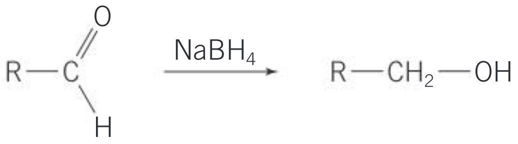
Benzene is the simplest arene (aromatic hydrocarbon), with six delocalized π electrons. Benzene (like other arenes) participates in *electrophilic substitution* (S_E) reactions. An electrophilic reagent, such as the nitronium ion ($^+NO_2$), attacks the ring of delocalized electrons and forms a carbocation, which releases a proton to give the substituted arene (figure 20.1.4).

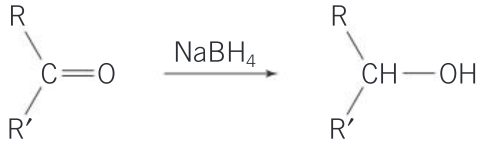


▲ Figure 20.1.4. A typical S_E reaction mechanism

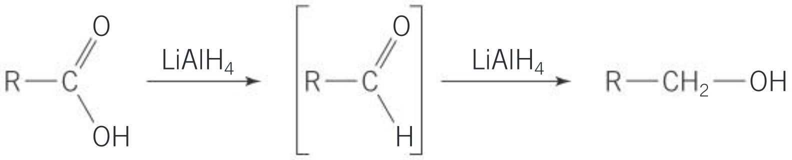
Reduction

Reduction reactions are typical for carbonyl compounds. Aldehydes and ketones are reduced by sodium borohydride ($NaBH_4$) to primary and secondary alcohols, respectively:





Carboxylic acids require a stronger reducing agent, lithium aluminium hydride ($LiAlH_4$), and form first aldehydes and then primary alcohols:



However, aldehydes cannot be isolated from the reaction mixture, as they react with $LiAlH_4$ faster than carboxylic acids.

Nitrobenzene can be reduced to phenylamine (commonly called aniline) in a two-step process. The first step produces a salt, phenylammonium chloride, which is then converted to phenylamine by reaction with a base:

$$C_6H_5NO_2(l) + 3Sn(s) + 7HCl(aq) \rightarrow [C_6H_5NH_3]^+Cl^-(aq) + 3SnCl_2(aq) + 2H_2O(l)$$

$$[C_6H_5NH_3]^+Cl^-(aq) + NaOH(aq) \rightarrow C_6H_5NH_2(l) + NaCl(aq) + H_2O(l)$$

Other metals, such as iron or zinc, can be used in the first step. Similarly, sodium hydroxide in the second step can be replaced with sodium carbonate.

Alternatively, the reduction of nitrobenzene can be carried out in one step using hydrogen gas and a transition metal catalyst (Ni or Pt) at high pressure and temperature:

$$C_6H_5NO_2(l) + 3H_2(g) \rightarrow C_6H_5NH_2(l) + 2H_2O(l)$$

The structure and reactivity of benzene are discussed in topic 10.1.

Assessment tip

The nitronium ion ($^+NO_2$) is formed in a mixture of concentrated nitric and sulfuric acids:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons {}^+NO_2 + H_3O^+ + 2HSO_4^-$$

It is essential to state that both acids must be concentrated, as $^+NO_2$ does not exist in dilute aqueous solutions.

Assessment tip

To score full marks, a diagram of this S_E mechanism must include the following elements:

- a curly arrow from the benzene ring to the nitrogen atom in $^+NO_2$;
- the structure of the intermediate carbocation;
- a curly arrow from the C–H bond to the ring;
- the structure of nitrobenzene and the leaving H^+ ion.

The reverse reactions, oxidation of alcohols, are described in topic 10.2.

Assessment tip

Although aldehydes and ketones react readily with $LiAlH_4$, they are usually reduced by the cheaper and less dangerous reagent $NaBH_4$, so this is the reagent you should specify.

Assessment tip

The reduction with hydrogen will not be accepted if the question requires a two-stage synthesis.

TOPIC 20.2 SYNTHETIC ROUTES

You should know:

- ✔ organic compounds are synthesized from readily available starting materials via a series of discrete steps;
- ✔ synthetic steps involve interconversions of functional groups;
- ✔ a synthesis can be designed by working back from the product (retrosynthesis).

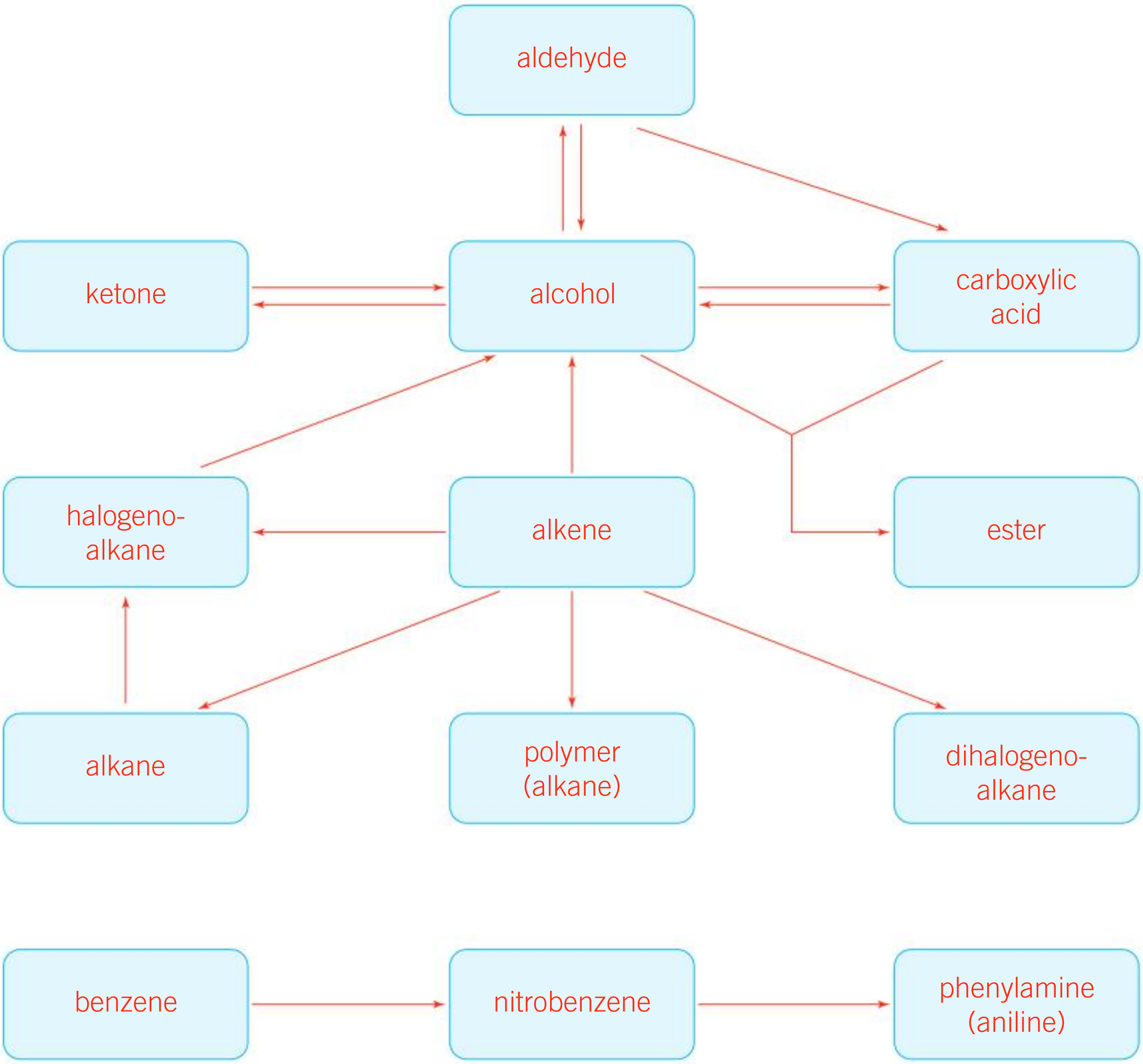
You should be able to:

- ✔ deduce multi-step synthetic routes from known starting material(s) to known product(s);
- ✔ outline the use of retrosynthetic analysis for planning an organic synthesis.

Assessment tip

In paper 2, you may be asked to design a synthetic pathway with up to four steps.

Every synthetic step has a yield of less than 100%, so an efficient synthesis must involve the smallest possible number of chemical transformations in order to maximize the yield of the final product. Typical synthetic pathways (figure 20.2.1) are based on the functional group interconversions summarized in table 20.2.1.



▲ Figure 20.2.1. Reaction pathways used in syntheses

▼ Table 20.2.1. Typical conversions of functional groups

Substrate		Reagent(s) and conditions*	Product	
Class	**Functional group**		**Class**	**Functional group**
alkane	none	Br_2, *hυ*	bromoalkane	–Br
alkene	C=C	H_2, Ni, heat, *p*	alkane	none
		Br_2	dibromoalkane	two –Br
		HBr	bromoalkane	–Br
		H_2O, H^+	alcohol	–OH
		X• or transition metal salt, heat	alkane (polymer)	none
arene (benzene)	C_6H_6	concentrated $HNO_3 + H_2SO_4$	nitro compound (nitrobenzene)	$C_6H_5NO_2$
nitro compound	$-NO_2$	a) Sn, HCl; b) NaOH	amine	$-NH_2$
halogenoalkane	–Cl, –Br, –I	dilute NaOH(aq)	alcohol	–OH
alcohol	–OH	RCOOH, H^+, heat	ester	–O–C(O)R
1° alcohol	$-CH_2-OH$	$K_2Cr_2O_7$, H^+, distillation	aldehyde	–CHO
		$K_2Cr_2O_7$, H^+, reflux	carboxylic acid	–COOH
2° alcohol	–CH(OH)–	$K_2Cr_2O_7$, H^+, heat	ketone	–C(O)–
aldehyde	–CHO	$NaBH_4$	1° alcohol	$-CH_2-OH$
		$K_2Cr_2O_7$, H^+, heat	carboxylic acid	–COOH
ketone	–C(O)–	$NaBH_4$	2° alcohol	–CH(OH)–
carboxylic acid	–COOH	ROH, H^+, heat	ester	–COOR
		$LiAlH_4$	primary alcohol	$-CH_2-OH$

**hυ* = light; *p* = pressure

All reactions included in table 20.2.1 are discussed in greater detail in topics 10.2 and 20.1.

Example 20.2.1.

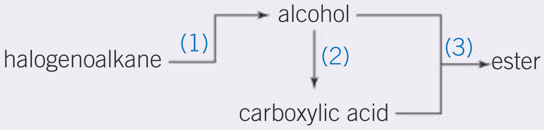
Deduce the synthetic route to prepare ethyl ethanoate from bromoethane.

Solution

Bromoethane (CH_3CH_2Br) is a halogenoalkane, and ethyl ethanoate ($CH_3COOCH_2CH_3$) is an ester. According to figure 20.2.1, the shortest pathway from halogenoalkane to ester includes two steps:

halogenoalkane ⟶ alcohol ⟶ ester

One of the reagents, the carboxylic acid, can be synthesized directly from the alcohol. Therefore, the synthetic pathway will look as follows:



Finally, we need to replace the class names with formulas and refer to table 20.2.1 for the reagents and reaction conditions required for each step:

(1) $CH_3CH_2Br \xrightarrow[-NaBr]{NaOH(aq)} CH_3CH_2OH$

(2) $CH_3CH_2OH \xrightarrow[reflux]{K_2Cr_2O_7,\ H^+} CH_3COOH$

(3) $CH_3COOH + CH_3CH_2OH \xrightarrow[-H_2O]{H^+,\ heat} \boxed{CH_3COOCH_2CH_3}$

Retrosynthetic analysis is an approach to designing a synthetic route to a given target molecule when the starting materials are not specified. The analysis begins from the target molecular structure, which is formally broken down into smaller fragments. This process is repeated until the fragments become simple enough for deduction of the starting materials. Although the retrosynthetic approach requires some practice and the ability to think “in reverse”, from products to reactants, it is a very powerful technique that allows planning of the synthesis of large molecules in a logical and systematic manner.

Assessment tip

You will be given the starting materials for all synthetic problems, so will not need to carry out retrosynthetic analysis yourself. Therefore, you can always follow the strategy outlined in example 20.2.1.

TOPIC 20.3 STEREOISOMERISM

You should know:

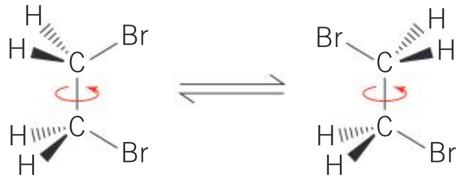
- ✔ conformational isomers interconvert by free rotation about a σ bond while configurational isomers interconvert only by breaking and reforming a bond;
- ✔ configurational isomers include *cis–trans*, *E*/*Z* and optical isomers;
- ✔ a chiral carbon atom is joined to four different atoms or groups of atoms;
- ✔ enantiomers are optical isomers that rotate the plane of polarized light by the same angle but in opposite directions.

You should be able to:

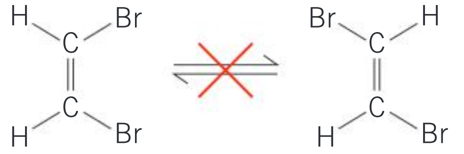
- ✔ construct real or virtual 3D models of stereoisomers;
- ✔ describe and explain the stereoisomerism in alkenes, cycloalkanes and chiral compounds;
- ✔ compare the physical and chemical properties of enantiomers and diastereomers;
- ✔ distinguish between optical isomers using a polarimeter.

- **Stereoisomers** differ in the arrangement of atoms in space but not in the connectivity or bond multiplicity (number of bonds).
- **Conformational isomers**, or **conformers**, can interconvert by free rotation about a single covalent bond.
- **Configurational isomers** cannot interconvert without breaking and reforming a bond.

Stereoisomers are subdivided into conformational and configurational isomers. *Conformational isomers* are difficult or impossible to isolate as individual compounds, as they quickly interconvert by free rotation about a σ (sigma) bond (figure 20.3.1, top). In contrast, *configurational isomers* can be isolated, as their interconversion would require breaking and reforming a σ or π (pi) bond (figure 20.3.1, bottom).



syn-1,2-dibromoethane *anti*-1,2-dibromoethane



cis-1,2-dibromoethene *trans*-1,2-dibromoethene

▲ **Figure 20.3.1.** Conformational (top) and configurational (bottom) isomers

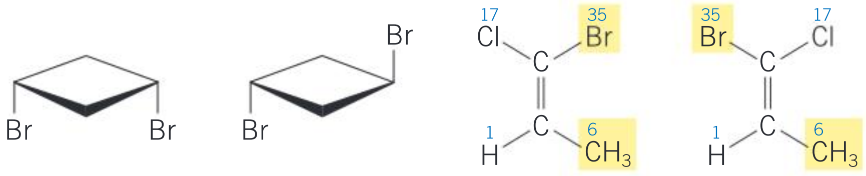
Assessment tip

The nomenclature of conformers will not be assessed in examinations.

Cis–trans and *E/Z* isomerism

Cis–trans isomerism is a form of configurational isomerism seen in alkenes and cycloalkanes, where two substituents can be positioned either on the same side (*cis*-isomer) or opposite sides (*trans*-isomer) of the C=C bond or the plane of the ring (figures 20.3.1, bottom, and 20.3.2, left). For alkenes with three or four different substituents at the doubly bonded carbon atoms, the *E*/*Z* nomenclature must be used (figure 20.3.2, right), following the *Cahn–Ingold–Prelog convention*.

- ***Cis*-isomers** have the two substituents on the same side of a C=C bond or a ring, while ***trans*-isomers** have the two substituents on opposite sides of a C=C bond or a ring.
- The **Cahn–Ingold–Prelog convention** defines the priority of substituents by the atomic numbers of their constituent elements.
- ***Z*-isomers** have the two groups of higher priority on the same side of a C=C bond, while ***E*-isomers** have the two groups of higher priority on opposite sides of a C=C bond.



cis-isomer *trans*-isomer *Z*-isomer *E*-isomer

▲ **Figure 20.3.2.** *Cis–trans* isomerism in 1,3-dibromocyclobutanes (left) and *E*/*Z*-isomerism in 1-bromo-1-chloropropenes (right)—atomic numbers in *E* and *Z* isomers are shown in blue, and the groups with higher priority are highlighted

Assessment tip

Since hydrogen has the lowest possible atomic number, any *cis*-alkene is a *Z*-isomer, and any *trans*-alkene is an *E*-isomer.

Assessment tip

It may help you to memorize the *E*/*Z* nomenclature if you remember that "*E*" comes from German *entgegen* ("in opposition to") while "*Z*" comes from German *zusammen* ("together").

Example 20.3.1.

Deduce, using the Cahn–Ingold–Prelog convention, the stereochemical configuration of each of the two alkenes shown in figure 20.3.1.

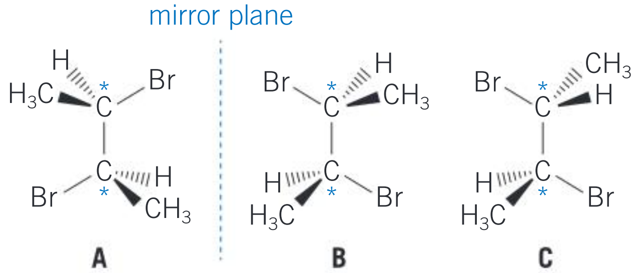
Solution

Bromine has an atomic number of 35 and thus a higher priority than hydrogen with an atomic number of 1. In *cis*-1,2-dibromoethene, the two bromine atoms are on the same side of the C=C bond, so it is a *Z*-isomer. In *trans*-1,2-dibromoethene, the bromine atoms are on opposite sides of the C=C bond, so it is an *E*-isomer.

- A **chiral carbon atom** is joined to four different atoms or groups of atoms.
- **Optical isomers** differ in configuration of one or more chiral centres.
- **Enantiomers** are non-superimposable mirror images of each other.
- **Diastereomers** are stereoisomers that are not mirror images of each other.

Optical isomerism

Optical isomers have one or more *chiral centres* (usually carbon atoms) with different arrangements of substituents. All chiral centres in a pair of *enantiomers* have opposite configurations, while *diastereomers* have different configurations of some but not all chiral centres (figure 20.3.3).



▲ **Figure 20.3.3.** Enantiomers (A and B) and diastereomers (A and C or B and C) of 2,3-dibromobutane (the chiral carbon atoms are marked with *)

Assessment tip

Chiral centres are often characterized by *R*/*S* nomenclature, but this will not be assessed in examinations. The D/L and α/β nomenclatures of biomolecules (topic B.10) will be assessed in Paper 3 only.

ATL Assemble 3D models of compounds **A**, **B** and **C** from figure 20.3.3 and verify for yourself that none of the three structures are superimposable. You can also use a mirror to verify that structures **A** and **B** are enantiomers while structure **C** is a diastereomer of both **A** and **B**.

Enantiomers have identical physical properties except that they rotate the plane of polarized light in opposite directions by the same angle. However, a mixture containing equal amounts of two enantiomers is optically inactive, as the effects of individual enantiomers cancel each other. Such mixture is known as *racemic mixture*, or *racemate*. The identity and purity of chiral compounds can be determined using a *polarimeter*, as explained in example D.7.1 in Option D.

The chemical properties of enantiomers are identical in reactions with non-chiral compounds but differ when a chiral reagent or solvent is used. Chirality is particularly important in biology and medicine, where one of the enantiomers can be beneficial for the organism while the other can be toxic or responsible for unwanted side effects.

- A **polarimeter** is an instrument that measures the angle of rotation of plane-polarized light.
- A **racemic mixture**, or **racemate**, contains equal amounts of two enantiomers of the same compound and thus is optically inactive (has a rotation angle of 0°).

Assessment tip

You should never say that enantiomers "bend" or "reflect" plane-polarized light; the only acceptable term is "rotate".

The properties and biological effects of chiral molecules are discussed in topics B.10 and D.7.

In contrast to enantiomers, diastereomers differ in both physical and chemical properties.

SAMPLE STUDENT ANSWER

One structural isomer of C_4H_9Br is a chiral molecule.

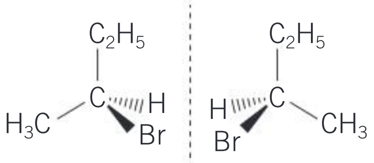
a) Draw the three-dimensional shape of each enantiomer of this isomer showing their spatial relationship to each other. [2]

b) When one enantiomer undergoes substitution by alkaline hydrolysis, approximately 75% of the product molecules show inversion of configuration. Comment on the mechanisms that occur. [2]

c) Suggest why the rate of alkaline hydrolysis of an enantiomer of iodobutane is greater than that of an enantiomer of bromobutane. [1]

This answer could have achieved 3/5 marks:

a)



b) The inversion occurs in S_N2 reactions,

so the mechanism is probably S_N2.

c) The electronegativity of I is lower than that of Br, so the C–I bond is less polar than C–Br.

▲ Correct structures

▲ Spatial relationship (mirror images) is shown clearly

▲ Correct statement about the inversion in S_N2

▼ The mechanism is a combination of S_N1 (50% inversion) and S_N2 (100% inversion), which is typical for secondary halogenoalkanes

▼ The reactivity is higher because the C–I bond is weaker than C–Br, and I^- is a better leaving group than Br^- because of its larger size

Practice problems for Topic 20

Problem 1

Which molecule can be both reduced by sodium borohydride, $NaBH_4$, and oxidized by warm acidified potassium dichromate(VI)?

A. $(CH_3)_3COH$

B. $(CH_3)_3CCHO$

C. $CH_3CH(OH)CH_2CH_3$

D. $(CH_3)_3CC(O)C(CH_3)_3$

Problem 2

a) Deduce the synthetic route for preparation of ethanal from ethane. State the reagents, conditions and reaction type for each synthetic step.

b) Construct the mechanism of the second synthetic step using curly arrows to denote the movement of electron pairs.

Problem 3

a) Deduce, giving a reason, whether 2-amino-3-methylbutan-1-ol or 3-amino-3-methylbutan-1-ol can show optical activity.

b) Draw the three-dimensional structures of the two enantiomers of the optically active compound in part (a).

c) Explain how the enantiomers in part (b) and the optically inactive compound in part (a) can be distinguished using a single analytical technique.

21 MEASUREMENT AND ANALYSIS (AHL)

TOPIC 21.1 SPECTROSCOPIC IDENTIFICATION OF ORGANIC COMPOUNDS

You should know:

- ✔ the spectroscopic analytical techniques IR, ^{1}H NMR and MS are used to deduce the structure of organic compounds;
- ✔ signals that appear as singlets in low-resolution ^{1}H NMR spectra often appear as multiplets in high-resolution spectra;
- ✔ X-ray crystallography is a structural technique used to identify the bond lengths and bond angles in crystalline solids.

You should be able to:

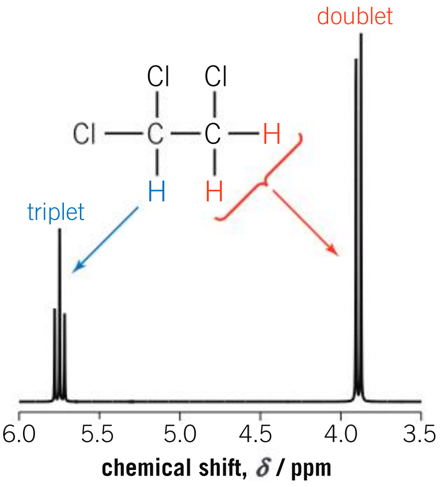
- ✔ explain why tetramethylsilane (TMS) is used as a reference standard in ^{1}H NMR spectroscopy;
- ✔ deduce the structure of an organic compound using data from several analytical techniques (X-ray crystallography, IR, ^{1}H NMR and MS).

The structural identification of an organic compound typically requires more than one analytical technique.

The principles underpinning the spectroscopic techniques of infrared (IR), proton nuclear magnetic resonance (^{1}H NMR) and mass spectrometry (MS) are discussed in topic 11.3.

^{1}H NMR

In low-resolution ^{1}H NMR spectra, single peaks (*singlets*) at different chemical shifts (δ) represent hydrogen nuclei in different chemical environments. When stronger magnetic fields are applied in high-resolution spectroscopy, some singlets resolve into multiplets. A multiplet of two close peaks is called a *doublet*, three peaks is a *triplet*, four peaks is a *quartet*, and so on. If a proton has n other protons as its nearest neighbours, then the signal for that proton will appear as $(n + 1)$ peaks. For example, the signal of the CH proton in 1,1,2-trichloroethane will be a triplet while the signal of the CH_2 protons will be a doublet (figure 21.1.1).



▲ **Figure 21.1.1.** Multiplets produced by spin–spin coupling in the ^{1}H NMR spectrum of 1,1,2-trichloroethane

Tetramethylsilane (TMS), $Si(CH_3)_4$, is used as a reference standard in ^{1}H NMR spectroscopy; its chemical shift δ is defined as 0 ppm. Because silicon has a lower electronegativity than carbon ($\chi(Si) = 1.9$, $\chi(C) = 2.6$), the ^{1}H signal of TMS appears much further upfield than the ^{1}H signals of most organic compounds. The twelve protons of TMS are all in the same chemical environment, so one strong signal is recorded. All other chemical shifts are measured in ppm relative to this signal. TMS is chemically inert, readily soluble in most organic solvents and volatile (boils just above room temperature), so it can be easily removed from a sample after measurement.

Example 21.1.1.

Using section 27 of the data booklet:

a) Predict the chemical shift, δ, in ppm, the integration for each signal, and the splitting pattern in the high-resolution ^1H NMR spectrum for ethanol.

b) Predict the integration for each signal and the splitting pattern in the high-resolution ^1H NMR spectrum for 2-methylpropan-2-ol.

Solution

a) For ethanol, CH_3CH_2OH, the integration trace (number of protons in each environment) is 3:2:1 and the splitting pattern is 3H triplet, 2H quartet, 1H singlet.

- -$\mathbf{CH_3}$: 0.9–1.0 ppm, with an integration of 3
- -$\mathbf{CH_2}$OR: 3.3–3.7 ppm, with an integration of 2; these two protons are located next to an electronegative oxygen, so the signal is shifted downfield (this *would not* occur if the protons were located in the chemical environment -$\mathbf{CH_2}$R)
- R–O**H**: 1.0–6.0 ppm, with an integration of 1.

b) The condensed structural formula of 2-methylpropan-2-ol is $(CH_3)_3COH$, so the integration trace is 9:1 and the splitting pattern is 9H singlet, 1H singlet.

In ethanol, the ^1H NMR signal for the hydroxyl proton occurs as a singlet at $\delta = 2.6$ ppm. The signal is not split into a triplet by the adjacent -CH_2- protons because trace amounts of acid and water in ethanol cause rapid proton-exchange reactions, for example:

$$CH_3CH_2OH + H_3O^+ \rightleftharpoons [CH_3CH_2OH_2]^+ + H_2O$$

At room temperature this proton transfer occurs faster than the NMR spectrum is recorded, so the hydroxyl protons generate a broad signal in which any splitting is averaged out.

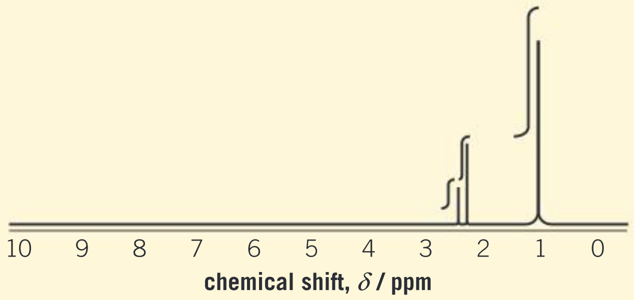
In the data booklet, the range of chemical shift values for R–OH is given as 1.0–6.0 ppm. The actual δ values for individual compounds depend on concentration, temperature and the strength of hydrogen bonding.

X-ray crystallography

X-ray crystallography is a structural technique in which the diffraction pattern of X-rays passed through a single crystal is used to identify the arrangement of atoms in the compound, revealing the bond lengths and bond angles. Crystallographic data are stored in international databases, which are used by both academic and industrial researchers.

SAMPLE STUDENT ANSWER

A compound with a molecular formula $C_7H_{14}O$ produced the following high-resolution ^1H NMR spectrum.



a) Deduce the following information from the ^1H NMR spectrum: [3]

- Number of hydrogen environments
- Ratio of hydrogen environments
- Splitting patterns

Assessment tip

The integration trace (curved line) shows the relative intensity of each signal in a ^1H NMR spectrum, which is proportional to the number of hydrogen atoms in each chemical environment. Use the length of each trace to find the ratio of hydrogen atoms in each environment.

b) Identify the functional group that shows stretching at 1710 cm^{-1} in the infrared spectrum of this compound using section 26 of the data booklet and the ^1H NMR. [1]

c) Suggest the structural formula of this compound. [2]

This answer could have achieved 5/6 marks:

a) Number of hydrogen environments: 3

Ratio of hydrogen environments: 2:3:9

Splitting patterns: All singlets

b) Aldehydes, ketones, carboxylic acids and esters

c) $(CH_3)_3CCH_2C(O)CH_3$

▲ All the answers are correct

▲ The second mark can be scored for any equivalent ratio, such as 9:3:2

▼ Four classes of compounds have been listed here, but the question asks for a functional group, so the correct answer is C=O or carbonyl; in addition, the compound $C_7H_{14}O$ contains only one oxygen atom, so its class cannot be ester or carboxylic acid

▲ Correct formula

▲ The question requires a structural formula, which can be full or condensed

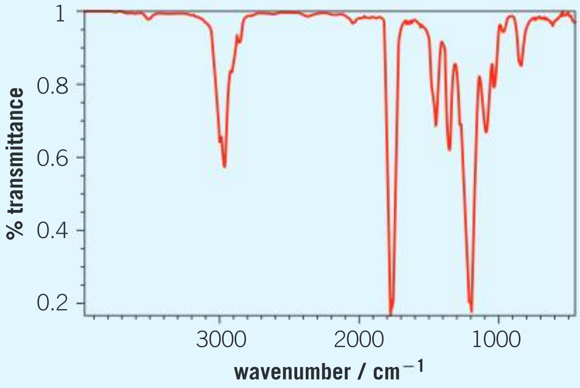
Practice problems for Topic 21

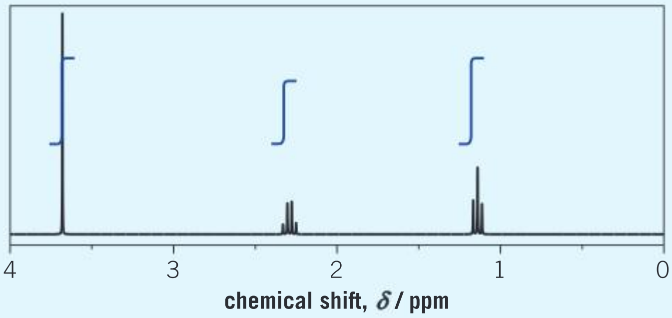
Problem 1

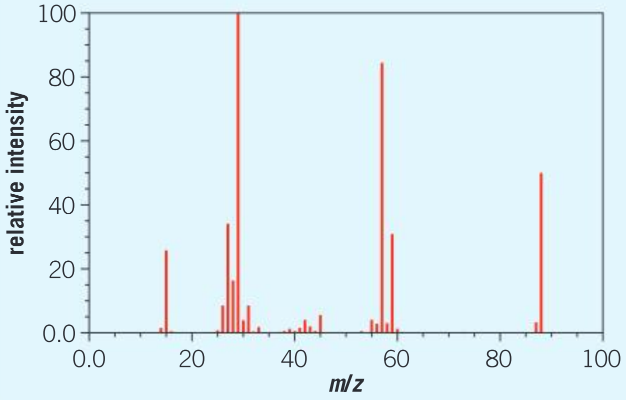
Predict the chemical shift, δ, in ppm, the integration for each signal, and the splitting pattern in the high-resolution ^1H NMR spectrum for propanal.

Problem 2

An unknown compound, X, of molecular formula $C_4H_8O_2$, has the following IR, ^1H NMR and MS spectra.







Deduce the structure of X using the information given and any other additional information from sections 26–28 of the data booklet. For each spectrum, assign as much spectroscopic information as possible, based on the structure of X.

22 DATA-BASED AND PRACTICAL QUESTIONS (SECTION A)

Assessment tip

Section A is identical in SL and HL papers, so most questions in that section are linked to the core material.

Section A of paper 3 usually contains one data-based question and several short-response questions related to practical work in a chemistry laboratory. Alternatively, the whole section can be based on a single experiment, in which case both the experimental design and the quantitative data obtained are discussed. Regardless of its structure, the primary aim of this section is to test your ability to interpret and analyse experimental data, identify qualitative trends, discuss the sources of errors or uncertainties and suggest improvements to experimental procedures.

PART 22.1 DATA-BASED QUESTIONS

You should know:

- ✔ experimental data can be obtained using a variety of physicochemical techniques;
- ✔ quantitative data are commonly recorded and communicated in tabular form;
- ✔ graphical techniques are an effective way of representing qualitative and quantitative data.

You should be able to:

- ✔ interpret and analyse experimental data presented in tabular and graphical forms;
- ✔ identify dependent and independent variables and their relationships;
- ✔ identify qualitative trends and sketch graphs using correctly labelled axes;
- ✔ estimate unknown quantities and their uncertainties from plots and diagrams.

Assessment tip

The experimental data can be taken from almost any area of science—from meteorological observations to properties of semiconductors. Do not panic if you are unfamiliar with that area—in most cases you will only need to work with numerical values and their units.

Data-based questions use real-life data from contemporary research or classroom experiments. The experimental results can be represented as tables, plots and/or diagrams. Tabular data usually require processing or analysis in order to identify a trend or correlation, which can be outlined in words or sketched as a graph.

Example 22.1.1.

The CT value is the dosage of a disinfectant needed to inactivate a certain percentage of a specific bacteria.

pH	Temperature/°C			
	5	10	15	20
6.0	69	52	35	26
7.0	97	73	49	37
8.0	140	105	70	53
9.0	201	151	101	75

▲ **Table 22.1.1.** The CT values for chlorine needed to inactivate 99% of bacteria A

a) With reference to table 22.1.1, suggest why it may be more difficult to disinfect water with chlorine in cold climates.

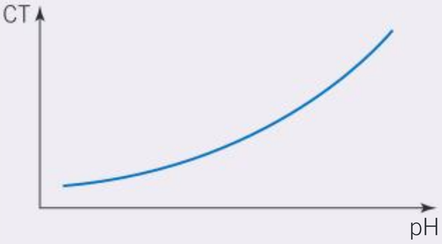
b) Sketch a graph to show how the CT value (at any temperature) varies with pH.

c) Comment on the relative CT values at pH 6.0 and pH 9.0 at each temperature.

Solution

a) The data in each row of the table show a clear trend: when the temperature increases, the CT value decreases. Conversely, the lower the temperature, the higher the dosage of chlorine needed for disinfection. Therefore, a dosage of chlorine that works in warm water may be ineffective in cold water.

b) The pH is an independent variable, so it will be shown at the *x*-axis. The CT is the dependent variable, so it will appear at the *y*-axis. Figure 22.1.1 represents the data for $T = 10°C$; the data at any other temperature would produce a similar curve.



▲ **Figure 22.1.1.** A sketch of a graph of CT against pH using the data from table 22.1.1

Note that the axes must be labelled, and the curve should have an increasing gradient. For a sketch, the scales on axes are not required, so a steeper or flatter curve would be equally acceptable.

c) The most obvious answer is that the CT for each temperature is higher at pH 9.0 than at pH 6.0. However, this answer would not be accepted, as the command term "comment" requires a more specific answer. Possible answers could state that the CT value for each temperature at pH 9.0 is approximately three times higher than that at pH 6.0, or that the CT values between pH 6.0 and 9.0 increase by approximately the same factor for all temperatures.

Assessment tip

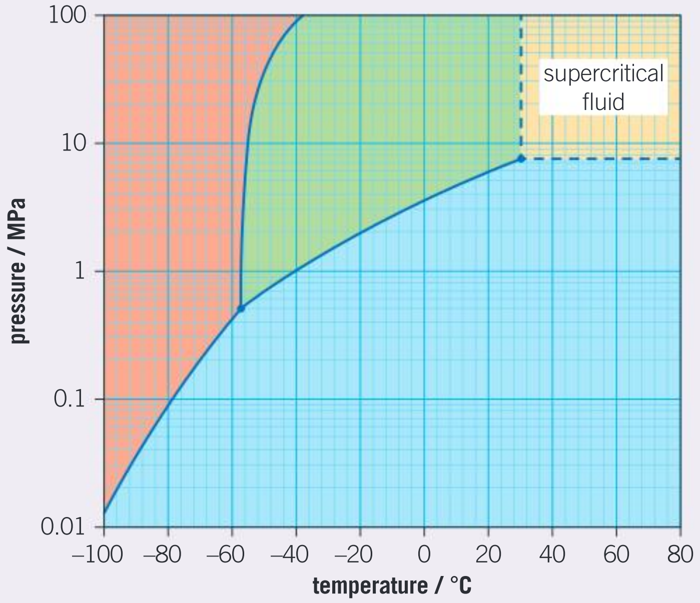
You must always pay attention to the command term used in the question. A list of the IB command terms is given in the introduction to this book. Make sure that you clearly understand the difference between apparently similar terms, such as "outline", "describe", "explain" and "comment", or "distinguish", "compare" and "compare and contrast".

If the question shows a plot or diagram, you are likely to be asked to estimate a numerical value, determine a range of values or make a qualitative statement.

Example 22.1.2.

Supercritical carbon dioxide is a non-toxic and inexpensive alternative to traditional solvents. As any supercritical fluid, it dissolves materials like a liquid and diffuses through solids like a gas.

In addition to supercritical state, carbon dioxide can exist as a gas, liquid or solid, which can be represented by a phase diagram (figure 22.1.2).



▲ **Figure 22.1.2.** A simplified phase diagram of carbon dioxide

a) Label the three blank areas of the diagram as “gas”, “liquid” and “solid”.

b) Estimate the temperature range where carbon dioxide can be liquefied.

c) Each line on the diagram represents the conditions (T, p) where two different phases can exist in equilibrium with each other. Estimate the temperature, in °C, and pressure, in MPa, where all three common phases (gaseous, liquid and solid) of carbon dioxide can exist at the same time.

d) Solid carbon dioxide is known as dry ice. Under ambient conditions, dry ice does not melt but sublimes, passing directly from solid to gaseous state. Estimate the sublimation point of carbon dioxide under standard pressure. Refer to section 2 of the data booklet.

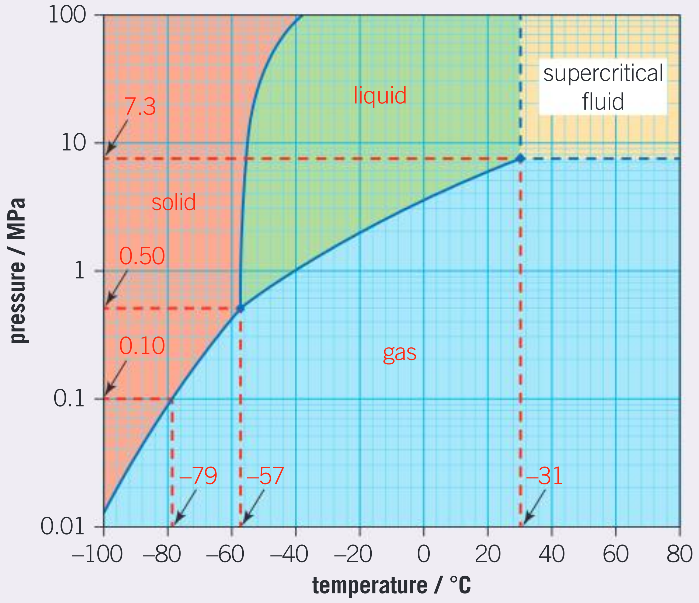
e) Predict whether liquid or supercritical carbon dioxide will have a higher density under the same pressure.

Solution

a) Even if you are unfamiliar with phase diagrams, you can answer this question using common knowledge. When the temperature increases, solids melt and form liquids, then evaporate and form gases. When pressure increases, gases turn first into liquids and then into solids. So we can expect that solid carbon dioxide will exist at low temperatures and high pressures (top left corner of the diagram) while gaseous carbon dioxide will exist at high temperatures and low pressures (bottom right corner). The remaining blank area (top middle part of the diagram) represents liquid carbon dioxide.

b) Liquid carbon dioxide can exist between approximately −57 and +31°C (figure 22.1.3).

➜



▲ **Figure 22.1.3.** Annotated phase diagram of carbon dioxide

c) All three phases can coexist at approximately –57°C and 0.50 MPa (note that the scale on the vertical axis is logarithmic). This set of conditions is known as *the triple point*, although you do not have to memorize this term.

d) According to section 2 of the data booklet, the standard pressure is 100 kPa, or 0.1 MPa. At this pressure, solid and gaseous phases can coexist at approximately –79°C, which is the sublimation point of carbon dioxide. Above –79°C, dry ice will spontaneously sublime and turn into gas without melting.

e) Once again, this qualitative question can be answered by reasoning. According to the diagram, supercritical fluid exists at higher temperatures than liquid. When heated, liquids and gases expand and thus become less dense. Therefore, under the same pressure the density of liquid carbon dioxide will be higher than that of supercritical carbon dioxide.

The above examples demonstrate that data-based questions do not require any specific knowledge beyond the core material. Ensure that you read the question carefully, take note of the column heading, axis labels and units, look for trends and correlations, think critically and use common sense in unfamiliar situations.

As a part of your preparation for data-based questions, you are advised to review topics 3.2 (periodic trends), 4.1 and 4.5 (ionic and metallic lattices), 5.1 (thermochemistry), 6.1 (chemical kinetics) and 11.2 (graphical techniques).

SAMPLE STUDENT ANSWER

The following data have been compiled for a range of molecules that may be found in the atmosphere.

Molecule	Integrated IR intensity* / km mol^{-1}	Molecular dipole moment / D	GWP** over 100 years
CO_2	25.7	0	1
CCl_4	433.7	0	1400
CCl_3F	705.2	0.45	4750
CCl_2F_2	970.1	0.51	10 900
$CClF_3$	1199	0.50	14 400
CF_4			

*Integrated IR intensity is a measure of the extent to which the molecule absorbs infrared radiation passing through the atmosphere.

**The global warming potential (GWP) is a relative measure of the total contribution of the compound to global warming over the specified time period.

i) Use the integrated IR intensity data in the table to estimate the value for CF_4. [1]

ii) Outline the relationship between GWP over 100 years and integrated IR intensity for CCl_4, CCl_3F, CCl_2F_2 and $CClF_3$. [1]

iii) Examine whether there is a general relationship between integrated IR intensity and molecular dipole moment. [1]

iv) CCl_2F_2 and $CClF_3$ were developed for use as refrigerants but are now being replaced by other chemicals. Comment on their use with reference to values in the table and other environmental concerns. [2]

This answer could have achieved 3/5 marks:

i) About 1450 km mol^{-1}, because the figure increases by 230–270 units after each Cl is replaced with F.

ii) When one value increases, another increases as well.

iii) There is no obvious relationship.

iv) They contribute to global warming. Also, they are chlorofluorocarbons (CFCs), so they cause ozone depletion.

▲ Correct. The explanation is also correct, but it is not required as the command term is "estimate"

▲ Correct. "Positive correlation" would also be accepted

▼ The statement is correct, but the command term "examine" requires a supporting argument. For example, CO_2 and CCl_4 have identical dipole moments but very different integrated IR intensities

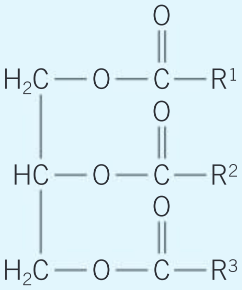
▲ Valid environmental concerns

▼ No reference to GWP values in the table

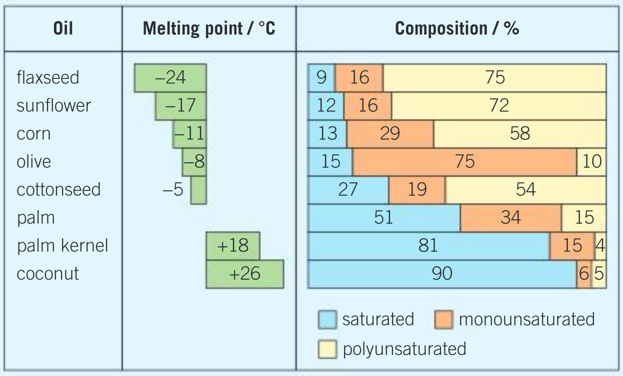
Practice problems for Part 1

Problem 1

Vegetable oils are composed of triglycerides, the organic molecules with long hydrocarbon chains R^1, R^2 and R^3 of the general formula C_nH_m:



Saturated triglycerides contain no C=C bonds, monounsaturated triglycerides contain one such bond per molecule, and polyunsaturated triglycerides contain two or more C=C bonds per molecule. The melting points and composition of common vegetable oils are shown in table 22.1.2.



Oil	Melting point / °C	Composition / %		
		saturated	monounsaturated	polyunsaturated
flaxseed	–24	9	16	75
sunflower	–17	12	16	72
corn	–11	13	29	58
olive	–8	15	75	10
cottonseed	–5	27	19	54
palm		51	34	15
palm kernel	+18	81	15	4
coconut	+26	90	6	5

▲ **Table 22.1.2.** Melting points and composition of common vegetable oils.

a) Examine whether there is a general relationship between the melting point of an oil and:

- **i)** the percentage of saturated triglycerides in that oil;
- **ii)** the percentage of monounsaturated triglycerides in that oil.

b) Estimate the melting point of palm oil using the data from table 22.1.2.

c) The actual melting point of palm oil is +35°C. Suggest, with a reference to intermolecular forces, why the actual melting point of palm oil differs from the value predicted in part (b).

d) The –OC(O)R fragments in triglycerides are the residues of fatty acids. The formulas and common names of three straight-chain fatty acids are given below.

$C_{15}H_{29}COOH$	$C_{17}H_{31}COOH$	$C_{19}H_{39}COOH$
palmitoleic acid	linoleic acid	arachidic acid

- **i)** Classify each of these acids as saturated, monounsaturated or polyunsaturated.
- **ii)** Suggest, with reference to table 22.1.2, which of the three acids has the highest melting point.

Problem 2

The physical properties and molecular geometry of hydrides and chlorides of Group 15 elements are shown in table 22.1.3.

▼ **Table 22.1.3.** Properties and structures of hydrides and chlorides of Group 15 elements

Compound	Molar mass / g mol^{-1}	Melting point / K	Boiling point / K	Molecular dipole moment / D	Bond length / pm	Bond angle / °
NH_3	17.04	195	240	1.42	102	108
PH_3	34.00	140	185	0.58	142	94
AsH_3	77.95	162	210	0.20	152	92
SbH_3	124.79	185	256	0.12	171	91
BiH_3	212.01	206	—*	0.04	178	90
NCl_3	120.36	233	344	0.60	176	107
PCl_3	137.32	179	349	0.97	204	100
$AsCl_3$	181.27	257	403	1.59	216	98
$SbCl_3$	228.11	346	497	3.9	233	97
$BiCl_3$	315.33	500	720	4.7	242	96

*Decomposes above 240 K.

a) Identify the compounds from table 22.1.3 that are liquid under SATP conditions. Refer to section 2 of the data booklet.

b) Using the same axes, sketch and label two curves to show how the boiling points of hydrides and chlorides vary with the molecular mass.

c) Comment on the shapes of the curves from part (b).

d) Explain, with a reference to VSEPR theory, why all molecules from table 22.1.3 are polar.

e) The molecular dipole moment is a measure of the separation of positive and negative charges within a molecule.

i) Outline how the molecular dipole moments of hydrides and chlorides from table 22.1.3 are related to bond lengths and bond angles in their molecules.

ii) The distribution of positive and negative charges within a molecule can be predicted using the electronegativity values of the elements. Suggest why the molecular dipole moments for hydrides and chlorides show opposite trends.

PART 22.2 PRACTICAL QUESTIONS

You should know:

- ✔ quantitative data are always associated with random errors caused by the apparatus and human limitations;
- ✔ experimental procedures often lead to systematic errors in measurement;
- ✔ the experimental setup affects the precision, accuracy and validity of the data obtained.

You should be able to:

- ✔ discuss the sources of errors in a laboratory experiment and estimate their impact on the experimental results;
- ✔ suggest how the accuracy and precision of a particular experiment can be improved;
- ✔ suggest and evaluate hypotheses using experimental evidence.

Many questions in section A are related to typical experiments performed by students in a classroom laboratory. The IB Chemistry diploma programme requires the candidates to complete a number of practical experiments, which are briefly described in table 22.2.1. You should be familiar with the laboratory techniques and equipment listed in the last column of this table, as nearly all practical questions in section A of paper 3 will be based on that material.

Topic	Practical skills	Typical experiments	Laboratory techniques
1.2	derive an empirical formula from a mass change in a chemical reaction	decomposition of a salt hydrate; combustion of magnesium or other active metal	using an electronic balance; heating a crucible to constant mass
1.3	calculate the molar mass of a gas using the ideal gas equation	determining the average M_r of the fuel gas from a disposable lighter; determining the average M_r of air	collecting an insoluble gas under water; using a measuring cylinder; using a gas syringe; using a vacuum pump
1.3 and 8.3	determine an unknown concentration by titration	acid–base titration using an indicator, pH-meter, conductivity probe or digital thermometer (temperature probe); analysis of an antacid; analysis of aspirin tablets	preparing a solution using a volumetric flask; taking a sample by a volumetric or graduated pipette; performing a titration using a burette, using an acid–base indicator; using a pH-meter; using a conductivity probe; using a digital thermometer; dissolving a solid sample with stirring and/or heating
2.2	observe and interpret emission spectra	flame tests for alkali metals and halogens; study of emission spectra of gas discharge tubes	performing flame tests; using coloured glass filters; using a spectroscope
5.1	determine the enthalpy of a reaction using a calorimeter	measuring the enthalpy change of a neutralization or redox reaction	assembling and using a coffee-cup calorimeter; extrapolating experimental data
5.3	determine the enthalpy of a reaction by heat transfer	measuring enthalpies of combustion of organic substances using a gas or spirit burner	using a gas or spirit burner; using a thermometer; identifying the source of a large systematic error
6.1	experimental study of reaction rates	determining and comparing reaction rates at different concentrations or different surface areas of reactants and with or without catalysts	measuring concentration changes indirectly (by changes in mass, volume, colour, pH or conductivity); using a colorimeter or spectrophotometer; using a data logger; determining the slope (gradient) of a graph
9.2	experimental study of voltaic cells	construction of voltaic cells using metal and/or metal-ion half-cells	assembling a voltaic cell; using a voltmeter; using an ammeter
10.1	construction of 3-D models of organic molecules	construction of real or virtual 3-D molecular models	using model kits; using molecular graphics software

▲ **Table 22.2.1.** The list of recommended laboratory experiments

Assessment tip

If you are not familiar with some experiments from table 22.2.1, you can easily find video demonstrations online using the second or third column of the table as key words. Listen carefully to the explanations and make notes about the purpose of each step in experimental procedures.

Assessment tip

In nearly all practical questions in Section A, the focus is on the methodology of experimental work rather than calculations. For example, when answering question (a) from example 22.2.1, your instinct may be to calculate the molar concentration of sodium hydroxide in the final solution. This would be irrelevant to the question—you are asked to outline an aspect of the experimental procedure, as opposed to performing any calculations.

Example 22.2.1.

A student wished to determine the concentration of sodium hydroxide in a solution by titrating it against a 0.100 mol dm^{-3} hydrochloric acid.

a) Outline, giving your reasons, how you would carefully prepare the 1.00 dm^3 aqueous solution from the 4.00 g sodium hydroxide pellets.

b) Outline, giving your reasons, the titration procedure that uses 10.0 cm^3 of the sodium hydroxide solution and bromothymol blue as the indicator. Refer to section 22 of the data booklet.

Note: before reading any further, you are strongly advised to write down your own answers and then compare them with the text below.

Solution

a) To score the full mark, it is sufficient to state any two of the following:

- wear laboratory coat, glasses and protection gloves because sodium hydroxide is highly corrosive;
- weigh sodium hydroxide pellets using an analytical balance because the precision of at least two decimal points is required;
- add sodium hydroxide to less than 1 dm^3 of deionized water in a beaker and stir the mixture until the pellets dissolve;
- transfer the solution from a beaker to a 1 dm^3 volumetric flask using a funnel to avoid any loss of the solution;
- rinse the beaker and the funnel with deionized water and add the washings to the volumetric flask to make sure that all sodium hydroxide has been transferred;

- add deionized water to the volumetric flask to the graduation mark, stopper the flask and turn it over at least ten times to stir the solution thoroughly;
- let the solution cool down to ambient temperature because sodium hydroxide dissolves in water exothermically.

b) As with the previous question, it is sufficient to state any two of the following:

- rinse the burette several times with the standard solution (0.100 mol dm^{-3} hydrochloric acid) to remove any possible contaminants;
- fill the burette above the top graduation mark with the standard solution and run down excess solution until the bottom of the meniscus touches the graduation mark "0";
- rinse a small conical flask several times with deionized water to remove any possible contaminants;
- transfer 10.0 cm^3 of the sodium hydroxide solution to the conical flask using a graduated or volumetric pipette because a precision of at least one decimal point is required;
- add several drops of the indicator solution to the conical flask and swirl the flask or use a magnetic stirrer to ensure that the solution is thoroughly mixed;
- keep swirling or stirring the flask and add the standard solution from the burette dropwise until the colour of the solution changes from blue to yellow;
- record the volume of the standard solution used to the nearest graduation mark of the burette;
- repeat the titration several times until two or three consecutive measurements agree within 0.1 cm^3 (or 0.05 cm^3 if a precise burette is used).

Note that a measuring cylinder cannot be used anywhere in parts (a) or (b), as its precision is insufficient for analytical experiments.

The above example illustrates the importance of experimental skills: if you have completed the mandatory practical works and taken effort to understand the purpose of what you were doing, you can approach any section A question with confidence. If not, there is still enough time to review the laboratory manuals and your own notes. Make sure that you can explain in your own words all typical experiments from table 22.2.1, state the names of common laboratory glassware and equipment, and outline the importance of safety precautions.

Quantitative data obtained from experiments or observations are always associated with *random* and *systematic errors*. Random errors are caused by the limitations of measuring devices and human operators. For example, the precision of burette readings in example 22.2.1 is limited to one-half of the graduation mark (typically 0.1 or 0.05 cm^3). Another source of random errors in titration is drop size, as the smallest portion of the standard solution cannot be less than one drop (0.04 to 0.05 cm^3). Finally, random errors of approximately the same magnitude (0.05 to 0.1 cm^3) are introduced by the analytical chemist whose ability to detect the colour change can vary slightly from experiment to experiment.

- **Random errors** are unpredictable variations of measurements between trials that can be reduced by repeating the measurement and averaging the results.
- **Systematic errors** are predictable and relatively constant deviations of the measurements from the true value; they cannot be reduced by repetition and averaging.

Random and systematic errors, uncertainties, accuracy and precision are discussed in greater detail in topic 11.1.

Random errors are unpredictable, so they cannot be eliminated completely. However, they can be reduced by repeating the experiment several times and averaging the measurements. In contrast, systematic errors are predictable and typically have a constant magnitude or vary proportionally to the true value. In a titration, systematic errors can be caused by imperfect calibration of the volumetric glassware, incorrectly determined concentrations of standard solutions, or human factors, such as unusual colour perception of the analytical chemist. Another common error in a titration experiment is discussed in example 22.2.2.

Example 22.2.2.

The student who performed a series of titrations from example 22.2.1 was adding the acid too quickly.

a) State the type of error introduced by the student.

b) Suggest, giving a reason, how this error could have affected the calculated concentration.

Solution

a) This is a systematic error, as it was introduced consistently in a series of experiments.

b) By adding the acid too quickly, the student missed the exact moment of the colour change and thus added too much acid. Using a larger volume of the standard solution in calculations would give a larger apparent concentration of sodium hydroxide.

Once identified, systematic errors can usually be eliminated by changing the equipment, materials or procedure, or by using a correction coefficient in calculations. Some typical systematic errors are listed in table 22.2.2. This list is not exhaustive, but it will give you an idea of what to look for in similar situations.

Experiment	Observation	Cause	Correction
decomposition of a salt or salt hydrate	mass loss is too large	loss of product	cover the crucible; heat up slowly
	mass loss is too small	incomplete reaction	increase the temperature or reaction time
combustion of an active metal	mass gain is too small		
	mass gain is too large	absorption of water or carbon dioxide from air	cool down the product in desiccator; determine the mass quickly
determining molar mass of a gas	M_r is too high	gas leaks out	use airtight connection and a gas syringe
	M_r is too low	air leaks in	
acid–base titration with an indicator	calculated concentration is too low or too high	incorrect choice of indicator	use a different indicator or a pH-meter
		old or wrong standard solution	prepare a new standard solution
using a coffee-cup calorimeter	ΔH is too low	heat loss to the environment	use nested caps; increase the solution volume
monitoring reaction rate by mass or volume of the gas released	mass loss is too large	evaporation/loss of solvent	close the flask with a loose piece of cotton
	volume change is too small	gas leak	use airtight connection and a gas syringe
isolating a reaction product	yield > 100%	wet or impure product	dry, recrystallize or redistill the product
	yield is very low	incomplete reaction	increase the reaction time or change the conditions
		product loss	alter the procedure

▲ **Table 22.2.2.** Typical systematic errors in chemical experiments

In many cases, you will be asked to make a comment on a particular set of experimental data or use these data for evaluating a hypothesis. Although it is impossible to give any specific recommendations for such questions, some typical situations are outlined in table 22.2.3 and the examples below.

Observation	Possible explanation
irreproducible results	large random errors; incorrect procedure
poor correlation	large random errors; no causal relationship between variables (incidental correlation)
no correlation	no causal relationship between variables
unexpected type of correlation (non-linear instead of linear, negative instead of positive, and so on)	wrong assumption; incorrect expression used in calculations; additional factors must be taken into account
good correlation between independent variables	variables are not independent
graph or calibration curve does not pass through origin	systematic error(s)
large deviation from expected results at high temperatures	heat loss to the environment; evaporation of solvent or volatile reactant/product
large deviation from expected results at low temperatures	heat gain from the environment; freezing of solvent (especially water); precipitation of reactant or product

▲ **Table 22.2.3.** Typical irregularities in experimental data

Example 22.2.3.

The series of titrations from example 22.2.1 was repeated very carefully, using freshly prepared standard solutions and correctly calibrated volumetric glassware. Despite all efforts, the reproducibility of results was very poor. Suggest **two** possible reasons for that.

Solution

Poor reproducibility is often a result of random errors, which could be introduced by external factors. For example, the temperature in the building could change during the experiment, affecting the concentrations of all reagents (as solutions would expand or contract, so their densities would change). If too little indicator was used, the colour change would be difficult to see, and the end point could be missed. The titrations could be performed by different students, who could have different colour perception and thus would stop the titration before or after the equivalence was reached. Another possibility is that the intermediate and final results in calculations could have been rounded incorrectly.

Similar to data-based questions, the practical questions in section A do not require any specific knowledge beyond the core material. Critical thinking and problem-solving experience are key elements for your success. The best way to develop these skills is to answer questions from past examination papers and the practice problems given at the end of this chapter.

Assessment tip

Remember that a hypothesis can be supported or disproved (falsified) by experimental evidence but can never be proved, as there is always a chance that another set of experimental data will not match the theoretical prediction.

Assessment tip

Note that detailed explanations are not required in this question, so an answer such as "temperature change and rounding errors" would be sufficient.

SAMPLE STUDENT ANSWER

Antacids react with hydrochloric acid in the stomach to relieve indigestion. A student investigated different brands of antacid to see which caused the largest increase in pH in a given time. She added the antacids to hydrochloric acid, and recorded the change in pH over five minutes.

Antacid brand	Active ingredient(s)	Recommended dosage	Dose used	Initial pH ±0.02	Final pH ±0.02	Change in pH
A	magnesium hydroxide, aluminium hydroxide	2–3 tablets	2 tablets	1.68	4.53	+2.85
B	sodium hydrogencarbonate, calcium carbonate	2–4 tablets	2 tablets	1.70	5.31	+3.61
C	calcium carbonate	1–2 tablets	1 tablet	1.70	4.52	+2.82
D	magnesium hydroxide, aluminium oxide, aluminium hydroxide	1–2 tablets	1 tablet	1.69	2.21	+0.52

a) State an equation for the reaction of magnesium hydroxide with hydrochloric acid. **[1]**

b) Suggest **two** variables, besides the time of reaction, which the student should have controlled in the experiment to ensure a fair comparison of the antacids. **[2]**

c) Calculate the uncertainty in the change in pH. **[1]**

d) The student concluded that antacid **B** was the most effective, followed by **A**, then **C** and finally **D**. Discuss **two** arguments that reduce the validity of the conclusion. **[2]**

This answer could have achieved 4/6 marks:

a) $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$

b) The mass of tablets needed to be the same in all experiments. Also, she needed to control whether the tablets were crushed or not.

c) $0.02 + 0.02 = \pm0.04$ pH units.

d) First, the ingredients in tablets were different. Second, two tablets were used in experiments A and B but only one tablet was used in experiments C and D.

▲ Correct equation

▲ The first statement is accepted

▼ "Crushed" not accepted as a specific variable is not described. "Surface area" would score the mark. Other acceptable variables: volume or concentration of HCl(aq); temperature of the solution

▲ Correct answer

▼ Not accepted, as the aim of this study was to compare the efficiency of different brands, regardless of their composition

▲ A good point. Other possible answers: each experiment was repeated only once; the difference in pH between experiments **A** and **C** (0.03 units) was smaller than the uncertainty (±0.04 units)

Practice problems for Part 2

Problem 1

The *iodine clock reaction* is often used as an illustration of chemical kinetics. The reaction involves two independent processes, **A** and **B**:

A: $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$

B: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Reaction **B** is much faster than reaction **A**, so the iodine, $I_2(aq)$, formed in reaction **A** immediately reacts with thiosulfate ions, $S_2O_3^{2-}(aq)$, in reaction **B**. Once all thiosulfate ions are consumed, free iodine appears in the solution, where it reacts with starch to form a characteristic blue-black complex.

a) A typical iodine clock reaction uses a mixture of the following solutions:

50.0 ± 0.1 cm³ of 0.00250 mol dm⁻³ potassium iodide, KI;

20.0 ± 0.1 cm³ of 0.0100 mol dm⁻³ sodium thiosulfate, $Na_2S_2O_3$;

20.0 ± 0.1 cm³ of 1.00 mol dm⁻³ sulfuric acid, H_2SO_4;

20.0 ± 0.1 cm³ of 0.500 mol dm⁻³ hydrogen peroxide, H_2O_2;

5.0 ± 0.1 cm³ of 1% aqueous starch.

i) The concentration of iodide ions, $I^-(aq)$, is assumed to be constant until the reaction mixture turns blue-black. Outline why this is a valid assumption.

➜

ii) The concentration of hydrogen peroxide, $H_2O_2(aq)$, is also assumed to be constant. Outline why this assumption is also valid.

iii) Determine the percentage uncertainty of the concentration of sulfuric acid, $H_2SO_4(aq)$, in the reaction mixture.

iv) The time required for the reaction mixture to change colour typically varies between 44 and 46 s. Apart from the concentration uncertainties, state **two** possible sources of error that could affect the reaction timing.

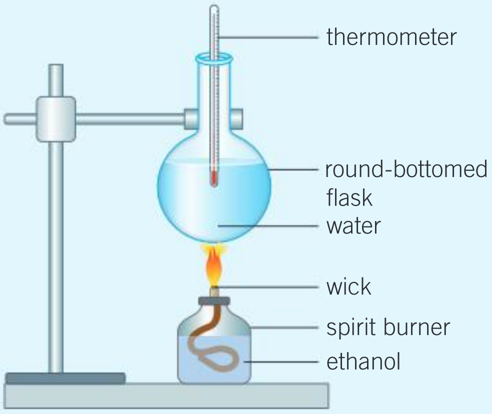
v) For each source of error in part (iv) state whether it is a random or a systematic error.

b) Outline, giving your reasons, how you would carefully prepare the solution of potassium iodide from part (a).

c) A group of students prepared several sets of flasks with the solutions from part (a). One of the students forgot to add the solution of sodium thiosulfate to his reaction mixture. Another student assumed that the spare solution was hers and added it to her reaction mixture, thus using twice as much sodium thiosulfate as was required. Predict the observations in each of the two erroneous experiments.

Problem 2

The enthalpy of combustion of ethanol can be determined experimentally in a school laboratory as illustrated below.



A student weighed the burner with ethanol to two decimal places, placed it under the flask, allowed the ethanol to burn for a short time and extinguished the flame.

a) Outline how the student could determine the mass of burned ethanol.

b) To calculate the amount of heat (q) produced by the combustion of ethanol, the student used the formula $q = m_w C_w \Delta T$, where m_w was the mass of water in the flask, C_w was the thermal capacity of water, and ΔT was the temperature change of the water. State **two** assumptions made by the student.

c) The enthalpy of combustion of ethanol determined in this experiment was -670 kJ mol^{-1}, which is approximately twice as low as the value given in section 13 of the data booklet. Suggest the most likely cause for such a large error.

d) The student hypothesized that the use of a more precise analytical balance would significantly improve the accuracy of the experimental ΔH_c value. Discuss the validity of this hypothesis.

e) Suggest **one** way of reducing random errors and **one** way of reducing systematic errors in this experiment.

A MATERIALS

A.1 MATERIALS SCIENCE INTRODUCTION

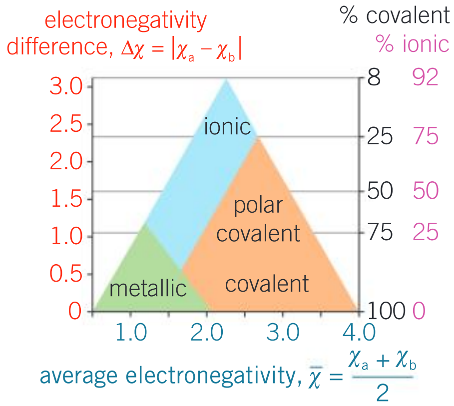
You should know:

- ✔ materials can be classified based on their bonding type, structure, properties or uses;
- ✔ composites are mixtures that consist of a reinforcing phase embedded in a matrix phase;
- ✔ the properties of a material based on the degree of metallic, ionic or covalent character can be deduced from the bonding triangle diagram.

You should be able to:

- ✔ apply the bonding triangle diagram to deduce the bonding type in a binary compound;
- ✔ relate the physical properties of a material (melting point, permeability, conductivity, elasticity, brittleness) to its bonding and structure;
- ✔ evaluate ways of classifying materials.

An understanding of electronegativity (χ) (topics 3.2 and 4.2), bonding types and structures (topic 4) is essential for option A.



▲ **Figure A.1.1.** The van Arkel–Ketelaar bonding triangle

The bonding triangle diagram can be found in section 29 of the data booklet.

Materials science is an interdisciplinary field of science and engineering that explores the physical and chemical properties of matter (materials) in the solid state and relates these macroscopic properties to the microscopic composition and structure of the material. Materials science enables the design of new materials with properties tailored to a specific use.

The properties of a pure material depend on its degree of metallic, ionic or covalent character. For binary compounds, this can be deduced from the bonding triangle diagram (figure A.1.1).

Example A.1.1.

Using the bonding triangle given in section 29 of the data booklet, deduce the type of bonding and predict the approximate percentage ionic character of the following materials: CsF, SiO_2 and Al_2O_3

Solution

For each material you need to work out the average electronegativity ($\bar{\chi}$) and the electronegativity difference ($\Delta\chi$) using the data given in section 8 of the data booklet. Then find its position on the bonding triangle to establish its class. The approximate percentage ionic character is $\frac{\Delta\chi}{3.2} \times 100\%$.

Material	$\bar{\chi}$	$\Delta\chi$	Classification	% Ionic character
CsF	$0.5(4.0 + 0.8) = 2.4$	$4.0 - 0.8 = 3.2$	ionic	$3.2/3.2 \times 100 = 100\%$
SiO_2	$0.5(3.4 + 1.9) = 2.7$	$3.4 - 1.9 = 1.5$	polar covalent	$1.5/3.2 \times 100 \approx 47\%$
Al_2O_3	$0.5(3.4 + 1.6) = 2.5$	$3.4 - 1.6 = 1.8$	ionic	$1.8/3.2 \times 100 \approx 56\%$

The physical properties of a material (melting point, permeability, conductivity, elasticity, brittleness) are related to its bonding and structure (the types of atoms and how they are packed together). The four types of material classified by bonding type are:

- *Metals* have metallic bonding.
- *Ceramics* can form both giant ionic and macromolecular structures. Ceramics are hard, brittle, and often porous because of gaps in their structures. Examples of ceramic materials are glass, spark-plug insulators, washbasins and roof-tiles. Ceramics are often aluminates, silicates, oxides, carbides or nitrides.
- *Polymers*, or plastics, are macromolecules.
- *Composites* are made of a combination of phases of metals, ceramics or polymers. Examples of composite materials include concrete and fibreglass.

Metallic bonding is covered in topic 4.5 and polymers in option A.5.

- **Metals** have high electrical conductivity, high thermal conductivity, are *malleable* (can be hammered into shape without breaking) and *ductile* (can be drawn into a wire).
- **Ceramics** are solid inorganic materials, excluding pure metals and their alloys. The elements found in ceramic materials may be metals or non-metals. They are typically hard, brittle and stable at high temperatures, and have high melting points.
- **Polymers** are long-chain, covalent molecules. Polymers are usually good electrical and thermal insulators.
- **Composites** are mixtures that consist of a reinforcing phase embedded in a matrix phase.

SAMPLE STUDENT ANSWER

Describe how the structures of ceramics differ from those of metals. [2]

This answer could have achieved 1/2 marks:

Ceramics have giant ionic structures, and metals contain a lattice of positive ions in a sea of delocalized electrons.

▼ The answer is not complete: ceramic materials can have giant ionic and/or giant covalent structures

▲ Correct description of the structure of a metal

Practice problems for Topic A.1

Problem 1

The bonding triangle is given in section 29 of the data booklet. For the substances F_2, KBr and $PbBr_2$:

a) deduce the type of bonding present in each substance

b) predict the approximate percentage ionic character.

Problem 2

Distinguish between alloys and composites.

Problem 3

Explain why platinum can be classified as a ductile metal.

A.2 METALS AND INDUCTIVELY COUPLED PLASMA (ICP) SPECTROSCOPY

You should know:

- ✔ metals can be extracted from their ores by reduction by coke or a more reactive metal, electrolysis or heating, depending on their positions in the activity series;
- ✔ Faraday's constant, *F*, relates the amount of substance produced by electrolysis to the charge passed through the electrolytic cell;
- ✔ alloys are homogeneous or heterogeneous mixtures of a metal with other metals or non-metals;
- ✔ materials can be classified as paramagnetic or diamagnetic on the basis of their behaviour in external magnetic fields;
- ✔ plasma is a high-energy state of matter that consists of isolated neutral atoms or molecules, free electrons or positive ions;
- ✔ trace amounts of metals can be identified and quantified by ionizing them with argon gas plasma in inductively coupled plasma (ICP) spectroscopy using mass spectrometry (MS) and optical emission spectroscopy (OES).

You should be able to:

- ✔ solve numerical problems on electrolysis using Faraday's law;
- ✔ deduce redox equations for the reduction of metals;
- ✔ explain the production of aluminium by the electrolysis of alumina in molten cryolite;
- ✔ explain how alloying changes the properties of metals;
- ✔ discuss paramagnetism and diamagnetism with respect to the electron structure of metals;
- ✔ identify metals and calculate their abundances from ICP-MS and ICP-OES data;
- ✔ explain the separation and quantification of metal ions by MS and OES.

This topic on metals and ICP requires understanding of oxidation and reduction (topic 9.1), line emission spectroscopy (topic 2.2) and mass spectrometry (topics 2.1 and 11.3).

Extraction of metals

Metals can be extracted from their ores by three methods, depending on their positions in the activity series:

- heating of ore (least reactive metals – Cu, Ag, Hg, Pt, Au)
- reduction of oxides of metal with a more reactive metal or with C(s)/CO(g) (metals of intermediate reactivity – Zn, Cr, Fe, Ni, Sn, Pb)
- electrolysis of molten compounds (very reactive metals – K, Na, Mg, Al).

Iron is reduced from its oxide with coke, C(s), and carbon monoxide, CO(g), in a blast furnace. The associated reactions are:

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

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

$$Fe_2O_3(s) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(l)$$

$$Fe_2O_3(s) + 3C(s) \rightarrow 3CO(g) + 2Fe(l)$$

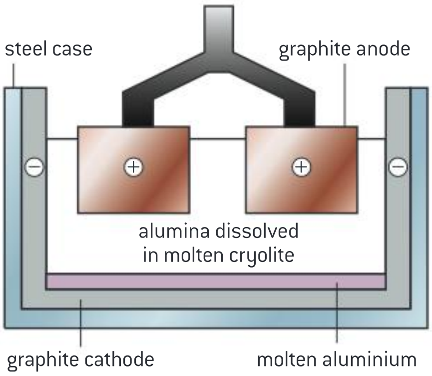
Molten iron is collected at the bottom of the furnace.

Metals can also be reduced by other metals higher up in the activity series, for example:

$$CuSO_4(aq) + Fe(s) \rightarrow Cu(s) + FeSO_4(aq)$$

The activity series is given in section 25 of the data booklet.

Metals that are higher in the activity series than carbon are usually extracted from their ores by electrolysis. Aluminium, for example, is obtained from its ore alumina, Al_2O_3, by the Hall–Héroult process (figure A.2.1).



▲ **Figure A.2.1.** The Hall–Héroult process for the extraction of aluminium

Example A.2.1.

The Hall–Héroult process is used for the industrial smelting of aluminium.

a) Explain why in the electrolysis of molten alumina, Al_2O_3, the molten electrolyte contains cryolite, Na_3AlF_6.

b) State the half-equation for the reaction taking place at the cathode.

c) State the half-equation for the reaction taking place at the anode, forming oxygen gas.

d) Formulate the overall equation for this process.

e) Suggest **one** problem associated with the use of cryolite in this process.

f) Compare the production of aluminium by this process with the process of recycling aluminium.

g) State **one** property of aluminium that makes it suitable for use as an alloy in the manufacture of aircraft.

Solution

a) Al_2O_3 has a very high melting point, above 2000°C, so the electrolysis of the molten ore would require too much energy. The use of molten cryolite as a solvent permits a much lower operating temperature of about 1000°C.

b) $Al^{3+} + 3e^- \rightarrow Al(l)$

c) $2O^{2-} \rightarrow O_2(g) + 4e^-$

d) $4Al^{3+} + 6O^{2-} \rightarrow 4Al(l) + 3O_2(g)$

e) Fluoride ions, F^-, from the cryolite, Na_3AlF_6, can be oxidized to fluorine gas, which can be dangerous to the environment if not appropriately recovered.

f) Production of aluminium by the Hall–Héroult process is much more energy-intensive than recycling aluminium, as the melting point of Al(s) is only 660°C, and no energy is spent on the electrolysis of recycled material.

g) Aluminium-based alloys are used because of their low density.

Assessment tip

- Environmental chemistry spans the entire chemistry curriculum of the IB Diploma Programme, so it is worth making a list of environmental aspects every time you spot them. Short questions on environmental chemistry often appear in section A of paper 3 or within the Options.
- Stating that "the alloys are lighter" would not score the mark as a response to question (g).

The quantity of metal produced in electrolysis can be calculated using *Faraday's law*. The amount of substance, n, produced at an electrode during electrolysis depends on the charge passed, Q (in turn dependent on the current, I, and the duration of electrolysis, t), and the charge on the ion, z. The charge in coulombs is related to the number of electrons passed by Faraday's constant, F, 96 500 C mol^{-1}.

$$n = \frac{Q}{Fz} = \frac{It}{Fz}$$

Faraday's law of electrolysis states that the amount of substance, in mol, formed at an electrode during electrolysis is directly proportional to the amount of charge, in C, passing through the electrolytic cell.

Alloys

Adding small amounts of another material to a metal to form an *alloy* can enhance its desired properties by altering its structure. Alloys often have greater mechanical strength than their individual components, as ions of different sizes form a less regular lattice in which it is more difficult for the cations to slide past each other. For example, steel is stronger than iron, and stainless steel resists corrosion; traces of titanium or scandium added to aluminium greatly increase its strength without compromising its low density for use in aircraft bodies.

Calculation of the amount of substance produced at an electrode during electrolysis is covered in topic 19.1.

Faraday's constant is given in section 2 of the data booklet.

Alloys are mixtures of a metal with other metals or non-metals and can be homogeneous or heterogeneous.

Paramagnetism and diamagnetism

Materials can be classified as *paramagnetic*, *diamagnetic* or *ferromagnetic* based on how they behave in an external magnetic field.

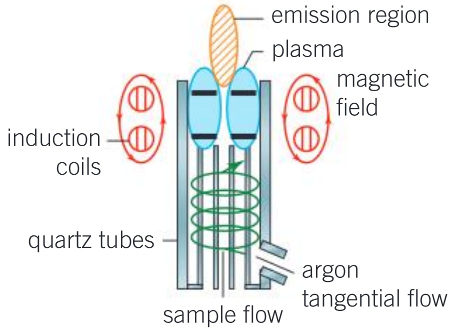
- **Paramagnetic** materials have unpaired electrons and are attracted by an external magnetic field.
- **Diamagnetic** materials have no unpaired electrons and are repelled by an external magnetic field.
- **Ferromagnetic** materials retain their permanent magnetic properties when outside an external magnetic field.

ICP

Inductively coupled plasma (ICP) is a spectroscopic technique used to determine very low concentrations of metals. A sample to be analysed is injected into argon gas *plasma*, which atomizes and ionizes any type of material (figure A.2.2). The mixture of excited atoms and ions is then analysed by optical emission spectroscopy (OES). Alternatively, mass spectrometry (MS) can be used. The limiting factor of concentration measurement with ICP-MS or ICP-OES is the accuracy of the calibration curve, which is generated by careful preparation of a standard solution and plotting of values obtained for the standard and its successive dilutions.

Plasma, one of the four states of matter, is a high-energy state that consists of isolated atoms or molecules, free electrons and positive ions.

MS is described in topic 11.3, and emission spectroscopy in topic 2.2.



▲ Figure A.2.2. Schematic diagram of an ICP torch: the sample is sprayed into the plasma, where it is ionized, and the emission region is analysed by MS or OES

SAMPLE STUDENT ANSWER

a) i) Nickel is used as a catalyst. It is processed from an ore until nickel(II) chloride solution is obtained. Identify **one** metal, using sections 24 and 25 of the data booklet, which will not react with water and can be used to extract nickel from the solution. [1]

ii) Deduce the redox equation for the reaction of nickel(II) chloride solution with the metal identified in (a)(i). [1]

b) Another method of obtaining nickel is by electrolysis of a nickel(II) chloride solution. Calculate the mass of nickel, in g, obtained by passing a current of 2.50 A through the solution for exactly 1 hour. Charge (Q) = current $(I) \times$ time (t). [2]

This answer could have achieved 3/4 marks:

a) i) Iron

ii) $Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$

b) $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$

$2\ F \equiv 1\ mol\ Ni(s)$

$1\ F \equiv 0.5\ mol\ Ni(s)$

$Q = It = (2.5\ A)(1\ hour) = 2.5\ C$

$96\,500\ C = 0.5\ mol\ Ni(s)$,

so $2.5\ C = 0.5 \times (2.5/96\,500) \times 59\ g$

$\approx 0.0008\ g\ Ni(s)$

▲ Iron is above nickel in the activity series; other possible metals include cobalt, cadmium, chromium or zinc, but *not* the alkali metals, as these react with water

▲ Correct ionic equation; a molecular equation would also be accepted

▼ The student had the right idea but failed to use the correct SI unit for time, where 1 h = 3600 s

▲ The second mark is awarded for the calculation method as an error carried forward

Practice problems for Topic A.2

Problem 1

Deduce whether Fe^{2+} ions and Zn^{2+} ions are diamagnetic or paramagnetic.

Problem 2

Determine the charge, *Q*, in C, needed to produce 2.000 kg of aluminium from alumina, Al_2O_3.

Problem 3

Other elements can be added to pure aluminium in an alloy to enhance its properties. With reference to the structure of such alloys, explain why they are less malleable than pure aluminium.

A.3 CATALYSTS

You should know:

- ✔ homogeneous catalysts chemically combine with reactants to form a reaction intermediate or an activated complex;
- ✔ reactants adsorb onto heterogeneous catalysts at active sites and the products desorb;
- ✔ catalytic particles are nearly always nanoparticles that have a large surface area per unit mass;
- ✔ transition metals act as inorganic catalysts because of their variable oxidation states and excellent adsorption ability;
- ✔ zeolites act as selective catalysts because of their cage-like structures.

You should be able to:

- ✔ explain the factors involved in choosing a catalyst for a reaction;
- ✔ describe how metals function as heterogeneous catalysts;
- ✔ describe the benefits of nanocatalysts in industrial processes.

A catalyst speeds up the reaction, without being used up itself in that reaction. Catalysts provide an alternative reaction pathway for the reaction with a lower activation energy, E_a.

Homogeneous catalysts chemically combine with reactants to form a reaction intermediate or an activated complex (a temporary transition state). Homogeneous catalysts work under mild conditions and have good selectivity for the desired products.

The basic principles of catalysis are introduced in topic 6.1. The way a catalyst can alter a reaction mechanism is discussed at higher level in topic 16.1, and activation energy is considered further in topic 16.2.

A **homogeneous catalyst** is in the same physical phase as the reactants, whereas a **heterogeneous catalyst** is in a different phase.

Heterogeneous catalysts provide active sites onto which reactants can be adsorbed, bringing them into the correct position and orientation to react. The products then desorb. The excellent ability of transition metals to adsorb other substances is one reason for their success as catalysts (the other, which applies to both homogeneous and heterogeneous catalysis, is their variable oxidation states). Heterogeneous catalysis is preferred in industrial processes, as the catalyst can be easily removed from the mixture by filtering, whereas homogeneous catalysis often requires costly methods of separation. However, the effectiveness of heterogeneous catalysis can be reduced by catalytic poisoning, when other compounds react with the surface of the catalyst, blocking the active sites. This is why leaded petrol cannot be used in cars with catalytic converters.

Nanoparticles have a large surface area per unit mass, so can provide a large area of active sites like heterogeneous catalysts, while being so small that they can be introduced into a reaction mixture like homogeneous catalysts. They can be engineered to be selective for the desired product and to have high conversion efficiency.

Zeolites are microporous materials of alumina silicate, Al_2O_3/SiO_2. Their cage-like structures offer a large surface area and give them a shape-selective catalytic nature; they also act as molecular sieves.

Factors that must be considered when a catalyst is selected are:

- cost
- life expectancy
- susceptibility to catalytic poisoning/impurities
- selectivity for the desired product
- conversion efficiency
- impact on the environment
- ability to work in mild/harsh conditions.

Assessment tip

This question is linked to core material covered in topic 10.2. This feature is very common within the options, where questions may involve testing part of the core and higher topics that underpin a given sub-topic in the options.

Example A.3.1.

Two important reactions in organic chemistry that involve catalysts are esterification and addition reactions involving the hydrogenation of an alkene.

a) Formulate a balanced equation for the reaction of ethanoic acid with methanol, including state symbols and an appropriate catalyst.

b) Formulate a balanced equation for the reaction of ethene with hydrogen, including state symbols and an appropriate catalyst.

c) State the type of catalysis involved in each process.

d) Describe the mode of action of the catalyst in each process.

Solution

a) $CH_3COOH(aq) + CH_3OH(aq) \xrightleftharpoons{H_2SO_4(conc.)} CH_3COOCH_3(aq) + H_2O(l)$

b) $H_2C{=}CH_2(g) + H_2(g) \xrightarrow{Ni(s)} CH_3CH_3(g)$

c) *Esterification:* Homogeneous (since the concentrated sulfuric acid catalyst is in the same phase as the reactants).

Hydrogenation: Heterogeneous (since the solid nickel catalyst is in a different phase to the gaseous reactants).

d) *Esterification:* Sulfuric acid catalyst reacts in one step of the mechanism and is regenerated in a later step.

Hydrogenation: The solid nickel catalyst provides a surface that absorbs the reactants and allows the products to desorb.

The physical states for ethene and ethane can be found in section 13 of the data booklet.

As well as Ni, other transition metal catalysts may also be used, such as Pt and Pd.

Practice problem for Topic A.3

Problem 1

The production of HDPE involves the use of homogeneous catalysts. Outline how homogeneous catalysts reduce the activation energy of reactions.

A.4 LIQUID CRYSTALS

You should know:

- ✔ liquid crystals are fluids with electrical, optical and elastic properties dependent on molecular orientation to a fixed axis in the material;
- ✔ nematic liquid crystals are rod-shaped molecules that are randomly distributed but on average are aligned in the same direction;
- ✔ thermotropic liquid crystals are pure substances that show liquid-crystal behaviour over a range of temperatures;
- ✔ lyotropic liquid crystals are solutions that show liquid-crystal behaviour over a set concentration range.

You should be able to:

- ✔ discuss the properties needed for a substance to be used in liquid-crystal displays (LCDs);
- ✔ explain liquid-crystal behaviour on a molecular level.

Liquid crystals (LCs) are a fluid state of matter intermediate between the crystalline and liquid states. Their molecules, often shaped like rods or flat discs, align regularly like in a crystal, but can flow freely like a liquid. Their physical properties (electrical, optical and elastic) depend on the orientation of the molecules. LC molecules are often polar, so align in a weak electric field. To have a useful LC phase, a molecule must be chemically stable, and the phase must exist over a range of temperatures (for *thermotropic LCs*) or concentrations (for *lyotropic LCs*).

Liquid crystal displays (LCDs) contain a thin film of *nematic liquid-crystal* molecules, which align in an applied electric field to either transmit or block plane-polarized light.

Thermotropic liquid crystals (e.g. biphenyl nitriles) can be designed to align and thus change colour over a given temperature range, making them useful as temperature indicators.

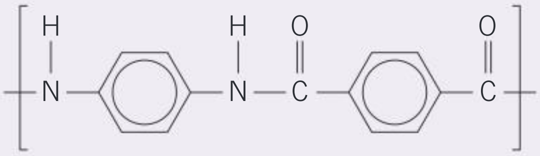
Some molecules with one hydrophilic and one hydrophobic end, like soap, can become *lyotropic liquid crystals* in high concentrations in aqueous solution, where they form regularly arranged rod-shaped *micelles*.

- The **nematic liquid-crystal** phase contains rod-shaped molecules randomly distributed, like in a liquid, but aligned in the same direction due to strong intermolecular forces of attraction.
- **Thermotropic liquid crystals** are pure substances that show liquid-crystal behaviour over a range of temperatures.
- **Lyotropic liquid crystals** are solutions that show liquid-crystal behaviour over a range of concentrations; they have a hydrophilic polar end and a hydrophobic non-polar end.
- **Micelles** are (often spherical) collections of molecules in solution, in which all the hydrophilic ends face outwards while the hydrophobic ends point inwards.

Plane-polarized light is covered in topic 20.3 in the discussion of optical isomerism.

Example A.4.1.

Kevlar, a condensation polymer, has liquid-crystal properties. A section of the polymer is shown here:



a) State a feature of Kevlar which allows it to show liquid-crystal properties.

b) Kevlar is used to make bulletproof vests. Explain the strength of Kevlar in terms of its structure and bonding.

c) Suggest why a bulletproof vest made of Kevlar should not be stored next to concentrated sulfuric acid.

Solution

a) The benzene rings in the polymer make it rigid and rod-shaped.

b) Hydrogen bonds form between N–H and O=C groups on adjacent Kevlar chains, resulting in an ordered and strong material.

c) The nitrogen and oxygen atoms in the Kevlar polymer could be protonated by the acid, thereby destroying the network of hydrogen bonds.

Assessment tip

Do not write "benzene" for "benzene ring". Benzene is the molecule C_6H_6. A benzene ring is a part of a larger molecule.

SAMPLE STUDENT ANSWER

Discuss **two** properties a substance should have to be suitable for use in liquid crystal displays. [2]

This answer could have achieved 1/2 marks:

The substance should be chemically stable and polar.

▲ Two properties identified correctly

▼ The command term "discuss" requires more detail; a complete answer would be "the substance must be chemically stable so that it will not degrade over time and polar so that the molecules change their orientation when an electric field is applied"

Practice problems for Topic A.4

Problem 1

Explain, using diagrams, the workings of a twisted nematic liquid crystal display (LCD) device.

Problem 2

State the property of carbon nanotubes that enables them to form a nematic liquid crystal phase.

A.5 POLYMERS

You should know:

- ✔ thermoplastics soften when heated and harden when cooled, so can be remoulded;
- ✔ a thermosetting polymer is a prepolymer in a soft solid or viscous liquid state that changes irreversibly into a hardened thermoset on curing;
- ✔ high-density polyethene, HDPE, has no branching in the polymer chain, so the chains are able to pack closely together;
- ✔ low-density polyethene, LDPE, has branches and is more flexible than HDPE;
- ✔ plasticizers added to a polymer weaken the intermolecular forces of attraction between the chains, increasing the flexibility;
- ✔ elastomers are flexible and deform under force, but return to their near-original shape when the stress is released;
- ✔ isotactic addition polymers have their substituents on the same side, whereas atactic addition polymers have substituents randomly placed.

You should be able to:

- ✔ evaluate the atom economy of a polymerization reaction;
- ✔ describe how the properties of polymers depend on their structure;
- ✔ describe how plasticizers are used in polyvinyl chloride;
- ✔ describe the role of volatile hydrocarbons in making expanded polystyrene;
- ✔ deduce structures of polymers of 2-methylpropene.

Plastics are polymers made up of repeating monomer units. Polymers can be classified in different ways—addition and condensation polymers, depending on how they are made, or thermoplastic and thermosetting plastics, based on how they behave when heated.

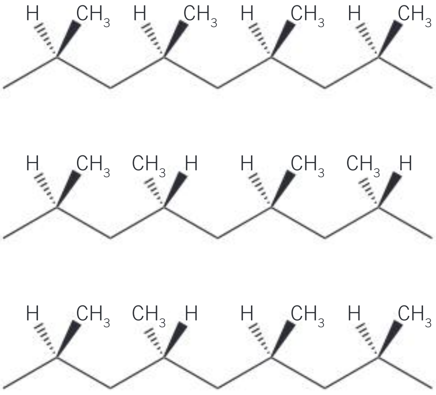
Addition polymerization is introduced in topic 10.2.

Thermoplastics soften when heated and can be remoulded simply by reheating. They consist of polymer chains held together by weak intermolecular forces of attraction. Thermosetting plastics, in contrast, have extensive covalent cross-linking between chains and are stronger as a result. They are moulded from a prepolymer in a soft solid or viscous liquid state and then cured to give a hardened solid that cannot be remoulded.

Elastomers, such as rubber, can be either thermoplastic or thermosetting polymers, and consist of long chains with a few cross-links. The chains are normally tangled into compact coils but can stretch out, enabling the polymer to deform under stress. When the stress is removed, the cross-links ensure that the polymer returns to its original shape.

The structure of polymers can be designed to produce materials with desired properties. For example, low-density polyethene (LDPE) has branched chains, which cannot pack closely, so LDPE has a low density and is flexible. In contrast, high-density polyethene (HDPE) consists of unbranched polymer chains that can pack closer together and thus experience stronger London (dispersion) forces. As a result, HDPE is denser and stronger than LDPE.

- **Isotactic polymers** have all substituents on the same side of the chain.
- **Syndiotactic polymers** have substituents that alternate from one side of the chain to the other.
- **Atactic polymers** have substituents randomly positioned on the chain.



▲ **Figure A.5.1.** Isotactic (top), syndiotactic (middle) and atactic (bottom) polypropene

Assessment tip

The list principle as applied in marking means that if a question asks for two responses, then only two should be given; if more than two are given and the additional responses are incorrect, marks may be lost. For example, if an answer to (c) here was "used in packing material, disposable cups and yoghurt pots", only one mark would be scored, as yoghurt pots are made of non-expanded polystyrene.

Assessment tip

The formula for % atom economy is given in section 1 of the data booklet.

Addition polymers made from asymmetric monomers, such as propene, $CH_3{-}CH{=}CH_2$, can polymerize in different arrangements under different conditions, to give *isotactic*, *syndiotactic* or *atactic* polymers (figure A.5.1).

Additives, too, can affect the structure and thus the properties of polymers. Plasticizers added to a polymer keep the chains apart, reducing the intermolecular London forces, decreasing the density, softening the polymer and making it flexible. Unplasticized polychloroethene, or polyvinyl chloride (PVC), is rigid and can be used, for example, to make window frames, whereas plasticized PVC is used in shower curtains and even clothing.

Polyphenylethene (polystyrene), made from $C_6H_5CH{=}CH_2$, is a clear, rigid thermoplastic addition polymer used, for example, as a material for CD cases. Expanded polystyrene is produced from a mixture of polystyrene and a gaseous blowing agent (usually carbon dioxide or a volatile hydrocarbon like pentane).

Example A.5.1.

a) Classify polystyrene as a polymer.

b) Describe how addition of a volatile hydrocarbon, such as pentane, during the formation of polystyrene has an impact on the properties of the polymer.

c) State **two** uses for expanded polystyrene.

Solution

a) Polystyrene is a thermoplastic addition polymer.

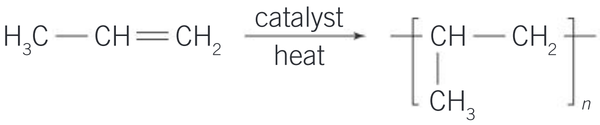
b) When the polymer mixture is heated, pentane evaporates, forming bubbles of gas. Their expansion in turn expands the polymer, forming low-density polystyrene foam.

c) Expanded polystyrene can be used in packing material and disposable coffee cups.

Atom economy is an important concept of *green chemistry* (Topic B.6) and a measure of the efficiency of a chemical or industrial process. It is calculated as follows:

$$\%\text{atom economy} = \frac{\text{total mass of desired product(s)}}{\text{total mass of reactants}} \times 100\%$$

For example, the addition polymerization (Topic 10.2) of propene has an atom economy of 100%, as all atoms from the reactant (propene) end up in the reaction product (polypropene):



$$H_3C{-}CH{=}CH_2 \xrightarrow[\text{heat}]{\text{catalyst}} \left[\underset{\displaystyle CH_3}{\underset{|}{CH}} {-} CH_2 \right]_n$$

In contrast, the atom economy of a condensation polymerization (Topic A.9) is always lower than 100%, as some of the atoms from the reactants end up in the reaction by-product.

SAMPLE STUDENT ANSWER

Chloroethene undergoes polymerization with a free-radical initiator to produce the atactic form of polychloroethene (PVC).

a) Sketch the atactic form of polychloroethene showing **four** units. [1]

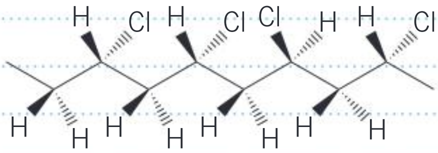
b) i) Explain, in molecular terms, why PVC becomes more flexible and softer when a plasticizer is added. [2]

ii) State one **type** of compound which can be added as a plasticizer. [1]

c) Suggest an environmental issue associated with the use of PVC. [1]

This answer could have achieved 2/5 marks:

a)



▲ Four repeating units are given, with the chlorine atom substituents randomly placed (atactic form), and continuation bonds are included to indicate the substance is polymeric

b) (i) Plasticizer molecules lower the density.

▼ Incomplete answer—a full answer would be "plasticizer molecules increase the space between the chains, thereby weakening the London forces of attraction between the chains"

(ii) Phthalate.

▲ A correct example

c) PVC is a toxic compound.

▼ This answer is too vague—the question asked for an environmental issue, so an acceptable answer might be "does not biodegrade"

Practice problems for Topic A.5

Problem 1

2-Methylpropene, also known as isobutylene, is an important industrial monomer.

a) Formulate an equation for the addition polymerization of 2-methylpropene.

b) Classify the reaction product in part (a) as a thermoplastic or thermosetting polymer.

c) Outline why the use of different catalysts in part (a) may produce polymers with different properties.

Problem 2

Draw the structure of the atactic form of polystyrene showing **five** repeating units.

Problem 3

Calculate the atom economy for the reaction below, assuming that the reaction yield is 100%.

$$CH_3C(O)Cl + H_2NCH_3 \rightarrow CH_3C(O)NHCH_3 + HCl$$

A.6 NANOTECHNOLOGY

You should know:

- ✔ molecular self-assembly is the bottom-up assembly of nanoparticles and can occur by selectively attaching molecules to specific surfaces, or spontaneously in solution;
- ✔ common methods of producing nanotubes are arc discharge, chemical vapour deposition (CVD) and high-pressure carbon monoxide disproportionation (HiPCO);
- ✔ arc discharge involves either vaporizing the surface of one of the carbon electrodes, or discharging an arc through metal electrodes submersed in a hydrocarbon solvent, which forms a small rod-shaped deposit on the cathode.

You should be able to:

- ✔ distinguish between physical and chemical techniques in forming molecules;
- ✔ describe the structure and properties of carbon nanotubes;
- ✔ explain why an inert gas is necessary for CVD preparation of carbon nanotubes;
- ✔ explain how carbon is produced from hydrocarbon solvents in the arc discharge method;
- ✔ deduce equations for the production of carbon atoms from HiPCO;
- ✔ discuss some of the applications and implications of nanotechnology;
- ✔ explain why nanotubes are strong and good conductors of electricity.

Intermolecular forces of attraction are covered in topic 4.4.

Nanotechnology involves the manipulation and control of atoms, molecules and objects with dimensions in the 1–100 nm range. There are two approaches to nanotechnology. The *top-down approach*, such as etching, starts with a bulk material and reduces it to the nanoscale. The *bottom-up approach* uses molecular self-assembly to build the material up from atoms and molecules by their selective attachment to specific surfaces, either in the solid state or in solutions. Self-assembly of viruses and carbon nanotubes are examples of the bottom-up approach.

Physical techniques allow atoms and molecules to be visualized, manipulated and positioned to specific requirements. Two such techniques are atomic force microscopy (AFM) and scanning tunnelling microscopy (STM).

Chemical techniques locate and manipulate atoms in molecules using chemical reactions. Nanotubes are self-assembled nanoparticles produced by arc discharge, chemical vapour deposition or high-pressure carbon monoxide disproportionation. In the *arc discharge* method, a plasma discharge produces carbon vapour either from the anode material (graphite) or, in the case of a metal anode, from a hydrocarbon solvent. The vaporized carbon deposits on the cathode in the form of nanotubes. When the graphite anode is doped with a transition metal catalyst, single-walled nanotubes are produced, while pure graphite forms multi-walled nanotubes.

In *chemical vapour deposition* (CVD), carbon atoms are produced by the decomposition of a gaseous hydrocarbon and deposited on the surface of a transition metal catalyst, where they form carbon nanotubes.

High-pressure carbon monoxide disproportionation (*HiPCO*) is a variant of CVD that uses carbon monoxide instead of a hydrocarbon. In this method, carbon atoms are produced by the disproportionation of carbon monoxide on the surface of iron nanoparticles, which in turn form by the thermal decomposition of vaporized iron(0) pentacarbonyl, $Fe(CO)_5$.

$Fe(CO)_5(g) \rightarrow Fe(s) + 5CO(g)$

$2CO(g) \xrightarrow{Fe(s)} C(s) + CO_2(g)$

Carbon nanoparticles also provide a surface for growing carbon nanotubes.

SAMPLE STUDENT ANSWER

Describe how carbon nanotubes are produced by chemical vapour deposition (CVD). [3]

This answer could have achieved 1/3 marks:

Decomposition of methane.

▲ Only one valid point is mentioned here so only one mark is awarded; all three marks could be scored by the answer "decomposition of methane over a transition metal catalyst at high temperature"

Practice problems for Topic A.6

Problem 1

a) Outline what is meant by the term *nanotechnology*.

b) State **two** applications of nanotechnology.

c) Discuss **two** risks associated with nanotechnology.

Problem 2

a) Describe the structure of carbon nanotubes.

b) State **two** physical properties of carbon nanotubes.

c) Explain why an inert gas, and not oxygen, is needed for the manufacture of carbon nanotubes by chemical vapour deposition (CVD).

A.7 ENVIRONMENTAL IMPACT—PLASTICS

You should know:

- ✔ plastics have strong covalent bonds, so do not decompose easily;
- ✔ combustion of PVC produces hydrogen chloride gas, dioxins and other toxic products;
- ✔ dioxins contain unsaturated six-membered heterocyclic rings with two oxygen atoms;
- ✔ chlorinated dioxins are hormone disruptors;
- ✔ recycling of plastics is more time- and energy-intensive than recycling other materials;
- ✔ plastics are recycled based on their resin identification codes (RICs).

You should be able to:

- ✔ deduce the products formed in a combustion reaction;
- ✔ discuss why recycling of plastics is such an energy-intensive process;
- ✔ discuss the environmental impact of the use of plastics;
- ✔ compare the structures of polychlorinated biphenyls and dioxins;
- ✔ discuss health concerns associated with the use of volatile plasticizers in polymers;
- ✔ distinguish polymers using infrared (IR) spectroscopy.

The environmental impact of plastics is an important theme within the Materials option that frequently appears in examination questions.

Plastics contain many strong C–C and C–H bonds and therefore do not decompose easily. Incomplete combustion of polymers can result in the formation of carbon monoxide gas and soot. The polymer polyvinyl chloride (PVC), used in window frames and doors, internal and external cladding and many other applications, produces hydrogen

The different functional groups are covered in topic 10.1 and IR spectroscopy is introduced in topic 11.3.

chloride gas and *dioxins* upon combustion. Chlorinated dioxins are hormone disruptors, and can damage cells. *Polychlorinated biphenyls (PCBs)*, formerly used as additives in plastics as well as for other purposes, have toxic effects similar to those of dioxins. The release of dioxins and other chlorinated compounds to the environment can be reduced by substituting PVC with chlorine-free plastics.

Plasticizers, such as phthalates, are added to polymers to make them more flexible. These additives are held within the polymer matrix by weak intermolecular forces and hence are eventually released into the environment. Phthalates may have carcinogenic properties.

The structures of dioxins and polychlorinated biphenyls are given in section 31 of the data booklet.

Resin identification codes are listed in section 30.

Recycling of plastics is a work- and energy-intensive process, as plastics need to be separated from other materials, sorted according to their resin identification codes (RICs), then shredded, melted or otherwise processed to give the desired product. Infrared spectroscopy (IR) can be used to identify different polymers.

Example A.7.1.

Polyvinyl chloride, PVC, is a widely used plastic.

a) State the condensed structural formula of the monomer used in the synthesis of PVC.

b) Formulate a balanced equation for the complete combustion of this monomer, including state symbols.

c) Infrared spectroscopy (IR) can be used to detect PVC during the sorting of plastics. Identify the wavenumbers, in cm^{-1}, and their associated bond types, for the IR spectrum of PVC, using section 26 of the data booklet.

d) State **two** uses of PVC.

e) Discuss the health concerns associated with the use of a phthalate plasticizer in PVC.

f) State the RIC for PVC.

Solution

a) $H_2C{=}CHCl$

b) $H_2C{=}CHCl(g) + 2.5O_2(g) \rightarrow 2CO_2(g) + H_2O(g) + HCl(g)$

c) C–H: 2850–3090 cm^{-1}; C=C: 1620–1680 cm^{-1}; C–Cl: 600–800 cm^{-1}

d) One possible answer is "credit cards and window frames".

e) Over time PVC may release phthalates, which can disrupt the human endocrine system, interfering with hormonal functions and causing damage to cells.

f) 3 (from section 30 of the data booklet).

Assessment tip

Be aware of the list principle in part (d)—an extra, incorrect answer can cost you a mark.

SAMPLE STUDENT ANSWER

Compare **two** ways in which recycling differs from reusing plastics. [2]

This answer could have achieved 2/2 marks:

Recycling is more energy intensive than reusing.

Recycling breaks the original product down to form a new product whereas reuse extends the life of the product.

▲ "Compare" means that the similarities between two or more items must be discussed, *referring to both of them throughout*, as has been done here for each separate point, securing both marks

Practice problem for Topic A.7

Problem 1

Polypropene, also known as polypropylene, is a common polymer. Waste materials containing polypropene can be disposed of by incineration or recycled.

a) Formulate balanced equations, including state symbols, for the complete and incomplete combustion of polypropene.

b) Suggest why polypropene waste should not be mixed with materials containing polyvinyl chloride (PVC).

c) Outline the meaning and purpose of resin identification codes (RICs).

d) Discuss the advantages and costs associated with recycling of polymers.

A.8 SUPERCONDUCTING METALS AND X-RAY CRYSTALLOGRAPHY (AHL)

You should know:

- ✔ superconductors have no resistance to electric current below a critical temperature;
- ✔ the Meissner effect is the ability of a superconductor to create a mirror-image magnetic field of an external field, thus expelling it;
- ✔ resistance in metallic conductors is caused by collisions between electrons and positive ions of the lattice;
- ✔ type 1 superconductors have sharp transitions to superconductivity, whereas type 2 superconductors have more gradual transitions;
- ✔ X-ray diffraction can be used to analyse the structures of compounds;
- ✔ crystal lattices contain simple repeating unit cells, which share atoms on their faces and edges;
- ✔ the number of nearest neighbours of an atom/ion is its coordination number.

You should be able to:

- ✔ analyse resistance versus temperature data for type 1 and type 2 superconductors;
- ✔ explain superconductivity in terms of Cooper pairs of electrons using the Bardeen–Cooper–Schrieffer (BCS) theory;
- ✔ deduce or construct unit cell structures from crystal structure information;
- ✔ apply the Bragg equation, $n\lambda = 2d\sin\theta$, to solve problems involving simple cubic metallic structures;
- ✔ determine the density of a pure metal from its atomic radius and crystal packing structure.

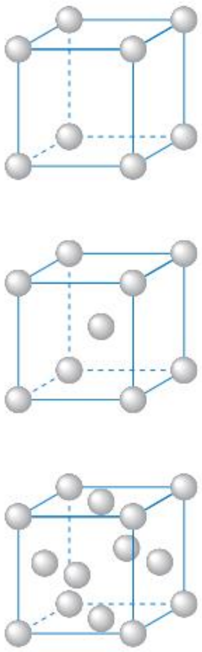
Superconductors conduct electricity with no resistance at very low temperatures. According to the *Bardeen–Cooper–Schrieffer (BCS) theory*, below their *critical temperature*, T_c, superconducting materials contain *Cooper pairs* of electrons, which can travel through the positive lattice without any energy loss.

Superconductors expel magnetic fields from their interiors (the *Meissner effect*). *Type 1 superconductors* (metals and metalloids) have sharp transitions from superconductivity when an applied magnetic field exceeds a critical value, H_c, characteristic of the material. *Type 2 superconductors* (alloys and metal oxide ceramics) lose superconductivity more gradually as the magnetic field increases.

Single-crystal X-ray crystallography is a structural technique in which the diffraction pattern of X-rays passed through a single crystal is used to identify the arrangement of atoms in a compound. The *Bragg equation* can be used to solve structures with a simple cubic *unit cell*.

- **Superconductors** conduct electricity with zero resistance below their **critical temperature**, T_c.
- The **Meissner effect** is the ability of a superconducting material to create a mirror image of an external field, thus expelling magnetic fields from the interior of the material.
- A **unit cell** is the smallest, regularly repeating, three-dimensional unit of a crystal lattice.
- The **coordination number** of an atom or ion is the number of other atoms or ions directly linked to that atom or ion in the crystal lattice.
- The **Bragg equation**, $n\lambda = 2d\sin\theta$, can be used to solve simple cubic metallic structures.

Topics 3.2 (atomic radii) and 21.1 (X-ray crystallography) underpin this sub-topic in option A.



▲ **Figure A.8.1.** Simple cubic (top), body-centred cubic (middle) and face-centred cubic (bottom) lattices

Example A.8.1.

a) Deduce the number of atoms per unit cell in each of the following cubic unit cells:

i) simple cubic

ii) body-centred cubic

iii) face-centred cubic

b) State the coordination number for each type of unit cell.

Solution

a) A diagram of each lattice type (figure A.8.1) might help you approach this problem.

i) simple: 8 corners $\times \frac{1}{8}$ atoms per corner $=$ 1 atom/unit cell.

ii) body-centred: 8 corners $\times \frac{1}{8}$ atoms per corner $+$ 1 atom at the centre $=$ 2 atoms/unit cell.

iii) face-centred: 8 corners $\times \frac{1}{8}$ atoms per corner $+$ 6 faces $\times \frac{1}{2}$ atom per face $=$ 4 atoms/unit cell.

b) i) simple cubic unit cell: 6

ii) body-centred unit cell: 8

iii) face-centred unit cell: 12

Example A.8.2.

α-Polonium crystallizes in a simple cubic unit cell, with side (edge) length $a = 0.336$ nm. Using sections 2, 5 and 6 of the data booklet, calculate the density of α-polonium, in g cm^{-3}.

Solution

Polonium, Po, has $M = 209$ g mol^{-1}

$$\text{mass per atom} = \left(\frac{1\ \text{mol}}{6.02 \times 10^{23}\ \text{atoms}}\right)(209\ \text{g mol}^{-1})$$

$$\approx 3.47 \times 10^{-22}\ \text{g atom}^{-1}$$

In a simple cubic unit cell, there is just 1 atom per cell, so $m(\text{unit cell}) \approx 3.47 \times 10^{-22}$ g

1 m $=$ 100 cm, so $a = 0.336\ \text{nm} = 0.336 \times 10^{-9}\ \text{m} = 3.36 \times 10^{-8}\ \text{cm}$

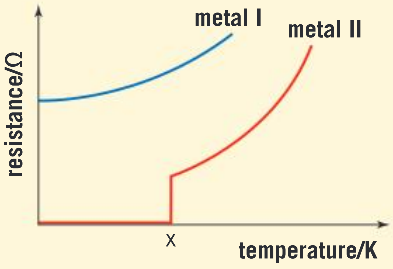
Volume $V = a^3 \approx 3.79 \times 10^{-23}\ \text{cm}^3$

$$\text{Density } \rho = \frac{m}{V} = \frac{3.47 \times 10^{-22}\ \text{g}}{3.79 \times 10^{-23}\ \text{cm}^3} \approx 9.16\ \text{g cm}^{-3}$$

SAMPLE STUDENT ANSWER

a) i) Outline the cause of electrical resistance in metallic conductors. [1]

ii) The resistance of two metals was measured as a function of temperature. The following graph was obtained.



Explain the behaviour of metal II below temperature X in terms of the Bardeen–Cooper–Schrieffer (BCS) theory. [3]

b) i) Polonium metal has a simple cubic structure. Construct a unit cell diagram and state the coordination number of each atom. [2]

ii) X-ray diffraction was carried out on polonium using radiation with a wavelength of 8.80×10^{-11} m. The first-order maximum in the diffraction pattern was observed at an angle of 13.0°. Determine the distance, in m, between layers of polonium atoms using section 1 of the data booklet. [1]

This answer could have achieved 5/7 marks:

a) (i) Electrical resistance is caused by the attraction between electrons and cations.

ii) Metal II is a superconducting material. As an electron passes through the metal the cations can be slightly displaced, deforming the lattice. This deformation creates a region of enhanced positive charge, which attracts another electron. The two electrons form a Cooper pair, which can travel through the lattice freely.

b) (i) coordination number = 6

ii) $n\lambda = 2d\sin\theta$, so $d = n\lambda/(2\sin\theta)$

$= 1 \times 8.80 \times 10^{-11}/(2 \times \sin 13.0°)$

$\approx 1.96 \times 10^{-10}$ m

▼ The terminology is not precise – "attraction" is not the same as "collision"

▲ The type of superconductor has been identified

▲ The formation of the Cooper pair in the lattice explained

▲ and its behaviour described

▼ The unit cell has not been shown

▲ The coordination number is correct

▲ A correct numerical answer using the Bragg equation

Practice problems for Topic A.8

Problem 1

a) State **two** differences between type 1 and type 2 superconductors.

b) Explain the principles of the Bardeen–Cooper–Schrieffer (BCS) theory for type 1 superconductors.

Problem 2

The density of nickel is 8.908 g cm^{-3}. The length of the side (edge) of its unit cell, *a*, is 352.4 pm. Deduce whether nickel crystallizes with a simple cubic unit cell, a body-centred unit cell or a face-centred unit cell.

A.9 CONDENSATION POLYMERS (AHL)

You should know:

- ✔ condensation polymers require two functional groups on each monomer;
- ✔ H_2O, NH_3 and HCl are common by-products of condensation reactions;
- ✔ the high tensile strength of the polyamide Kevlar is a result of its ordered structure stabilized by a network of hydrogen bonds.

You should be able to:

- ✔ distinguish between addition and condensation polymers;
- ✔ complete and describe equations for the formation of condensation polymers;
- ✔ deduce the structures of polyamides and polyesters from their respective monomers;
- ✔ explain the strength of Kevlar and why it dissolves in concentrated sulfuric acid.

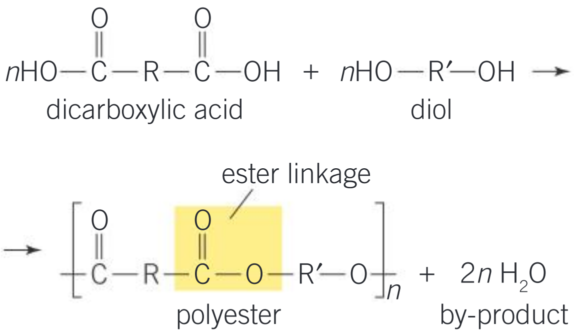
- **Addition polymerization** is the reaction of many small molecules (monomers) containing C=C bonds to form a single macromolecule (polymer).
- **Condensation polymerization** is the reaction of monomers with different functional groups to form a polymer with the loss of a small molecule (such as H_2O, HCl or NH_3) at each new bond.

Polymers can be formed by addition or condensation reactions (Table A.9.1).

Type	Monomer	Main product	By-product	Polymer backbone
addition	alkene	macromolecule	none	carbon atoms only
condensation	difunctional molecule(s)		H_2O, HCl, NH_3, etc.	carbon atoms and heteroatoms

▲ **Table A.9.1.** Addition and condensation polymerization

Condensation polymers require monomers with two functional groups that can react with one another. For example, polyesters can be produced from dicarboxylic acids and diols:

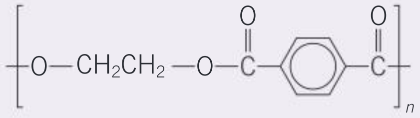


$$n\text{HO}-\overset{\overset{\displaystyle O}{\|}}{C}-R-\overset{\overset{\displaystyle O}{\|}}{C}-\text{OH} + n\text{HO}-R'-\text{OH} \rightarrow \left[\overset{\overset{\displaystyle O}{\|}}{C}-R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'-O\right]_n + 2n\,H_2O$$

Addition and condensation reactions are covered in topic 10.2, and the various types and general properties of polymers are discussed in topic A.5.

Example A.9.1.

The structure of the condensation polymer, polyethylene terephthalate (PET), is shown below.



a) Deduce the condensed structural formulas of **two** monomers used to form this polymer.

b) State the name of the other product formed in the reaction of the two monomers to form PET.

Solution

a) Identify the position of the ester linkage and then "break" it apart to generate the dicarboxylic acid and diol from the original esterification reaction.

The two monomers are $HOCH_2CH_2OH$ and $HOOCC_6H_4COOH$.

b) The condensation polymerization releases a small molecule as the by-product, in this case water.

The structure and hydrogen bonding in another condensation polymer, the polyamide Kevlar, are discussed in Example A.4.1.

Assessment tip

Note that "H_2O" would not suffice, as the name of the product is asked for.

SAMPLE STUDENT ANSWER

Deduce, giving a reason, whether the atom economy of a condensation polymerization would be greater or less than an addition polymerization, such as the formation of HDPE. [1]

This answer could have achieved 0/1 marks:

Addition polymerization has 100% atom economy.

▼ The question requires deduction of the atom economy for condensation polymerization, which will be lower, and a reason: the small molecule released is not the desired product

Practice problem for Topic A.9

Problem 1

a) Sketch **two** repeating units of the polymer formed from the monomers propanedioic acid, $HOOCCH_2COOH$, and ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

b) State the formula for the other product formed in this condensation polymerization.

c) Calculate the percent atom economy of this reaction, assuming that the reaction yield is 100%.

A.10 ENVIRONMENTAL IMPACT—HEAVY METALS (AHL)

You should know:

- ✔ toxic doses of transition metals can disturb the normal redox balance in cells;
- ✔ the various methods used to remove heavy metals are chelation, precipitation and adsorption;
- ✔ polydentate ligands form more stable complexes than similar monodentate ligands due to the chelate effect, which can be explained by entropy changes.

You should be able to:

- ✔ deduce the number of coordinate bonds a ligand can form with a central metal ion;
- ✔ solve solubility product, K_{sp}, problems involving the precipitation of metals ions;
- ✔ compare and contrast the Haber–Weiss and Fenton reaction mechanisms.

Heavy metals, such as lead (Pb), cadmium (Cd) and mercury (Hg), are toxic in high concentrations and can cause cancer. These metals readily form coordination complexes, have different oxidation states and can act as catalysts in the human body. Toxic doses of transition metals can disturb the normal redox balance in cells through various mechanisms that often involve radicals, species with an unpaired electron.

Heavy metal ions can be removed from solutions by *chelation*, *adsorption* and *precipitation*.

Chelate complexes contain *ligands* capable of forming more than one coordinate bond with the metal ion. Common chelates include *bidentate* ligands such as ethane-1,2-diamine (also written as en) and ethanedioate (oxalate, ox), and the *hexadentate* ligand ethylenediaminetetraacetate ($EDTA^{4-}$). Chelate complexes are very stable because their formation increases the entropy of the system. For example, the ΔS value for the following reaction is positive due to the increasing number of dissolved species (four on the reactant side and seven on the product side):

$$[Ni(NH_3)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6NH_3(aq)$$

Redox chemistry is outlined in topic 9.1, and the properties of transition metals are discussed in topic 13.2.

- A **chelate ligand** can form more than one coordinate bond with the metal ion. A **bidentate** ligand forms two such bonds, a **tridentate** ligand forms three bonds, and so on.
- **Adsorption** is the adhesion of species from a gas or solution to the surface of a material (**adsorbent**), such as a zeolite.
- **Precipitation** is the separation of a solid phase from a solution.

The structures of chelate ligands are given in section 16 of the data booklet.

Example A.10.1.

a) Formulate a balanced equation for the reaction of the hexaaquairon(II) complex, $[Fe(H_2O)_6]^{2+}$, with the ethylenediaminetetraacetate ion in aqueous solution.

b) Predict the entropy change, ΔS, for the reaction.

Solution

a) The ion of EDTA is $EDTA^{4-}$. This is a hexadentate ligand (section 16 of the data booklet), so it will replace all six monodentate H_2O ligands:

$$[Fe(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^{2-}(aq) + 6H_2O(l)$$

b) The number of species has increased from two to seven, so $\Delta S > 0$.

The catalytic properties of zeolites are discussed in topic A.3.

Typical *adsorption* agents are zeolites, which are microporous alumina silicates. Due to their cage-like structure, zeolites have large surface area and can selectively adsorb ions or other species according to their sizes and shapes.

Many salts and hydroxides of heavy metals have low solubility in water, so heavy metal ions can be removed from waste water by *precipitation*. For example, when calcium oxide, CaO, is added to water, hydroxide ions are produced and heavy metal ions can subsequently be removed:

$$CaO(s) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

$$Cr^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Cr(OH)_3(s)$$

K_{sp} values are listed in section 32 of the data booklet.

The *solubility product*, K_{sp}, for the electrolyte MX_y can be defined as follows:

$$MX_y(s) \rightleftharpoons M^{y+}(aq) + yX^-(aq)$$

$$K_{sp} = [M^{y+}(aq)][X^-(aq)]^y$$

Haber–Weiss and Fenton reactions

In the *Haber–Weiss* and *Fenton reactions* (table A.10.1), the highly reactive hydroxyl radical, •OH, is generated. This radical can damage DNA but at the same time can be used to break down pollutants, such as pesticides dissolved in water.

	Haber–Weiss	**Fenton**
active product	hydroxyl radical, •OH	
net equation	$H_2O_2 + \bullet O_2^- \rightarrow O_2 + \bullet OH + OH^-$	$2H_2O_2 \rightarrow \bullet OH + \bullet OOH + H_2O$
reaction mechanism	$Fe^{3+} + \bullet O_2^- \rightarrow Fe^{2+} + O_2$ $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OOH + H^+$
role of Fe^{3+}	catalyst	intermediate
role of Fe^{2+}	intermediate	catalyst

▲ Table A.10.1. The Haber–Weiss and Fenton reactions

SAMPLE STUDENT ANSWER

Metal ions may cause unwanted environmental effects.

a) The presence of iron(III) ions can catalyse the formation of hydroxyl radicals from O_2^- and H_2O_2 in the Haber–Weiss reaction. State the equations for this process. [2]

b) Zinc ions, toxic to aquatic life, may be removed by adding a solution containing hydroxide ions. Determine the concentration of zinc ions in a saturated solution of zinc hydroxide at 298 K using information from section 32 of the data booklet. [2]

This answer could have achieved 3/4 marks:

a) $Fe^{3+} + \bullet O_2^- \rightarrow Fe^{2+} + O_2$

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$

b) $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Zn^{2+}][OH^-]^2 = 3.0 \times 10^{-17}$

$x(2x)^2 = 3.0 \times 10^{-17}$

$x \approx 2.0 \times 10^{-6}$ mol dm^{-3}

▲ Both equations are correct

▼ Use of the radical symbol is inconsistent: the dot symbol was used for the superoxide radical ion in the first equation, so a dot should also have been used for the hydroxyl radical:
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$

▲ This is a perfect answer

▲ and includes units

Practice problems for Topic A.10

Problem 1

a) State an expression for the solubility product, K_{sp}, of nickel(II) hydroxide.

b) Calculate the solubility, in mol dm^{-3}, of nickel(II) hydroxide in water at 298 K.

c) Calculate the highest possible concentration, in mol dm^{-3}, of nickel(II) ions in 0.010 mol dm^{-3} aqueous solution of sodium hydroxide at 298 K.

Problem 2

Outline the principles of adsorption, chelation and precipitation as methods for removing heavy metals in an environmental context.

B BIOCHEMISTRY

B.1 INTRODUCTION TO BIOCHEMISTRY

You should know:

- ✔ the functions of biological molecules depend on their structures and shapes;
- ✔ metabolism is the sum of chemical reactions that take place within a living organism;
- ✔ catabolic reactions, such as cellular respiration and digestion, produce energy by breaking down large organic molecules into smaller units;
- ✔ anabolic reactions, such as photosynthesis and tissue growth, require energy to synthesize larger molecules from smaller units;
- ✔ biopolymers are typically produced by condensation reactions and broken down by hydrolysis reactions.

You should be able to:

- ✔ explain the difference between condensation and hydrolysis reactions;
- ✔ define oxidation and reduction in terms of the gain or loss of oxygen and hydrogen atoms;
- ✔ identify whether a given biochemical reaction is a catabolic or anabolic process;
- ✔ use the summary equations of photosynthesis and respiration to explain oxygen and carbon dioxide exchange with the atmosphere;
- ✔ state the names and outline the composition of common biopolymers.

Common biopolymers and their structural units are discussed in topics B.2 (proteins and amino acids), B.3 (fats, fatty acids and glycerol), B.4 (poly- and monosaccharides) and B.8 (nucleic acids, nucleotides and nitrogenous bases).

- **Hydrolysis** is the reaction of a large molecule with water to produce two or more simpler molecules.
- **Condensation** is a reaction in which two or more molecules combine together into a larger molecule and release water or another simple by-product.
- **Oxidation** is the loss of two hydrogen atoms or the gain of an oxygen atom.
- **Reduction** is the gain of two hydrogen atoms or the loss of an oxygen atom.

Metabolic processes are essential for life. Catabolic reactions provide energy for living organisms by *hydrolysing* large molecules of nutrients (proteins, fats and carbohydrates) into smaller units (amino acids, fatty acids, glycerol and monosaccharides) and then *oxidizing* these units into carbon dioxide and water. This energy is used by the organism for performing physical activity, maintaining constant body temperature and carrying out anabolic reactions, which are opposite to catabolism and typically involve *condensation* and *reduction*.

Example B.1.1.

Aerobic respiration of sucrose ($M_r = 342.34$) is a complex catabolic process that can be summarized as follows:

Step 1: $\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$

Step 2: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

a) State, with a reason, the reaction type for each step.

b) Suggest whether energy is released or consumed at each step.

c) Calculate the mass, in grams, of water produced by aerobic respiration of 10.0 g of sucrose.

➜

Solution

a) The first step is a hydrolysis reaction, as a larger molecule reacts with water to produce two smaller molecules. The second step is an oxidation reaction, as the organic molecule gains oxygen atoms.

b) Both steps are catabolic processes, so they are likely to release energy.

c) Water is consumed in Step 1 and released in Step 2. To simplify the calculations, it is convenient to combine both steps into a single equation:

$$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$$

Now we can see that one mole of sucrose produces 11 moles of water. Therefore:

$n(C_{12}H_{22}O_{11}) = 10.0\ \text{g}/342.34\ \text{g mol}^{-1} \approx 0.0292\ \text{mol};$

$n(H_2O) = 11 \times 0.0292\ \text{mol} \approx 0.321\ \text{mol};$

$m(H_2O) = 0.321\ \text{mol} \times 18.02\ \text{g mol}^{-1} \approx 5.78\ \text{g}.$

Both condensation and hydrolysis reactions are variants of nucleophilic substitution. However, the latter term is not used in biochemistry, as the opposite nature of these reactions is more important than the similarity of their mechanisms. Similarly, oxidation and reduction in biochemistry are usually discussed in terms of lost or gained hydrogen or oxygen atoms, as the oxidation states of carbon atoms in organic molecules are difficult to calculate.

The summary equation of photosynthesis is the reverse of Step 2 from example B.1.1. Together with respiration, photosynthesis is a part of the carbon cycle that maintains a balance of carbon dioxide and oxygen in the atmosphere.

SAMPLE STUDENT ANSWER

Describe what is meant by a condensation reaction. [2]

This answer could have achieved 1/2 marks:

A condensation reaction is an anabolic reaction that builds a polymer from a monomer. Water is formed as a reaction by-product.

▼ "a monomer" is not clear enough, as it implies a single reacting species, while a condensation must involve at least two reacting species, which can be identical or different molecules or ions

▲ "Water" is accepted as the most common by-product, although the answer "a small molecule" would be more accurate

Practice problems for Topic B.1

Problem 1

The peptidase enzyme in the digestive system hydrolyses peptide bonds. Identify the type of metabolic process that occurs when a peptide undergoes hydrolysis.

Problem 2

Depending on the substrate, the standard enthalpy changes for both hydrolysis and condensation reactions can be either positive or negative. However, nearly all hydrolysis reactions in living organisms release energy while nearly all condensation reactions in living organisms consume energy. Suggest a possible reason for this fact, with a reference to Le Châtelier's principle.

B.2 PROTEINS AND ENZYMES

You should know:

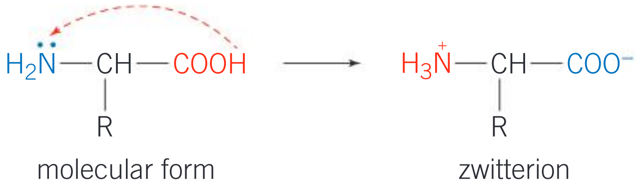
- ✔ amino acids are amphoteric species that can exist as cations, zwitterions and anions;
- ✔ proteins and peptides are polymers of 2-amino acids, in which the units are joined by amide links (–C(O)–NH–), also known as peptide bonds;
- ✔ protein structures can be described at primary to quaternary levels, and the shapes of proteins relate to their roles;
- ✔ enzymes are biological catalysts, usually protein-based, that provide an active site for binding to a specific substrate;
- ✔ enzymes lose their shape and thus activity outside the optimum ranges of pH and temperature, or in the presence of heavy metal ions.

You should be able to:

- ✔ explain the solubilities and melting points of amino acids in terms of zwitterions;
- ✔ deduce equations and structural formulas for condensation and hydrolysis reactions involving amino acids and peptides;
- ✔ apply the relationships between charge, pH and isoelectric point to explain the properties of amino acids and proteins;
- ✔ explain how amino acids and proteins can be separated and identified by paper chromatography and gel electrophoresis;
- ✔ describe the four levels of protein structure, including the types of bonds and interactions at each level;
- ✔ deduce and interpret plots of enzyme activity against substrate concentration, pH and temperature.

Amino acids

Amino acids are polyfunctional compounds that contain a basic amino group (–NH_2) and an acidic carboxyl group (–COOH) in the same molecule. In the solid state and in neutral aqueous solutions, amino acids exist as *zwitterions*:



$$H_2\ddot{N}-\underset{\displaystyle R}{\underset{|}{CH}}-COOH \longrightarrow H_3\overset{+}{N}-\underset{\displaystyle R}{\underset{|}{CH}}-COO^-$$

- A **zwitterion** is an ion that carries both a positive and a negative charge.
- The **isoelectric point (pI)** is the pH at which an amino acid carries no overall charge, that is, exists as a zwitterion.

The pH at which nearly all amino acid species exist as zwitterions is known as the *isoelectric point* (pI). The pI value depends on the side chain (R) so is specific for each amino acid.

Example B.2.1.

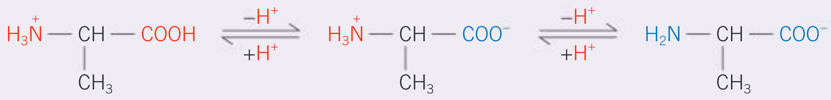
The molecular formulas and isoelectric points of 2-amino acids are given in section 33 of the data booklet.

a) Draw the structural formulas of organic species that are present in aqueous solutions of alanine at pH 4.5 and 7.5.

b) Explain, with a reference to the bonding, why alanine is readily soluble in water and has a high melting point.

Solution

a) The pI of alanine is 6.0 (section 33 of the data booklet). At pH 4.5 this amino acid will exist as a mixture of cationic and zwitterionic species, while at pH 7.5 it will form zwitterionic and anionic species:



$$\overset{+}{H_3N}-\underset{\underset{CH_3}{|}}{CH}-COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \overset{+}{H_3N}-\underset{\underset{CH_3}{|}}{CH}-COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_2N-\underset{\underset{CH_3}{|}}{CH}-COO^-$$

cation (pH < pI) zwitterion (pH = pI) anion (pH > pI)

b) Alanine has two polar groups, amino and carboxyl, which can form hydrogen bonds with water. In the solid state, the zwitterions of alanine form ionic and hydrogen bonds with one another. The non-polar side chain of alanine is small, so it does not affect the overall polar nature of this compound.

Assessment tip

Note that zwitterions exist in solutions at any pH, but their proportion will be the highest at pH = pI and become very low at pH << pI or pH >> pI.

A mixture of amino acids can be separated by *paper chromatography*. A spot of the sample to be analysed is placed on a piece of paper (*stationary phase*) and eluted with a solvent (*mobile phase*). Because of the differences in solubility and affinity for the stationary phase, amino acids travel along the paper at different speeds and separate into individual colourless spots, which can be developed by staining the paper with ninhydrin. Each amino acid has a unique *retention factor* (R_f), the ratio of the distances travelled by the amino acid (l_A) and the solvent front (l_0). The composition of the mixture can be deduced by comparing the R_f value of each spot with known R_f values for amino acids under the same conditions.

Example B.2.2.

A mixture of amino acids was analysed by paper chromatography. After development with ninhidrin, three spots were detected at distances of 3.3, 6.1 and 7.0 cm from the start line, while the solvent front was at 10.3 cm from the start line.

a) Using the table on the right, identify **two** amino acids in the original mixture.

b) Suggest **two** possible changes in the experimental conditions that could enable determination of the number of amino acids in the mixture.

Amino acid	Lys	Gly	Ala	Asp	Ser
R_f	0.14	0.24	0.32	0.32	0.39
Amino acid	**Cys**	**Val**	**Met**	**Leu**	**Phe**
R_f	0.59	0.64	0.68	0.76	0.92

Solution

a) The spot at 6.1 cm is produced by cysteine ($R_f = 6.1/10.3 \approx 0.59$), and the spot at 7.0 cm by methionine ($R_f = 7.0/10.3 \approx 0.68$). The spot at 3.3 cm ($R_f = 3.3/10.3 \approx 0.32$) cannot be identified, as it might be produced by alanine, aspartic acid, or a mixture of both.

b) To determine whether the spot at 3.3 cm contains one or two amino acids, we can repeat the experiment using different solvent and paper. We can also vary solvent pH and temperature. If any of these changes produce a chromatogram with four spots, the mixture contains four amino acids. Otherwise, it is likely to contain only three.

Gel electrophoresis is another technique used for the analysis of amino acids. A mixture of amino acids is placed in the centre of a gel saturated with a buffer solution (topic B.7) of a certain pH. When a potential difference is applied, the amino acids move at different rates towards one or the other electrode or remain stationary depending on their charges and sizes.

- **Gel electrophoresis** is a technique that allows one to separate a mixture of amino acids according to their charge and size.

Example B.2.3.

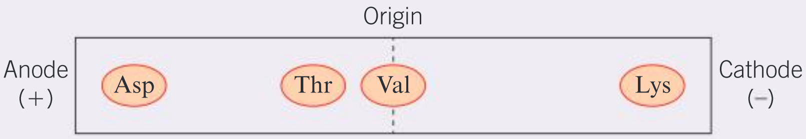
A mixture of amino acids was separated by gel electrophoresis at pH 6.0.

a) On the diagram below, draw the relative positions of aspartic acid, lysine, threonine and valine. Explain your reasoning.

b) Suggest why alanine and isoleucine separate slightly at pH 6.5.

Solution

a) The pI values of Asp, Lys, Thr and Val are 2.8, 9.7, 5.6 and 6.0, respectively (section 33 of the data booklet). At pH 6.0, aspartic acid will exist predominantly as negatively charged anions (pH >> pI) and thus move to the positive electrode (anode). Threonine will also move to the anode but more slowly, as its pI is only slightly below the solution pH. Valine (pH = pI) will exist in the form of zwitterions with zero net charge, so it will stay at the origin. The positively charged cations of lysine (pH << pI) will move to the negative electrode (cathode):

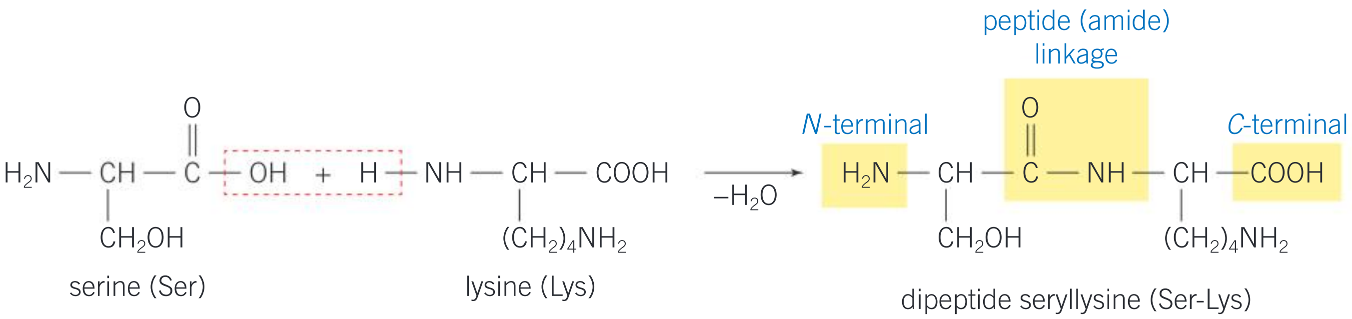


b) Alanine and isoleucine have identical isoelectric points (pI = 6.0) and thus identical net ionic charges at pH = 6.5. However, isoleucine has a larger side chain and thus will move through the gel slower than alanine.

- **Peptides** are polycondensation polymers of 2-amino acids containing up to 50 structural units.
- **Proteins** contain over 50 amino acid units and can spontaneously adopt specific three-dimensional shapes.

Proteins

Amino acids undergo condensation reactions (topic B.1), producing *peptides* and *proteins*. The side chains of amino acids in such reactions usually remain unchanged.



$$H_2N-CH(CH_2OH)-C(=O)-OH + H-NH-CH((CH_2)_4NH_2)-COOH \xrightarrow[-H_2O]{} H_2N-CH(CH_2OH)-C(=O)-NH-CH((CH_2)_4NH_2)-COOH$$

In turn, peptides and proteins can be hydrolysed to amino acids in the presence of enzymes or hot concentrated hydrochloric acid.

Proteins are polycondensation polymers containing 50 or more 2-amino acid units. In contrast to peptides that typically have no permanent three-dimensional shape, proteins can have up to four structural levels of increasing complexity (table B.2.1).

Structure	Description	Bonding types	Examples
primary	sequence of amino acid units	covalent bonds (peptide linkages)	Ala–Glu–Arg–Ser–…
secondary	regular folding pattern of the protein backbone	hydrogen bonds between peptide linkages	α-helix (coil) and β-pleated sheet (twisted ribbon)
tertiary	overall three-dimensional shape of the polypeptide chain	van der Waals' interactions; ionic, hydrogen and disulfide bonds between side chains of amino acids	globular (insulin and hemoglobin) and fibrous (keratin and collagen) proteins
quaternary	three-dimensional arrangement of several polypeptide chains and non-protein units	van der Waals' interactions; ionic, hydrogen and sometimes covalent bonds	insulin (two polypeptide chains); hemoglobin (four polypeptide chains with one non-protein unit each)

▲ **Table B.2.1.** The four levels of protein structure

The three-dimensional shapes of proteins determine their roles in living organisms. Fibrous proteins have structural, supportive and protective functions, while globular proteins act as biological catalysts (enzymes), messengers (hormones) and carriers of biologically important molecules and ions.

Enzymes

Most *enzymes* are protein-based molecules that provide an *active site* for binding to a specific *substrate*. The activity of an enzyme depends on the shape of its active site, which in turn is affected by the overall *native structure* of the enzyme. Maximum enzyme activity is achieved within narrow ranges of pH and temperature. Outside these ranges or in the presence of heavy metal ions the enzyme becomes *denatured* – it changes shape and loses its activity.

Example B.2.4.

Enzyme activity depends on many factors. Explain how pH change causes the loss of activity of an enzyme.

Solution

When the pH changes, some amino, carboxyl and other ionizable groups in the side chains of amino acid units lose or gain protons. This alters ionic and hydrogen bonds between different parts of the enzyme and distorts its native structure. The distortion affects the conformation and charge of the active site, which no longer fits the substrate, so no reaction takes place.

Assessment tip

When discussing enzymes, remember to mention that the substrate binds to the active site. In many examination questions this statement alone will score a mark.

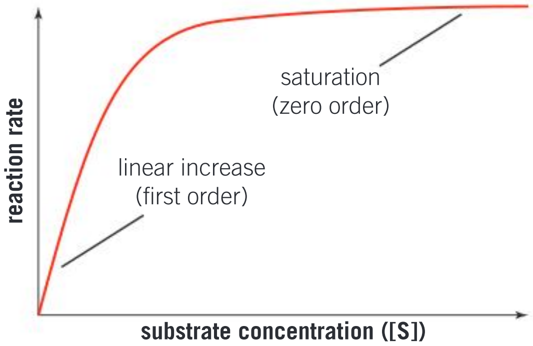
In a typical enzymatic reaction, enzyme E and substrate S form an intermediate enzyme–substrate complex ES. While this complex exists, the enzyme is temporarily unavailable for other substrate molecules. At low [S], only a few active sites are occupied by the substrate, so the reaction rate is proportional to [S]. At high [S], nearly all active sites are occupied, so further increase in [S] does not affect the reaction rate (figure B.2.1).

Assessment tip

The intermolecular forces between hydrocarbon side chains of amino acid units in proteins are often referred to as "hydrophobic interactions". This is a general term and not precise enough for examination answers. The acceptable term is "van der Waals forces", which includes London (dispersion) forces, dipole–induced dipole and dipole–dipole interactions (topic 4.4).

- An **enzyme** is a biological catalyst, typically a globular protein-based molecule.
- A **substrate** is a molecule or ion that is changed by an enzyme.
- The **active site** is the part of an enzyme that binds to the substrate by non-covalent interactions.
- **Native structure** is the three-dimensional (tertiary and quaternary) structure of a functional (active) protein.
- **Denaturation** is the loss of the native structure and activity of a protein.

Scientific theories are often modified or superseded. The specificity of enzyme–substrate interactions was once described by the "lock and key" hypothesis, which suggested that the shape of the active site ("lock") matched exactly the shape of the substrate ("key"). According to the latest "induced fit" theory, the active site does not fit the substrate perfectly but changes its conformation slightly upon binding, like a glove stretches to fit a hand.



▲ **Figure B.2.1.** Kinetics of a typical enzyme-catalysed reaction

The rates of enzyme-catalysed reactions are discussed in more detail in topic B.7.

SAMPLE STUDENT ANSWER

A tripeptide Ala-Asp-Lys was hydrolysed and electrophoresis of the mixture of the amino acids was carried out at a pH of 6.0. Refer to section 33 of the data booklet.

a) Identify the name of the amino acid that does not move under the influence of the applied voltage. [1]

b) Deduce, giving a reason, which amino acid will develop closest to the negative electrode. [2]

This answer could have achieved 1/3 marks:

a) Alanine (Ala)

b) Aspartic acid (Asp), because its pI is less than the pH (2.8 < 6.0), so it will form an anion with two negative COO^- groups and one positive NH_3^+ group.

▲ Correct, as this amino acid has a pI of 6.0 and thus has zero charge at pH 6.0 (note that the answer "Ala" alone would not be accepted, as the name was required)

▼ The anion will have a net negative charge as stated, but will therefore be attracted to the positive electrode. The correct answer is lysine (pI = 9.7), as at pH < pI lysine will have a net positive charge with one COO^- and two NH_3^+ groups

Practice problems for Topic B.2

Problem 1

The structures of amino acids are given in section 33 of the data booklet.

a) State the IUPAC names for glycine and leucine.

b) Suggest, with a reason, the best method for separating a mixture of these two amino acids.

c) Deduce the number of different dipeptides that can be made from glycine and leucine.

d) Draw the structural formula of **one** dipeptide from part (c).

e) Amino acids are usually identified by their common names. Discuss the advantages and disadvantages of this approach.

Problem 2

The fibrous protein keratin has a secondary structure with a helical arrangement.

a) State the type of interaction responsible for holding the protein in this arrangement.

b) Identify the functional groups responsible for these interactions.

Problem 3

Bioplastics are broken down by enzyme-catalysed reactions. Sketch a graph illustrating how the rate of this reaction varies with pH.

B.3 LIPIDS

You should know:

- ✔ fats are more reduced than carbohydrates and thus produce more energy when oxidized;
- ✔ fatty acids can be saturated, monounsaturated or polyunsaturated;
- ✔ triglycerides are triesters produced by condensation of glycerol with fatty acids;
- ✔ triglycerides and their derivatives phospholipids form cell membranes, store energy, provide insulation and transport lipid-soluble vitamins around the body;
- ✔ triglycerides and phospholipids can be hydrolysed by enzymes, acids or bases;
- ✔ lipids act as structural components of cell membranes, in energy storage, thermal and electrical insulation, as transporters of lipid-soluble vitamins and as hormones.
- ✔ steroids have a characteristic fused ring structure (the steroidal backbone) and act as hormones.

You should be able to:

- ✔ compare carbohydrates and lipids as energy storage molecules with respect to their solubility and energy density;
- ✔ deduce the structural formulas of reactants and products in condensation and hydrolysis reactions involving glycerol, fatty acids, triglycerides and phospholipids;
- ✔ predict the relative melting points of fats and oils from their structures;
- ✔ compare the processes of hydrolytic and oxidative rancidity in fats and oils;
- ✔ apply the iodine number to determine the unsaturation of a lipid;
- ✔ discuss the physiological effects of saturated, unsaturated and *trans*-fats, HDL and LDL cholesterol, and the use and abuse of steroids.

Lipids are a diverse group of biomolecules with large hydrocarbon backbones and very few polar functional groups. Unlike carbohydrates (topic B.4), lipids are predominantly non-polar and thus insoluble in water, as they cannot form enough hydrogen bonds with the solvent. Lipids have a low ratio of oxygen to carbon atoms, so they are less oxidized than carbohydrates and thus store more energy per unit mass than other dietary compounds.

Common lipids are *fatty acids*, *triglycerides* (fats and oils, found in living organisms), phospholipids and steroids. Saturated fatty acids contain no C=C bonds, monounsaturated acids contain one C=C bond, and polyunsaturated acids contain two or more C=C bonds. Two polyunsaturated fatty acids, linoleic and linolenic (see section 34 of the data booklet), are *essential fatty acids*, as they cannot be synthesized in the human body and must be obtained from food.

Assessment tip

Lipids are not biopolymers. In biopolymers the structural units are linked by covalent bonds. In contrast, the molecules of lipids are held together by weak London (dispersion) forces and other van der Waals interactions (topic 4.4).

- **Fatty acids** are long-chain carboxylic acids containing more than three carbon atoms.
- **Triglycerides** (oils and fats) are esters of glycerol with fatty acids.

Fatty acids

Unsaturated fatty acids have lower melting and boiling points than their *saturated* analogues. The C=C fragments in naturally occurring molecules usually have *cis*-configuration, so they form kinks in the hydrocarbon chains. These kinks prevent the chains from packing closely and thus weaken the intermolecular London (dispersion) forces. The melting and boiling points of fatty acids increase with chain length, as the strength of London (dispersion) forces increases with the number of electrons.

Assessment tip

All fatty acids contain a C=O fragment, so it is incorrect to say that saturated acids have no double bonds. The correct statement is "saturated fatty acids contain no double *carbon–carbon* bonds". The same is true for triglycerides.

Iodine number is the mass of molecular iodine that reacts with 100 g of the lipid.

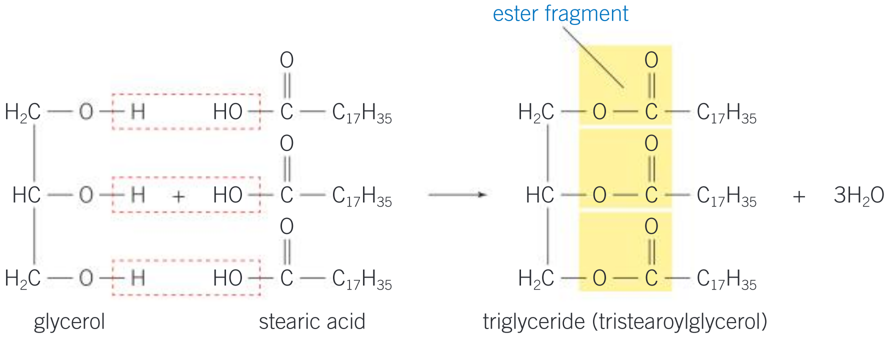
The number of C=C bonds in a lipid (its degree of unsaturation) can be determined from its reaction with iodine.

Unsaturated fatty acids can be saturated by hydrogenation in the presence of a nickel catalyst, at high temperature and pressure:

$$\underset{\text{linolenic acid}}{CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH} + 3H_2 \xrightarrow[p,\ \text{heat}]{Ni} \underset{\text{stearic acid}}{CH_3(CH_2)_{16}COOH}$$

Triglycerides and phospholipids

Triglycerides are triesters of fatty acids and glycerol. They are produced by condensation reactions, for example:



Phospholipids are similar to triglycerides but one fatty acid is replaced with phosphoric acid. Hydrolysis reactions of triglycerides and phospholipids are catalysed by enzymes, strong acids or strong bases.

Melting points of triglycerides and phospholipids, like those of fatty acids, decrease as the number of C=C bonds they contain increases. Liquid triglycerides (*oils*) contain a larger proportion of unsaturated fatty acid residues than solid triglycerides (*fats*). Oils can be converted to fats by catalytic hydrogenation. Incomplete hydrogenation may produce *trans*-isomers of the unsaturated fatty acid residues. Like saturated fatty acids, these increase the risk of heart disease by lowering the ratio of HDL to LDL cholesterol (see below) in the blood, thus contributing to the formation of atherosclerotic plaque. *Cis*-unsaturated fatty acids and their derivatives have the opposite effect and are beneficial for health.

Dietary fats and oils can develop unpleasant odours and flavours due to *rancidity* (table B.3.1). Hydrolytic rancidity (also known as microbial rancidity when caused by bacteria) affects all triglycerides, while oxidative rancidity affects polyunsaturated compounds, such as vegetable and fish oils.

Rancidity type	Group affected	Products	Conditions	Prevention
hydrolytic	ester linkages	fatty acids, glycerol, mono- and diglycerides	moisture, acids, heat, bacterial enzymes	freezing or refrigeration, sterilization
oxidative	double carbon–carbon bonds	volatile aldehydes and ketones	exposure to air and sunlight	airtight and light-proof packaging, protective atmosphere, antioxidants

▲ **Table B.3.1.** Types of rancidity

Assessment tip

Each ester link formed in a condensation reaction requires one molecule of a fatty acid and releases one molecule of water. Similarly, hydrolysis reactions usually require one molecule of water per ester link. Each unbalanced equation will cost you a mark!

Another common error is the incorrect representation of ester links. Make sure that glycerol (X) and the side chain of the fatty acid (R) are connected as X–O–C(O)–R, not as "X–C(O)–O–R" or "X–COOR".

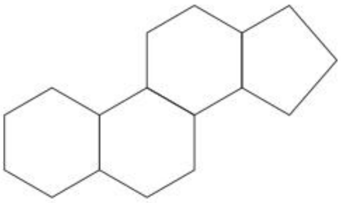
- A **fat** is a triglyceride that is solid at room temperature.
- An **oil** is a triglyceride that is liquid at room temperature.
- **Saturated fats** contain very few or no C=C bonds in fatty acid residues.
- **Monounsaturated fats** contain fatty acid residues with one C=C bond each.
- **Polyunsaturated fats** contain fatty acid residues with two or more C=C bonds each.
- ***Trans*-fats** contain a significant proportion of *trans*-C=C bonds in fatty acid residues.
- **Rancid** fats have been hydrolyzed or oxidized to produce unpleasant odours or flavours.

Steroids and cholesterol

Most *steroids* act as chemical messengers (hormones) that regulate metabolism, immune responses and reproductive functions. Anabolic steroids stimulate the growth of muscle tissue and have many medical uses, but are also abused in sports as performance-enhancing drugs.

All steroids in the human body are synthesized from cholesterol, shown in section 34 of the data booklet, which is also an important component of cell membranes.

Steroids have a characteristic arrangement of four fused rings, known as the *steroidal backbone* (figure B.3.1).



▲ **Figure B.3.1.** The steroidal backbone

Example B.3.1.

Cholesterol is synthesized in the liver and has various biological functions.

a) Suggest, with a reason, whether cholesterol is soluble in water or not.

b) Describe how cholesterol is transported around the body.

Solution

a) The cholesterol molecule has a large hydrocarbon backbone and only one hydroxyl group. Its overall polarity is low, so it is insoluble in water.

b) Cholesterol is transported from the liver to body tissues by the blood in the form of complexes with low-density lipoproteins (LDL). High-density lipoproteins (HDL) form more stable complexes with cholesterol and transport it back to the liver, where it is metabolized.

Assessment tip

HDL cholesterol (HDL-C) and LDL cholesterol (LDL-C) are sometimes called “good cholesterol” and “bad cholesterol”, respectively. You should never use such colloquial names in examinations, as they will not be accepted.

SAMPLE STUDENT ANSWER

Sunflower oil contains stearic, oleic and linoleic fatty acids. The structural formulas of these acids are given in section 34 of the data booklet.

a) Explain which one of these fatty acids has the highest boiling point. [2]

b) 10.0 g of sunflower oil reacts completely with 123 cm^3 of 0.500 mol dm^{-3} iodine solution. Calculate the iodine number of sunflower oil to the nearest whole number. [3]

This answer could have achieved 4/5 marks:

a) Stearic acid, as it is saturated and so molecules can pack closer together, giving stronger London dispersion forces between molecules.

b) $n(I_2) = 0.123 \times 0.500 = 0.0615$ mol;

$m(I_2) = 126.9 \times 0.0615 \approx 7.8$ g

10.0 g acid → 7.8 g iodine,

100 g acid → 78 g iodine.

Iodine number is 78.

▲ Correct; the question requires an explanation, so the nature of intermolecular forces must be stated for the second mark

▲ Correct amount of iodine

▼ Atomic mass of iodine (126.9) is used instead of its molecular mass (253.8)

▲ The last step is correct, so the third mark is awarded with “error carried forward”; the correct answer is 156 (whole number without units)

Practice problems for Topic B.3

Problem 1

Triglycerides are commonly classified as fats and oils.

a) State **one** difference in physical properties and **one** difference in chemical composition between fats and oils.

b) Fats can clog the drains of kitchen sinks. Explain, using a chemical equation, how sodium hydroxide unblocks the drains.

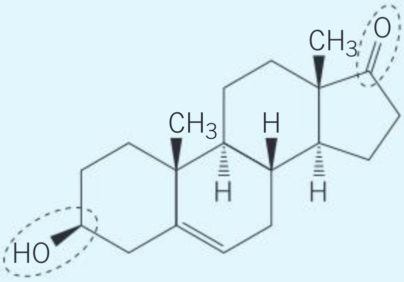
c) Outline how an oil can be converted into a fat.

d) State **one** health concern about the product obtained in (c).

Problem 2

DHEA (dehydroepiandrosterone) is banned for use by athletes under the World Anti-Doping Code.

a) State the names of the functional groups circled in the DHEA molecule shown here.



b) Identify the characteristic of DHEA that classifies it as a steroid.

c) Suggest, with a reason, whether DHEA will be more or less soluble in water than cholesterol.

d) The production of banned steroids has ethical implications. State **one** reason why steroid research might be supported.

B.4 CARBOHYDRATES

You should know:

- ✔ carbohydrates have the general formula $C_x(H_2O)_y$ and function as energy sources and reserves;
- ✔ monosaccharides contain several –OH groups and a carbonyl group;
- ✔ straight-chain and cyclic forms of monosaccharides interconvert in solutions;
- ✔ monosaccharides join together via glycosidic bonds to form di- and polysaccharides.

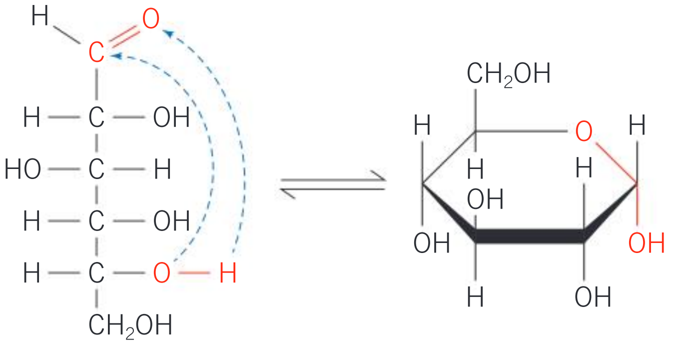
You should be able to:

- ✔ deduce Haworth projections of cyclic monosaccharides;
- ✔ deduce the structural formulas of di- and polysaccharides from given monosaccharides;
- ✔ discuss the properties and functions of mono- and polysaccharides in relation to their chemical structure.

- **Carbohydrates** have the general formula $C_x(H_2O)_y$.
- **Monosaccharides** are organic molecules with one C=O and two or more OH groups.
- An **aldose** is a monosaccharide with a CHO group.
- A **ketose** is a monosaccharide with a C=O group at the second carbon atom.

Carbohydrates ("hydrates of carbon") are oxygen-rich biomolecules with multiple hydroxyl groups and the general formula $C_x(H_2O)_y$. Broader terms *saccharides* and *sugars* include other structurally similar compounds. Monosaccharides have a single carbon chain with a carbonyl group either at the end of the chain (*aldoses*) or at the second carbon atom (*ketoses*). For example, glucose is an aldose while fructose is a ketose (see section 34 of the data booklet).

Most monosaccharides can exist in straight-chain and cyclic forms that interconvert rapidly in solution, where the carbonyl and one of the hydroxyl groups join in a *hemiacetal* group, –O–CH(OH)–. The –OH part of the hemiacetal group can be *trans* or *cis* to the $-CH_2OH$ group, producing α- and β-isomers, respectively (see topic B.10).



glucose, straight-chain form

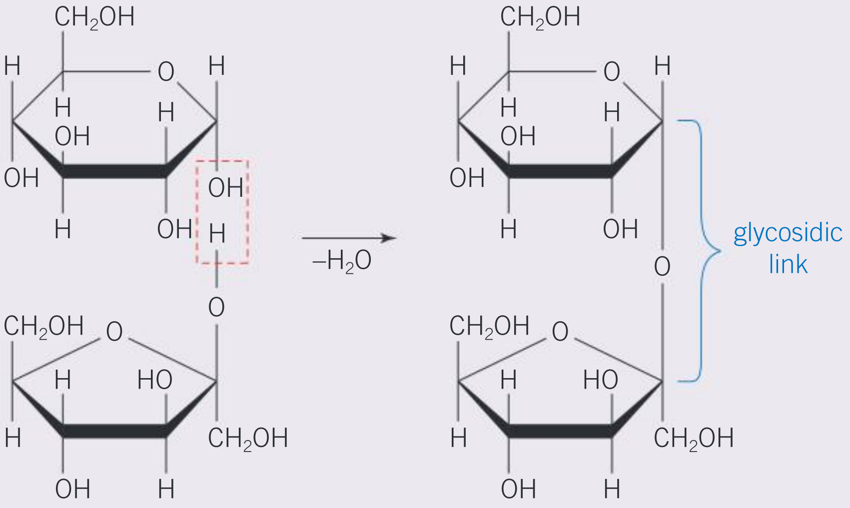
α-glucose, cyclic form (Haworth projection)

Monosaccharides participate in condensation reactions to give di- and *polysaccharides*, in which the structural units are joined by *glycosidic* links.

Example B.4.1.

Sucrose is a disaccharide formed from α-glucose and β-fructose. Deduce the structural formula of sucrose and identify the glycosidic link in its molecule.

Solution



Assessment tip

Make sure that you use correct functional group names, such as hydroxyl (not "hydroxide" or "alcohol") for –OH and carbonyl (not "aldehyde" or "ketone") for C=O. It is also important to state that a sugar contains two or more –OH groups (not just "an –OH group").

Polysaccharides are condensation products of monosaccharides.

Assessment tip

It is incorrect to call the C–O–C fragment in a cyclic monosaccharide an "ether linkage" or "ether group", as it is a part of the larger hemiacetal group.

Carbohydrates are more oxidized than fats (topic B.3) and thus store less energy per unit mass. However, they have many hydroxyl and other polar functional groups that can participate in a wide range of reactions. Hydroxyl groups can form hydrogen bonds with water, so all mono- and disaccharides are readily soluble in water and can be quickly delivered to cells by the blood. Therefore, glucose is used as a source of energy in many biological processes. Polysaccharides, such as glycogen and starch (topics B.6 and B.10), are less water-soluble, so they are used for storing energy and hydrolysed into glucose when needed.

SAMPLE STUDENT ANSWER

Glucose, $C_6H_{12}O_6$, is a monosaccharide that our body can use as a source of energy. Calculate the energy, in kJ, produced from 15.0 g of glucose if its enthalpy of combustion is −2803 kJ mol^{-1}. [2]

This answer could have achieved 2/2 marks:

$M(C_6H_{12}O_6) = 180.18\ g\ mol^{-1}$;

$n(C_6H_{12}O_6) = \frac{15.0}{180.18} \approx 0.0833\ mol$;

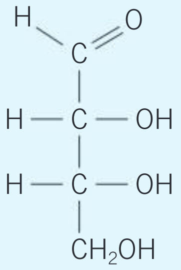
$E = 0.0833 \times 2803 \approx 233\ kJ$

▲ Correct; note that the value must be positive – the enthalpy change of a reaction is independent of the pathway (topic 5.2), so the respiration of glucose will produce the same amount of energy as its combustion

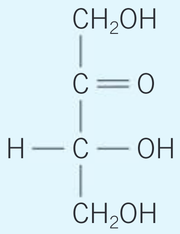
Practice problems for Topic B.4

Problem 1

Carbohydrates are the primary source of energy in living organisms. The structures of threose and erythrulose are shown below.



threose



erythrulose

a) Justify why threose and erythrulose are carbohydrates.

b) Distinguish between these molecules in terms of their functional groups.

c) Suggest, with reference to intermolecular forces, whether carbohydrates are more soluble in water or in hydrocarbons.

Problem 2

Amylose is an unbranched polysaccharide composed of repeating units of α-glucose.

a) Draw the structure of the repeating unit of amylose. Use section 34 of the data booklet.

b) Deduce a balanced equation for the hydrolysis of an amylose molecule with *n* repeating units.

B.5 VITAMINS

You should know:

- ✔ vitamins are organic micronutrients that must be obtained from food;
- ✔ most vitamins are sensitive to heat, light and atmospheric oxygen;
- ✔ vitamin deficiencies cause particular diseases that affect many people worldwide.

You should be able to:

- ✔ compare the structures of vitamins A, C and D;
- ✔ predict the solubility of a vitamin in water and fats from its structure;
- ✔ discuss the causes and effects of vitamin deficiencies and suggest preventive measures.

Vitamins are small organic molecules with diverse functions (table B.5.1). With the exception of vitamin D, they cannot be synthesized by the body and must be obtained from food. Vitamin deficiencies affect health and can be fatal, even if all other nutrients (proteins, fats, carbohydrates, minerals, and water) are present in the diet.

Table B.5.1. Properties and functions of vitamins*

Vitamin	Solubility	Biological role	Deficiency disease
A	fats	vision, immune system, tissue growth and development	night blindness
C	water	collagen synthesis, tissue repair, energy transfer, immune and nervous systems	scurvy
D	fats	calcium absorption, bone and muscle development, immune system	rickets

* Structures of these vitamins are given in section 35 of the data booklet.

Vitamins A and D have large hydrocarbon backbones, so they are predominantly non-polar and thus insoluble in water. In the human body, both vitamins accumulate in fatty tissues, where their molecules are retained by London (dispersion) forces. In contrast, vitamin C (ascorbic acid) has many polar groups that can form hydrogen bonds with water. As a result, vitamin C is soluble in water but insoluble in fats, so it cannot be stored in the body for long and requires regular uptake.

Assessment tip

When the question does not specify the solvent, you should discuss the vitamin solubility in both water and fats. The phrase "at the molecular level" means that you must state the nature and polarity of the vitamin molecule and the type of interactions (London forces or hydrogen bonding) between the vitamin and solvent.

Example B.5.1.

Vitamin A is an essential micronutrient.

a) Suggest why a low-fat diet can result in a deficiency of this vitamin even if it is consumed in sufficient quantities.

b) State **three** methods of preventing vitamin deficiencies.

Solution

a) Vitamin A is insoluble in water but soluble in fats, so its absorption from the gastrointestinal tract requires the presence of fats and lipoproteins (see topic B.3).

b) The use of vitamin supplements (pills), fortification (addition of vitamins to milk and other dietary products) and changes in diet (selection of foods rich in certain vitamins). Another method is the use of food made from genetically modified organisms (topic B.8) with increased vitamin content.

Many vitamins, especially ascorbic acid, are sensitive to heat, light and atmospheric oxygen, so fried or overcooked food loses most of its vitamin content. The decomposition of vitamins is catalysed by metal ions, which are always present in canned food. To reduce loss of vitamins, food must be cooked quickly, stored in airtight glass or plastic packaging, protected from light and refrigerated or frozen.

SAMPLE STUDENT ANSWER

Vitamins can be water-soluble or fat-soluble.

a) Explain, at the molecular level, why vitamin D is soluble in fats. Use section 35 of the data booklet. [2]

b) State **one** function of vitamin D in the body. [1]

This answer could have achieved 1/3 marks:

a) It contains a long chain, similar to long chains in fats. Like dissolves like.

▼ The answer is too vague: "long *hydrocarbon* chain" would score one mark; a reference to specific intermolecular interactions (London forces) is required for the second mark

b) It strengthens the bones.

▲ The answer is accepted; other possible answers are listed in table B.5.1

Practice problems for Topic B.5

Problem 1

a) State **one** structural and **one** physical characteristic of vitamins A and D that make them more similar to each other than they are to vitamin C.

b) Deduce which of the three vitamins (A, C or D) is more soluble in water.

Problem 2

Although small quantities of vitamin D are synthesized in the human body, most people need to obtain this vitamin from their diet.

a) Using sections 34 and 35 of the data booklet, identify the precursor in the biosynthesis of vitamin D.

b) Explain why vitamin D deficiency in northern countries is more common during the winter.

B.6 BIOCHEMISTRY AND THE ENVIRONMENT

You should know:

- ✔ xenobiotics are chemicals that are foreign to an organism or ecosystem;
- ✔ some industrial and domestic waste, such as oil spills, can be broken down by enzymes;
- ✔ biodegradable plastics can be consumed by bacteria;
- ✔ enzymes are included in many detergents to clean at lower temperatures, reducing energy consumption;
- ✔ host–guest chemistry mimics enzyme–substrate chemistry in terms of binding to a specific guest;
- ✔ biomagnification is the increase in concentration of a substance along a food chain;
- ✔ green chemistry aims to minimize the environmental impact of chemical industry and research.

You should be able to:

- ✔ discuss the problem of xenobiotics such as antibiotics in waste water;
- ✔ describe the biomagnification of heavy metals and pesticides;
- ✔ apply the concept of host–guest chemistry to the removal of a specific pollutant;
- ✔ describe the role of starch in biodegradable plastics;
- ✔ discuss the criteria and challenges in assessing the "greenness" of a substance.

A **xenobiotic** is a substance foreign to an organism or ecosystem.

Xenobiotics are chemicals that are released to the environment and enter living organisms with food, water or air. Some xenobiotics are toxic themselves or produce toxic metabolites.

Many, such as DDT, dioxins and polychlorinated biphenyls (PCBs), are very resistant to *biodegradation* and accumulate in plant cells or animal fatty tissues, eventually reaching dangerous concentrations. These concentrations increase exponentially along food chains, which is known as *biomagnification*. As a result, top predators are particularly affected by xenobiotics.

Another class of xenobiotics, antibacterial drugs, do not accumulate in living organisms but cause antibiotic resistance in bacteria.

Certain heavy metals, such as arsenic and mercury, can also undergo biomagnification, especially in aqueous ecosystems. Therefore, these metals must be removed from industrial waste water by various techniques, including precipitation, chelation (topic A.10) and *host–guest chemistry*.

- **Biodegradation** is the breaking down of a substance by bacteria or other organisms.
- **Biomagnification** is the exponential increase of a substance concentration along a food chain.
- In **host–guest chemistry** one chemical species is “recognized” by another, which forms non-covalent bonds with it.

Example B.6.1.

Heavy metals are a serious environmental concern.

a) Explain how host–guest chemistry can be used to selectively remove mercury(II) ions from an aqueous solution.

b) State **two** similarities and **one** difference between host–guest chemistry and the action of enzymes.

Solution

a) The “host” material must have pores or channels of a size and shape that closely match the size and shape of $Hg^{2+}(aq)$ ions. These “guest” ions will enter the pores and be held tightly by multiple non-covalent interactions with the host. Larger ions will not fit into the pores while smaller ions will be held loosely and return to the solution.

b) Similarity 1: active sites in enzymes and pores in host materials both have specific sizes and shapes, so they selectively bind to specific targets (substrates or guests, respectively).

Similarity 2: in both cases, the species are held together by non-covalent interactions (such as van der Waals forces, ionic and hydrogen bonds).

Difference: enzymes select substrates not only by their size and shape but also by their chemical nature (identity and orientation of functional groups), while hosts select guests by size and shape only.

Plastics constitute a large proportion of landfill waste. Polyethene and other hydrocarbon-based plastics are non-biodegradable, so they remain in soil or seawater for hundreds of years. Birds and marine animals often die because they swallow pieces of plastic or get entangled in plastic debris. Biodegradable plastics contain carbohydrates (options B.4 and B.10) that can be broken down by bacteria.

Some industrial wastes, such as oil spills, can be broken down by artificial enzymes or genetically engineered microorganisms (option B.8). Enzymes in biological detergents accelerate the hydrolysis of fats (option B.3) to clean effectively at low temperatures.

Example B.6.2.

Explain how the inclusion of starch in hydrocarbon-based plastics makes them biodegradable.

Solution

Starch-based plastics are hydrophilic due to the presence of hydroxyl groups in carbohydrate units. Bacterial enzymes hydrolyse glycosidic bonds in starch and produce glucose, which is then catabolized by the bacteria. In addition, starch fragments prevent hydrocarbon chains from packing closely and thus weaken the London dispersion forces between these chains. This makes the plastic more permeable to oxygen and water and thus more accessible to microorganisms that decompose it.

Green chemistry

Green chemistry is an approach to chemical research and engineering that seeks to minimize the production and release to the environment of hazardous substances. Common practices of green chemistry include atom economy (topic A.5) and the use of aqueous or solvent-free reactions, renewable starting materials, mild reaction conditions, energy-saving techniques and efficient catalysts, and utilization of by-products.

Non-hazardous substances, such as biodegradable plastics, are often marketed as "green" but still require toxic chemicals or large amounts of energy for their production. In addition, the use of plant oils and starch in industry takes up agricultural land, affects biodiversity and increases the cost of food. Therefore, the "greenness" of a product must be assessed using all direct and indirect environmental implications of its entire life cycle.

Green chemistry has developed alongside growing awareness of the environmental and ethical implications of science and technology. The high cost of some "green" technologies is compensated by lower spending on environmental remediation, waste management and energy.

SAMPLE STUDENT ANSWER

Glucose is the basic building block of starch that can be used to make bioplastics. Outline **two** advantages and **two** disadvantages of biodegradable plastics. [4]

This answer could have achieved 2/4 marks:

Two advantages:

1. The plastic will be quickly digested by bacteria and free up landfills.
2. The plastic will be recycled by returning to the environment for use by organisms.

Two disadvantages:

1. Lots of starch needed, for which lots of crop has to be grown.
2. Uses land to grow the crop.

▲ Correct point; "quickly" and "by bacteria" (or other organisms) are required for the mark

▼ Both answers refer to the same point, and the term "recycled" is incorrect in this context – possible answers could refer to renewable resources used for making starch, reduced use of petrochemicals and non-toxic products of starch metabolism

▲ Again, both answers refer to the same point, but the statement "uses land" scores the mark

▼ Possible answers could refer to the use of fertilizers or pesticides, reduced lifetime of plastic (it can break down before the end of use) and the release of methane if the plastic is buried or composted

Practice problems for Topic B.6

Problem 1

Biodegradable boxes made from polylactic acid, PLA, disintegrate when exposed to water.

$$\left[O - CH(CH_3) - CO \right]_n$$

polylactic acid

State the formula of the product formed when water reacts with PLA.

Problem 2

Suggest how lead ions could be removed from an individual suffering from lead poisoning.

B.7 PROTEINS AND ENZYMES (AHL)

You should know:

- ✔ inhibitors regulate the activity of enzymes;
- ✔ amino acids and proteins can act as acid–base buffers;
- ✔ the concentration of a protein can be determined by UV-vis spectroscopy.

✔ You should be able to:

- ✔ determine K_m and V_{max} from a plot and explain the importance of these values;
- ✔ compare competitive and non-competitive inhibition of enzymes;
- ✔ calculate the pH of buffer solutions involving amino acids;
- ✔ determine the concentration of a protein using the Beer–Lambert law.

Rates of enzyme reactions

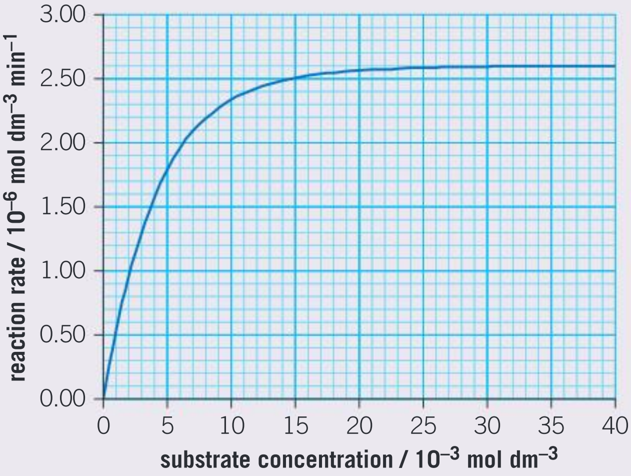
The composition and action of enzymes are discussed in topic B.2. The rates of enzymatic reactions are quantitatively described by the *Michaelis–Menten equation*,

$$\upsilon = \frac{V_{max}[S]}{K_m + [S]},$$

where υ and V_{max} are the actual and *maximum reaction rates*, respectively, [S] is the substrate concentration and K_m is the *Michaelis constant*, which is equal to [S] at $\upsilon = \frac{1}{2}V_{max}$.

Example B.7.1.

The graph in figure B.7.1 shows a Michaelis–Menten plot for an enzymatic reaction.



▲ **Figure B.7.1.** Michaelis–Menten plot

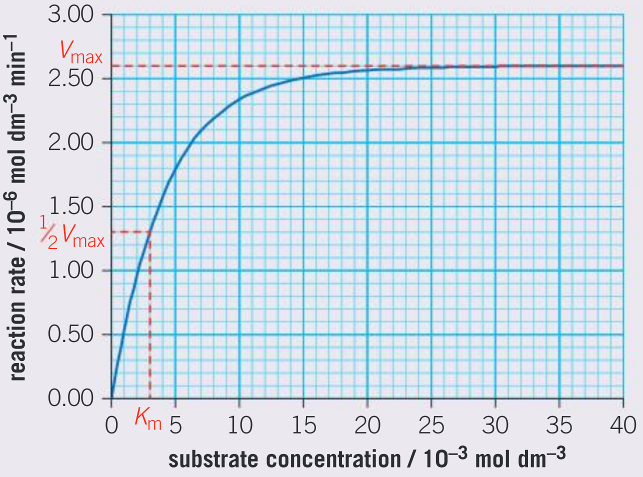
- **Saturation** occurs when all active sites are occupied by substrate molecules.
- **Maximum rate (V_{max})** is the highest possible rate of an enzymatic reaction at given [E].
- The **Michaelis constant (K_m)** is the substrate concentration at $\upsilon = ½V_{max}$.

a) Determine the V_{max} and K_m values for this reaction.

b) Outline the significance of these values for a particular enzyme–substrate pair.

Solution

a)



$V_{max} = 2.60 \times 10^{-6}$ mol dm^{-3} min^{-1}

$½V_{max} = 1.30 \times 10^{-6}$ mol dm^{-3} min^{-1}

$K_m = 3.0 \times 10^{-3}$ mol dm^{-3}

(Note that K_m has the same units as [S].)

b) The V_{max} value characterizes the enzyme activity. It is proportional to the number of substrate molecules that can be converted to product by one molecule of enzyme per unit time.

The K_m value is an inverse measure of the substrate's affinity for the enzyme. A small K_m indicates high affinity, because the enzyme–substrate complex (topic B.2) is particularly stable and the reaction rate approaches V_{max}, even at low [S].

An **inhibitor** is a molecule or ion that decreases the rate of an enzymatic reaction.

Inhibitors regulate metabolic processes by reducing the activity of enzymes. A *competitive inhibitor* binds to the active site, making the enzyme temporarily unavailable for the substrate. A *non-competitive inhibitor* binds to an *allosteric site* (away from the active site), altering the shape of the whole enzyme molecule and distorting the active site so enzyme–substrate binding is less effective. The type of inhibition can be determined from the effects of the inhibitor concentration on V_{max} and K_m (table B.7.1).

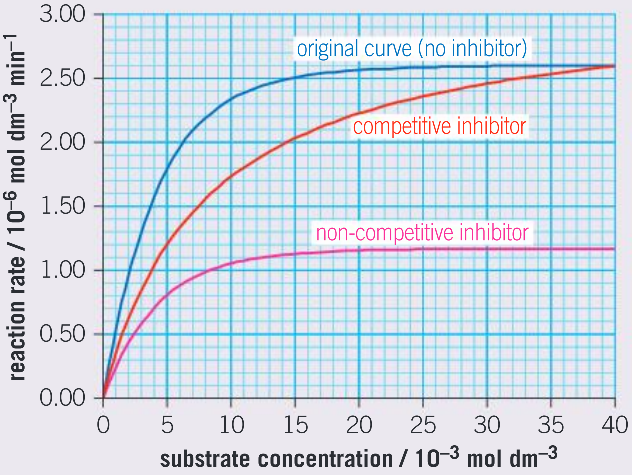
Inhibitor	Structure and shape	Binding site	V_{max}	K_m
competitive	similar to substrate	active	no change	increases
non-competitive	dissimilar to substrate	allosteric	decreases	no change

▲ **Table B.7.1.** Competitive and non-competitive inhibition of enzymes

Example B.7.2.

On the graph from the previous example, sketch and label two curves to show the effect of adding a competitive and a non-competitive inhibitor to the enzyme.

Solution



Assessment tip

The product of an enzymatic reaction can itself act as a competitive or non-competitive inhibitor, providing negative feedback to metabolic processes. Inhibition by the product is a biochemical equivalent of Le Châtelier's principle (topic 7.1): excess product slows the forward reaction until the product concentration returns to its normal physiological level.

Amino acid buffers

Amino acids and proteins can act as acid–base buffers (topic 18.3). An amino acid buffer consists of a zwitterion and either the cation or the anion of the same amino acid (table B.7.2).

Solution pH	Conjugate acid	Conjugate base	Reaction with a strong acid	Reaction with a strong base
pH < pI (acidic)	cation	zwitterion	zwitterion + $H^+ \longrightarrow$ cation	cation + $OH^- \longrightarrow$ zwitterion + H_2O
pH > pI (alkaline)	zwitterion	anion	anion + $H^+ \longrightarrow$ zwitterion	zwitterion + $OH^- \longrightarrow$ anion + H_2O

▲ **Table B.7.2.** Amino acid buffers

The pH of a buffer solution can be calculated using the *Henderson–Hasselbalch equation*:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

Example B.7.3.

A buffer solution contains 0.200 mol dm^{-3} of the cation and 0.500 mol dm^{-3} of the zwitterion of glycine. Calculate the pH of this solution if the pK_a of glycine is 2.34.

Solution

The cation in this solution is the conjugate acid, as it contains one more proton than the zwitterion. Therefore:

$$\text{pH} = 2.34 + \log\frac{0.500}{0.200} \approx 2.74$$

Assessment tip

The Henderson–Hasselbalch equation is given in section 1 of the data booklet. Remember that in acidic solutions the zwitterion acts as a base, so its concentration appears in the numerator. In alkaline solutions the zwitterion acts as an acid, so its concentration appears in the denominator.

UV-vis spectroscopy

Proteins absorb UV light because of electron conjugation (topic B.9) in the aromatic rings of phenylalanine, tyrosine and tryptophan residues. The absorbance (A) of a protein is proportional to its concentration (c) in the solution and the cuvette length (l) (the *Beer–Lambert law*):

$$A = \varepsilon l c$$

The constant ε depends on the solvent and the temperature of the solution. In a typical experiment, the unknown protein concentration is determined from a calibration curve.

Example B.7.4.

UV-vis spectroscopy is commonly used for protein assay. The absorbances of a series of standard protein solutions are given below.

Concentration (c) / mmol dm^{-3}	0.20	1.10	2.00	2.90	3.80
Absorbance (A)	0.047	0.259	0.470	0.682	0.893

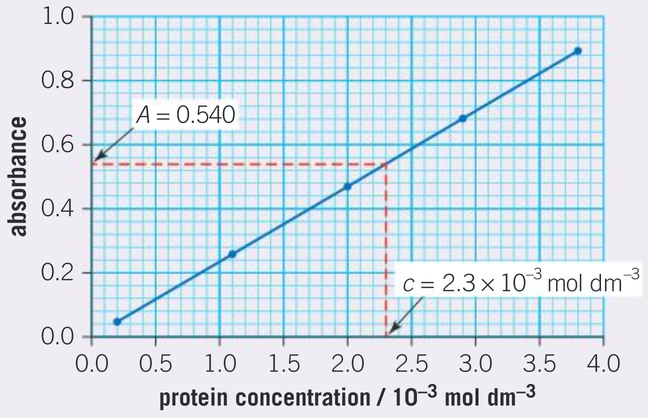
a) Using graph paper, construct the calibration curve.

b) Determine the extinction coefficient (ε), in mol^{-1} dm^2, if the cuvette used in all experiments has a length of 1.00 cm. Refer to section 1 of the data booklet.

c) Determine the concentration of a protein solution with an absorbance of 0.540 measured under the same experimental conditions.

Solution

a)



b) The Beer–Lambert law: $A = \varepsilon l c$, so $\varepsilon = \frac{A}{lc}$. Since the concentration is given in mol dm^{-3}, we need to convert the cuvette length to dm: 1.00 cm = 0.100 dm. The calibration curve is linear, and all points are on the line, so we can use any pair of A and c values from the table, for example:

$$\varepsilon = \frac{0.470}{0.100\ \text{dm} \times 2.00 \times 10^{-3}\ \text{mol dm}^{-3}} = 2.35 \times 10^{3}\ \text{mol}^{-1}\ \text{dm}^{2}$$

c) We can find the unknown concentration from the calibration curve, or calculate it using the Beer–Lambert law:

$$c = \frac{A}{\varepsilon l} = \frac{0.540}{2.35 \times 10^{3}\ \text{mol}^{-1}\ \text{dm}^{2} \times 0.100\ \text{dm}} \approx 2.3 \times 10^{-3}\ \text{mol dm}^{-3}$$

SAMPLE STUDENT ANSWER

Enzymes are biological catalysts. The data shows the effect of substrate concentration, [S], on the rate, υ, of an enzyme-catalysed reaction.

[S] / mmol dm^{-3}	0.0	0.67	1.5	2.0	4.0	6.0	8.0	10.0
υ / mmol dm^{-3} min^{-1}	0.0	0.4	0.6	0.68	0.78	0.8	0.8	0.8

a) Determine the value of the Michaelis constant (K_m) from the data. A graph is not required. [1]

b) Outline the action of a non-competitive inhibitor on the enzyme-catalysed reaction. [2]

This answer could have achieved 1/3 marks:

a) $V_{max} = 0.80$, so $K_m = \frac{1}{2}V_{max} = 0.40$

b) Non-competitive inhibitor binds to allosteric site and changes active site's shape. Substrate cannot bind to changed active site, so reaction stops.

▼ This is a very common error: K_m is not $\frac{1}{2}V_{max}$; it is the [S] value at $\upsilon = \frac{1}{2}V_{max}$, so $K_m = 0.67$ mmol dm^{-3}

▲ The first sentence is correct, so one mark is scored

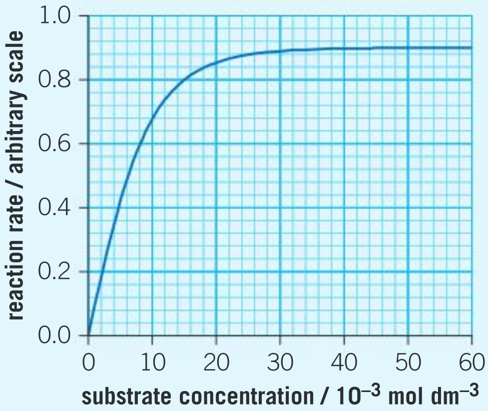
▼ The substrate can still bind to the distorted active site (although less efficiently), so the reaction continues at a reduced rate; V_{max} decreases but does not fall to zero

Practice problems for Topic B.7

Problem 1

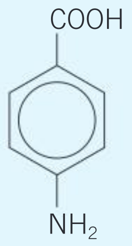
Para-aminobenzoic acid (PABA) plays an important role in the growth of bacteria and fungi.

The rate of an enzyme-catalysed reaction between PABA and glucose depends on the PABA concentration as shown below.



a) Determine the Michaelis constant, K_m, by annotating the graph.

b) Sulfanilamide acts as an inhibitor for the enzyme. The structures of PABA and sulfanilamide are shown right.



4-aminobenzoic acid (PABA)

4-aminobenzenesulfonamide (sulfanilamide)

Suggest, on the molecular level, how sulfanilamide is able to inhibit the enzyme.

c) Sketch a curve on the graph in part (a) showing the effect of sulfanilamide on the reaction rate.

Problem 2

An aqueous buffer solution contains 0.250 mol dm^{-3} of the zwitterion and 0.100 mol dm^{-3} of the anionic form of phenylalanine.

a) Calculate the pH of this buffer solution if the pK_a for phenylalanine is 9.13.

b) Explain how the concentration of phenylalanine in solution can be determined by UV-vis spectroscopy.

B.8 NUCLEIC ACIDS (AHL)

You should know:

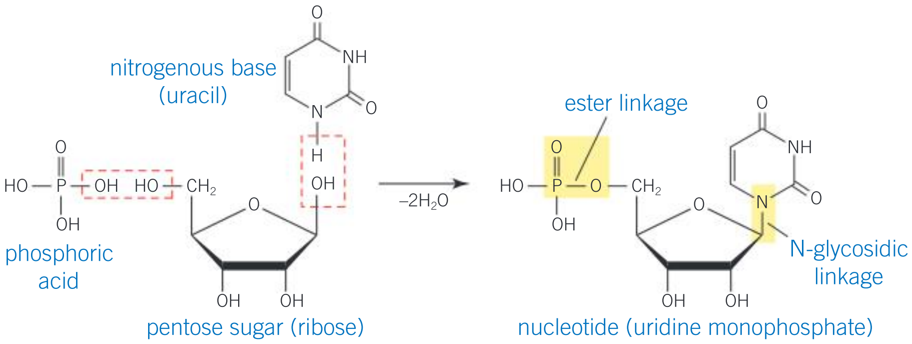
- ✔ a nucleotide contains residues of a nitrogenous base, pentose sugar and phosphoric acid;
- ✔ polynucleotides form by condensation reactions involving phosphate units;
- ✔ RNA is typically a single polynucleotide chain containing ribose and four nitrogenous bases (adenine, uracil, guanine and cytosine);
- ✔ DNA is a double helix of two polynucleotide strands containing deoxyribose instead of ribose and thymine instead of uracil;
- ✔ a sequence of three nitrogenous bases (triplet) in DNA or RNA encodes one amino acid in a protein;
- ✔ genetically modified organisms (GMOs) have artificially altered DNA or RNA.

You should be able to:

- ✔ explain the stability of DNA in terms of the interactions between its hydrophilic and hydrophobic components;
- ✔ explain the origin of the negative charge on DNA and its association with basic proteins (histones) in chromosomes;
- ✔ deduce the nucleotide sequence in a complementary strand of DNA or an RNA molecule;
- ✔ explain how the complementary pairing between bases enables DNA to replicate itself;
- ✔ discuss the benefits and concerns of using genetically modified foods.

Nucleotides and nucleic acids

Nucleotides are formed by condensation of *nitrogenous bases* (section 34 of the data booklet) with a pentose sugar (ribose or deoxyribose) and phosphoric acid (figure B.8.1).



▲ **Figure B.8.1.** Structural units in a nucleotide

Mononucleotides can further condense with one another, producing nucleic acids (table B.8.1).

Polynucleotide	Sugar	Nitrogenous bases	Strands
ribonucleic acid (RNA)	ribose	A, C, G, U	usually one
deoxyribonucleic acid (DNA)	deoxyribose	A, C, G, T	two (double helix)

▲ **Table B.8.1.** Nucleic acids

Nucleic acid structure and function

The two polynucleotide chains (known as *strands*) in *DNA* form a *double helix*, which is stabilized by hydrogen bonds between *complementary* nitrogenous bases of opposite strands. Adenine forms two hydrogen bonds with thymine (A=T), while guanine forms three hydrogen bonds with cytosine (G≡C).

- **Nitrogenous bases** are adenine (A), thymine (T), guanine (G), cytosine (C) and uracil (U).
- A **nucleotide** is the condensation product of a nitrogenous base, a pentose and phosphoric acid.
- **RNA** contains ribose and all nitrogenous bases except thymine.
- **DNA** contains deoxyribose and all nitrogenous bases except uracil.
- A **strand** is a polynucleotide chain in DNA or RNA.
- Two DNA strands spontaneously adopt the **double helix** configuration .
- A **complementary pair** is a pair of nitrogenous bases that form two or three stable hydrogen bonds with each other (A=T, G≡C and A=U).

When the strands are separated, two identical copies of the original DNA can be produced by adding the sequence of complementary nucleotides to each strand.

Example B.8.1.

A fragment of a DNA strand has the nucleotide sequence –ATTGCGTAC–.

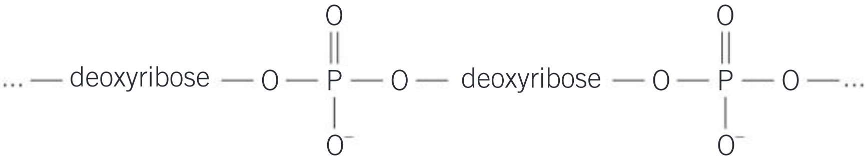
a) Deduce the nucleotide sequence in the complementary strand of this DNA.

b) The DNA strand from part (a) was used as a template for creating an RNA molecule. State **two** differences between this RNA and the first DNA strand (–ATTGCGTAC–).

Solution
a) To construct a complementary DNA strand, we need to replace each adenine residue with thymine, thymine with adenine, guanine with cytosine and cytosine with guanine: –TAACGCATG–.

b) The RNA will be complementary to the second strand. Therefore, it will have the same nucleotide sequence as the first strand except that all thymine residues will be replaced with uracil: –AUUGCGUAC–. In addition, the RNA will contain ribose instead of deoxyribose.

At physiological pH, the phosphodiester bridges in DNA are almost completely ionized:



$$\ldots-\text{deoxyribose}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\text{deoxyribose}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\ldots$$

Negatively charged phosphato groups repel one another and form multiple hydrogen bonds with surrounding water molecules. In addition, phosphato groups can form ionic bonds with basic chromosomal proteins, histones, which are positively charged at physiological pH. The hydrogen and ionic bonds further stabilize the double-helical shape of DNA and protect the strands from damage.

The sequence of nitrogenous bases in DNA is used by the cell as a program for synthesizing specific proteins. Three consecutive bases (*triplet*) encode one amino acid. The genetic information from a DNA strand is first copied (*transcribed*) into a complementary RNA molecule before the RNA is decoded (*translated*) into the amino acid sequence of a protein.

- A **triplet** is the sequence of three nucleotides in DNA or RNA that encodes a single amino acid in a protein.
- **Transcription** is the assembly of a complementary RNA chain from a DNA template.
- **Translation** is the process of building an amino acid sequence from an RNA template.

GMOs

Genetically modified organisms (GMOs) have artificially altered genetic material. Common genetic modifications include transferring useful DNA fragments between species or deleting parts of existing DNA. The most common GMOs, transgenic plants, are resistant to pests, viruses and harsh weather, have higher crop yields or increased nutritional value.

Alongside their advantages, the use of GMOs raises many issues, including the unknown long-term effects of GM foods on health and the possibility of transferring altered genetic material to wild species.

SAMPLE STUDENT ANSWER

The sequence of nitrogenous bases in DNA determines hereditary characteristics. Calculate the mole percentages of cytosine, guanine and thymine in a double-helical DNA structure if it contains 17% adenine by mole. [2]

This answer could have achieved 2/2 marks:

Each adenine in DNA pairs with a thymine, so mole percentage of adenine is the same as thymine (17%).

Together adenine and thymine make up 17 + 17 = 34 mole % of DNA.

Cytosine and guanine make up the rest: 100 – 34 = 66 mole %.

Each cytosine pairs up with a guanine, so their percentages are the same: 66 / 2 = 33% each.

▲ A perfect answer: note that it is sufficient to know the mole percentage of only one nitrogenous base in the DNA to calculate the mole percentages of the three other bases

Practice problems for Topic B.8

Problem 1

DNA is a biological macromolecule.

a) Explain, with reference to functional groups, why it is negatively charged in the body.

b) Deduce the nucleotide sequence of the complementary strand of a DNA fragment with the nucleotide sequence –TCAATGGAC–.

Problem 2

Hereditary information is stored in DNA and transferred by RNA.

a) State **two** differences in composition and **one** difference in structure between DNA and RNA.

b) The mole ratio of adenine to guanine in a double helical DNA sample is 2 : 3. Determine the mole percentage of cytosine in this DNA sample.

B.9 BIOLOGICAL PIGMENTS (AHL)

You should know:

- ✔ biological pigments are coloured compounds produced by living organisms;
- ✔ pigments absorb visible light due to extensive electron conjugation;
- ✔ heme is a chelate complex of iron with a large macrocyclic ligand (porphyrin);
- ✔ hemoglobin, myoglobin and cytochrome are heme-containing proteins;
- ✔ chlorophyll is similar to heme but contains magnesium instead of iron;
- ✔ carotenoids are non-aromatic lipid-soluble pigments involved in photosynthesis;
- ✔ anthocyanins are aromatic water-soluble pigments occurring in plants.

You should be able to:

- ✔ explain the sigmoidal shape of the oxygen saturation curve of hemoglobin in terms of cooperative binding;
- ✔ discuss the factors that affect oxygen saturation of hemoglobin;
- ✔ describe the higher affinity of oxygen for fetal hemoglobin over adult hemoglobin;
- ✔ explain the action of carbon monoxide on hemoglobin in terms of competitive inhibition;
- ✔ describe the function of pigments in photosynthesis;
- ✔ explain the ability of anthocyanins to act as acid–base indicators.

Biological pigments are coloured compounds produced by living organisms. Pigments absorb certain wavelengths of visible light because of extensive electron conjugation in their molecules, the result of the presence of many alternating single and double bonds, aromatic rings and/or heteroatoms with lone electron pairs. The more electrons are involved in conjugation, the longer the wavelength of the absorbed light.

Porphyrin is a nitrogen-containing macrocyclic ligand that forms chelate complexes with iron (hemes), magnesium (chlorophyll) and other metals. Hemes are non-protein components of hemoglobin, myoglobin and cytochromes. The iron(II) ion in hemes can be reversibly oxidized to iron(III) when it binds to oxygen (in hemoglobin and myoglobin) or participates in other redox reactions (in cytochromes).

Hemoglobin consists of four structurally similar subunits (two α and two β in adult hemoglobin; two α and two γ in fetal hemoglobin), which are held together by non-covalent (hydrogen, ionic and van der Waals) interactions. Each subunit contains a heme, which forms a part of the binding site for oxygen.

The structure of carotene, with a chain of conjugated double bonds, is shown in section 35 of the data booklet.

Assessment tip

In answers, it is essential to state that electron conjugation in coloured pigments is *extensive* or involves *many* electrons/atoms/bonds. Similarly, it is important to state that pigments absorb *visible* light (not just “light”) and transmit/have the *complementary* colour (which is opposite the absorbed colour in the colour wheel).

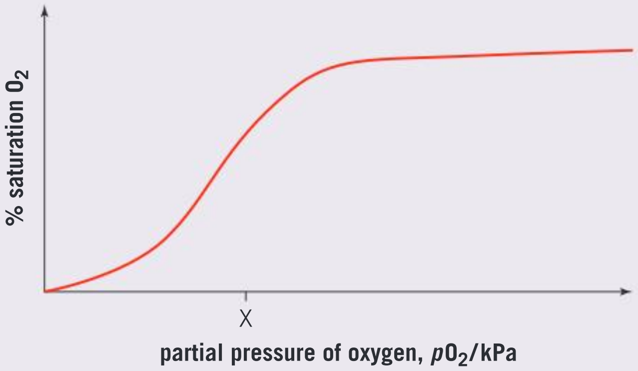
Example B.9.1.

Hemoglobin is a metalloprotein that carries oxygen from lungs to tissues.

a) Explain the sigmoidal shape of the oxygen saturation curve of hemoglobin (figure B.9.1).

b) Describe how the oxygen saturation of hemoglobin is affected by changes in the cell.

c) Outline why fetal hemoglobin has a greater affinity for oxygen.



▲ **Figure B.9.1.** The oxygen saturation curve for hemoglobin

Solution

a) At low $p(O_2)$, hemoglobin is deoxygenated and its affinity for oxygen is low, so the curve rises slowly. When an O_2 molecule binds to iron(II) in any hemoglobin subunit, the conformation of that subunit changes. This affects the conformations of all other subunits and their binding sites, increasing their affinities for oxygen so that the saturation curve rises steeply at medium $p(O_2)$. At high $p(O_2)$, the hemoglobin is nearly saturated, so the curve flattens out again.

b) The oxygen saturation of hemoglobin decreases when temperature increases or pH decreases due to unfavourable changes in the conformation of binding sites. It also decreases in the presence of carbon dioxide and organic phosphates, which act as non-competitive inhibitors (topic B.7).

c) Fetal hemoglobin has a different amino acid sequence and is less sensitive to inhibitors than adult hemoglobin. Therefore, it can work at low $p(O_2)$ and receive oxygen from partly deoxygenated blood.

Carbon monoxide (CO) is highly toxic because it is a competitive inhibitor of oxygen binding in hemoglobin. It replaces one oxygen molecule in hemoglobin by binding to the iron(II) ion and prevents the release of other oxygen molecules to tissues, causing hypoxia.

Chlorophyll is similar to heme but contains a magnesium ion instead of iron(II) ion. Together with carotenoids (long-chain polyunsaturated hydrocarbons), chlorophyll initiates the process of photosynthesis (topic B.1 and table B.9.1). Almost all plant pigments are sensitive to photo-oxidation.

Pigment	Metal ion	Colour	Function
chlorophyll	Mg^{2+}	green	absorbs light energy in photosynthesizing cells
carotenoids	none	orange	extend the absorption spectrum of chlorophyll
anthocyanins	none	various	natural antioxidants, UV-protectors and colourants in plants

▲ **Table B.9.1.** Plant pigments

Carotenoids have no polar groups in their molecules (section 35 of the data booklet) and thus are insoluble in water but soluble in lipids. In contrast, anthocyanins are soluble in water because they have many polar groups that can form hydrogen bonds with the solvent.

In aqueous solutions, anthocyanins act as weak acids and/or bases that gain protons at low pH and lose protons at high pH. These processes affect the extent of electron conjugation in anthocyanins and thus change the wavelength of light they absorb. Therefore, anthocyanins (for example, from red cabbage juice) can be used as acid–base indicators.

SAMPLE STUDENT ANSWER

The heme groups in cytochromes contain iron ions that are involved in the reduction of molecular oxygen.

a) State the half-equation for the reduction of molecular oxygen to water in acidic conditions. [1]

b) Outline the change in oxidation state of the iron ions in heme groups that occurs when molecular oxygen is converted to water. [1]

This answer could have achieved 1/2 marks:

a) $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

b) The oxidation state of iron can vary between +2 and +3.

▲ Correct equation; fractional coefficients would also be acceptable

▼ A specific *change* is required, so an acceptable answer would be "The oxidation state *increases* from +2 to +3."

Practice problems for Topic B.9

Problem 1

A hemoglobin–oxygen saturation curve does not follow the same model as enzyme–substrate reactions (see figure B.9.1).

a) Explain the shape of the curve from 0 to X kPa.

b) Sketch a curve on the axes in figure B.9.1 to show the effect of decreasing pH on the oxygen saturation of hemoglobin.

c) Explain why carbon monoxide is toxic to humans.

Problem 2

Anthocyanins are pigments that give colour to many flowers and fruits. The general structures of two forms of anthocyanins, quinoidal base and flavylium cation, are given in section 35 of the data booklet.

a) State, with a reason, which of the two forms will exist in an aqueous solution at low pH.

b) Explain, with a reference to specific functional groups, why anthocyanins are soluble in water.

c) Outline why quinoidal base and flavylium cation absorb light of different wavelengths.

d) Deduce the colour of a quinoidal base that strongly absorbs visible light in the range 600–640 nm (see section 3 of the data booklet).

B.10 STEREOCHEMISTRY IN BIOMOLECULES (AHL)

You should know:

- ✔ all proteinogenic amino acids except glycine have L-configuration;
- ✔ naturally occurring sugars usually have D-configuration;
- ✔ ring forms of sugars can exist as α- and β-isomers;
- ✔ natural unsaturated fats usually have *cis*-configuration but can be converted to *trans*-fats by incomplete hydrogenation;
- ✔ *cis*-retinal in rhodopsin can be converted to *trans*-retinal by absorbing a photon.

You should be able to:

- ✔ compare the structures and properties of starch and cellulose;
- ✔ discuss the importance of cellulose as a structural material and in the diet;
- ✔ describe the hydrogenation of unsaturated fats and discuss the advantages and disadvantages of this process;
- ✔ outline the role of vitamin A in vision, including the roles of opsin, rhodopsin and retinal.

Most biological molecules have specific configurations of *chiral* carbon atoms. All proteinogenic amino acids (topic B.2) except glycine are L-isomers, while naturally occurring sugars (topic B.4) are predominantly D-isomers (figure B.10.1).

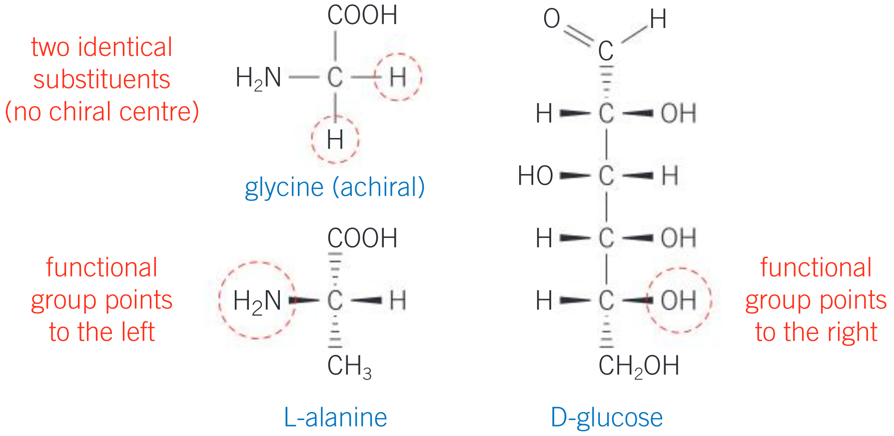
Glycine is non-chiral, as it contains two identical substituents at the central carbon atom (figure B.10.1). In Fischer projections of L-amino acids, the amino group *closest* to the carboxyl group points to the left. In Fischer projections of D-sugars, the hydroxyl group *furthest* from the carbonyl group points to the right.

Chirality is introduced in topic 20.3.

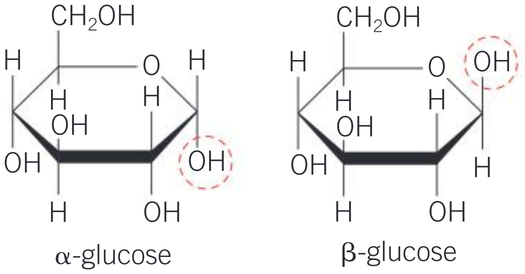
- **Chiral** carbon atoms have four different substituents.
- **Enantiomers**, such as L- and D-isomers, are non-superimposable mirror images of each other.
- **Diastereomers**, such as α- and β-sugars, are stereoisomers that are not mirror images of each other.

Assessment tip

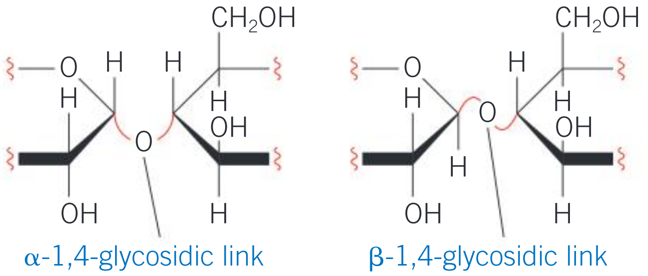
In Fischer projections, the carbon chain must be drawn vertically, with the senior substituent (COOH, CHO or C=O) at the top. Horizontal lines represent the bonds pointing toward you while vertical lines represent the bonds pointing away from you. If you need to show a three-dimensional structure, always draw these bonds as wedges and dashed lines, respectively.



▲ **Figure B.10.1.** Fischer projections of amino acids and a sugar, showing chirality



▲ **Figure B.10.2.** Cyclic forms of sugars are represented by Haworth projections: in α-isomers, the hydroxyl group at carbon 1 (in aldoses) or carbon 2 (in ketoses) points down while in β-isomers it points up



▲ **Figure B.10.3.** Starch is a polymer of α-glucose, while cellulose is a polymer of β-glucose (the glycosidic links are shown curved to maintain the Haworth projections)

- ***Cis*-isomers** are *Z*-isomers with two hydrogen atoms at the same side of a double bond.
- ***Trans*-isomers** are *E*-isomers with two hydrogen atoms at opposite sides of a double bond.

Example B.10.1.

Starch and cellulose are biologically important carbohydrates.

a) Compare and contrast the structures of starch and cellulose.

b) Discuss the importance of cellulose in human diet.

Solution

a) Both starch and cellulose are polymers of glucose. Both polymers have 1,4-glycosidic links between repeating units. However, in starch these links have α-configuration while in cellulose they have β-configuration (figure B.10.3).

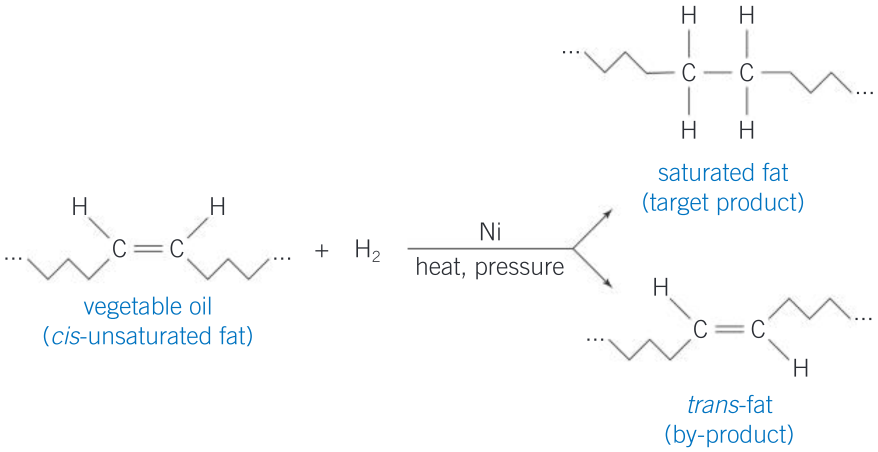
Starch consists of unbranched (amylose) and branched (amylopectin) polysaccharides. The branching in amylopectin occurs due to additional α-1,6-glycosidic links. The chains in starch have coiled, compact conformations. In contrast, cellulose contains only unbranched chains that adopt more extended, rod-like conformations. The conformations of starch and cellulose are stabilized by hydrogen bonds between hydroxyl groups of adjacent chains.

b) Cellulose is a major component of dietary fibre, which facilitates the passage of food through the intestine, preventing constipation. By adding bulk to food, dietary fibre reduces appetite and helps prevent obesity. It also reduces the risk of hemorrhoids, diverticulosis, Crohn's disease, irritable bowel syndrome (IBS) and bowel cancer.

Assessment tip

When discussing the melting points of oils and fats, do not forget to state the nature of the interactions (London forces) between the hydrocarbon chains in triglycerides and the fact that these interactions are intermolecular.

Double carbon–carbon bonds in natural oils and fats have predominantly *cis*-configuration. Margarine and other butter-like dietary products are obtained by hydrogenation of vegetable oils in the presence of a nickel catalyst. Incomplete hydrogenation at high temperatures produces *trans*-fats (figure B.10.4), which increase the risk of heart disease by lowering the ratio of HDL to LDL cholesterol in the blood (topic B.3).



▲ **Figure B.10.4.** Incomplete hydrogenation of vegetable oils

Vision chemistry involves the light-activated interconversion of *cis*- and *trans*-isomers of retinal, a form of vitamin A (topic B.5). In photoreceptor cells, retinal forms a complex with the protein opsin, producing a light-sensitive pigment, rhodopsin. Opsin extends the system of electron conjugation in retinal and allows it to absorb photons across the whole spectrum of visible light.

SAMPLE STUDENT ANSWER

Retinal is the key molecule involved in vision. Explain the roles of *cis*- and *trans*-retinal in vision and how the isomers are formed in the visual cycle. [3]

This answer could have achieved 2/3 marks:

When we look at something, *cis*-retinal transforms into *trans*-retinal, which is unable to bind to rhodopsin and hence detaches. This changes the conformation of rhodopsin and triggers a nerve impulse, providing us with vision. The dissociated *trans*-isomer converts naturally to *cis*-isomer. The *cis*-isomer returns to rhodopsin and restores its 3D conformation, making it ready for the new cycle.

▼ No mark, as the absorption of a photon is not mentioned, and the name of the complex (rhodopsin) is erroneously used instead of the protein name (opsin)

▲ Correct point; the words "an electrical signal" instead of "a nerve impulse" would also be acceptable

▼ "naturally" is not accepted, as this conversion requires enzymes

▲ Again, "rhodopsin" is used instead of "opsin", but the mark is awarded for stating that *trans*-retinal detaches and *cis*-retinal reattaches to the protein

Practice problems for Topic B.10

Problem 1

Serine is a chiral amino acid.

a) Draw both enantiomers of serine.

b) State the enantiomeric form of serine found in proteins.

Problem 2

The structures of biologically important carbohydrates are given in section 34 of the data booklet.

a) Draw the Haworth structures of α-deoxyribose and β-fructose.

b) Identify, by marking with asterisk (*) symbols, all chiral carbon atoms in the structures from part (a).

Problem 3

Retinal reacts with opsin to produce rhodopsin. Refer to section 35 of the data booklet for one structure of retinal.

a) Identify the structural feature that enables rhodopsin to absorb visible light.

b) Outline the change that occurs in the retinal residue during the absorption of visible light.

c) Rhodopsin is commonly called "visual purple" while pure retinal is a bright-yellow solid. Suggest why the colours of these two biological pigments are different.

C ENERGY

C.1 ENERGY SOURCES

You should know:

- good energy sources release energy at a reasonable rate and produce minimal pollution;
- renewable energy sources are naturally replenished while non-renewable sources are finite;
- the quality of energy degrades as heat is transferred to the surroundings;
- specific energy $= \dfrac{\text{energy released from fuel}}{\text{mass of fuel consumed}}$;
- energy density $= \dfrac{\text{energy released from fuel}}{\text{volume of fuel consumed}}$;
- energy transfer efficiency $= \dfrac{\text{useful output energy}}{\text{total input energy}} \times 100\%$.

You should be able to:

- determine the energy density and specific energy of a fuel;
- discuss the use of different energy sources and how the choice of fuel is influenced by its energy density or specific energy;
- discuss the advantages and disadvantages of various energy sources;
- determine the efficiency of an energy transfer process.

Specific energy and energy density are defined in section 1 of the data booklet.

Specific energy and *energy density* of a fuel can be calculated from the standard enthalpy of combustion ($\Delta H_c^{\ominus}$), density (ρ) and the molar mass (M) of the fuel. Together with the *energy transfer efficiency*, specific energy and energy density influence the choice of fuel for specific applications.

Example C.1.1.

A hybrid car uses gasoline (petrol) and a lithium ion battery.

a) The specific energy and energy density of gasoline are similar to those of octane, C_8H_{18}, which has a density of 0.703 kg dm^{-3} and a standard enthalpy of combustion of –5470 kJ mol^{-1}. Calculate the specific energy and energy density of octane.

b) Calculate the specific energy of the lithium ion battery, in kJ kg^{-1}, if it has a mass of 80.0 kg and can store 1.58×10^7 J of energy.

c) The efficiency of energy transfer by the lithium ion battery is four times greater than that of gasoline. Determine the distance, in kilometres, the car can travel on the battery power alone if the car uses 1.00 dm^3 of gasoline to travel 32.0 km. Assume that gasoline has the same energy density as octane.

d) Discuss the advantages and disadvantages of gasoline and the lithium ion battery as energy sources.

Solution

a) $M(C_8H_{18}) = 114.26\ \text{g mol}^{-1} = 0.11426\ \text{kg mol}^{-1}$

$$\text{Specific energy}(C_8H_{18}) = 5470\ \text{kJ mol}^{-1}/0.11426\ \text{kg mol}^{-1} \approx 4.79 \times 10^4\ \text{kJ kg}^{-1}$$

Note that specific energy must be positive.

$$\text{Energy density}(C_8H_{18}) = 4.79 \times 10^4\ \text{kJ kg}^{-1} \times 0.703\ \text{kg dm}^{-3} \approx 3.37 \times 10^4\ \text{kJ dm}^{-3}$$

$$\text{Specific energy(battery)} = 1.58 \times 10^7\ \text{J}/80.0\ \text{kg} \approx 1.98 \times 10^5\ \text{J kg}^{-1} = 1.98 \times 10^2\ \text{kJ kg}^{-1}$$

b) The battery can store 1.58×10^7 J, or 1.58×10^4 kJ of energy, which is $\frac{3.37 \times 10^4}{1.58 \times 10^4} \approx 2.13$ times less than the energy released by 1 dm^3 of gasoline. But the efficiency of a battery is four times greater than that of gasoline, so:

$$l = 32.0\ \text{km} \times \frac{4}{2.13} \approx 60.1\ \text{km}$$

c) Gasoline is relatively cheap and has a higher specific energy than the lithium ion battery. However, gasoline is flammable and non-renewable; it also produces greenhouse gases upon combustion, whereas a battery can be charged from renewable resources. The battery can be recharged while gasoline can be used only once. Finally, the battery has a higher energy transfer efficiency than gasoline.

The enthalpies of combustion and the combustion reactions of hydrocarbons are discussed in topics 5.1 and 10.2, respectively.

Every energy transformation disperses heat to the surroundings, so only a fraction of the initial energy can be used for doing work. All forms of energy can be converted into heat with nearly 100% efficiency, while heat can be converted into other forms of energy with less than 100% efficiency. Generally, the *quality of energy* decreases as follows:

electricity > light > chemical energy > heat

The quality of energy is characterized by the percentage of this energy that can be converted into useful work or other forms of energy.

SAMPLE STUDENT ANSWER

There are many sources of energy available.

a) Calculate the specific energy of hydrogen, stating its units. Refer to sections 1, 6 and 13 of the data booklet. [2]

b) Hydrogen has a higher specific energy than petrol (gasoline) but is not used as a primary fuel source in cars. Discuss the disadvantages of using hydrogen. [2]

This answer could have achieved 2/4 marks:

a) $M(H_2) = 2 \times 1.01 = 2.02\ \text{g mol}^{-1}$

$SE(H_2) = -286\ \text{kJ mol}^{-1}/2.02\ \text{g mol}^{-1}$

$\approx -142\ \text{kJ g}^{-1} = -1.42 \times 10^5\ \text{kJ kg}^{-1}$

b) Hydrogen is flammable and more dangerous to handle than petrol. It also has to be stored in a thick metal cylinder, which is heavy, so energy is wasted on moving this cylinder along with the car.

▼ A specific energy must be positive

▲ Units are correct

▼ Petrol is also flammable, and "more dangerous" is not specific enough ("explosive" would score a mark); the main disadvantage of $H_2(g)$ is its low energy density, so a large volume of this gas is required to power a car

▲ "heavy cylinder" accepted for mark

Practice problems for Topic C.1

Problem 1

Biodiesel and ethanol are renewable fuels.

a) Determine the specific energy, in kJ g^{-1}, and energy density, in kJ cm^{-3}, of a biodiesel using the following data: $\rho = 0.850$ g cm^{-3}; average $M = 299$ g mol^{-1}; $\triangle H_c^\circ = 12.0$ MJ mol^{-1}.

b) The specific energy of ethanol is 29.67 kJ mol^{-1}. Evaluate the addition of ethanol to biodiesel for use as a fuel in motor vehicles, giving **two** advantages and **two** disadvantages.

Problem 2

A coal power plant produces 11.0 GJ of electrical energy per 1.00 tonne (1000 kg) of coal.

a) Calculate the efficiency of energy transfer when the chemical energy of coal is converted into electricity. Assume that coal contains 93% of graphite and 7% of non-combustible material.

b) Suggest **two** methods of increasing the efficiency of this coal power plant.

C.2 FOSSIL FUELS

You should know:

- crude oil (petroleum) is a mixture of hydrocarbons that can be separated by fractional distillation;
- the tendency of a fuel to auto-ignite, which leads to "knocking" in a car engine, is related to molecular structure and measured by the octane number;
- the performance of a hydrocarbon fuel is improved by catalytic cracking and reforming;
- a carbon footprint is the total amount of carbon dioxide produced by human activities.

You should be able to:

- identify the various fractions of petroleum, their relative volatility and their uses;
- deduce equations for cracking and reforming reactions, coal gasification and coal liquefaction;
- discuss the effects of chain length and chain branching on the octane number;
- calculate how much carbon is added to the atmosphere when fuel is burned;
- discuss the advantages and disadvantages of the different fossil fuels.

Natural gas, petroleum (crude oil) and coal are fossil fuels formed over millions of years by the reduction of biological compounds. Petroleum consists of hydrocarbons, which can be separated into fractions (table C.2.1) by fractional distillation. Coal is an impure form of carbon (graphite).

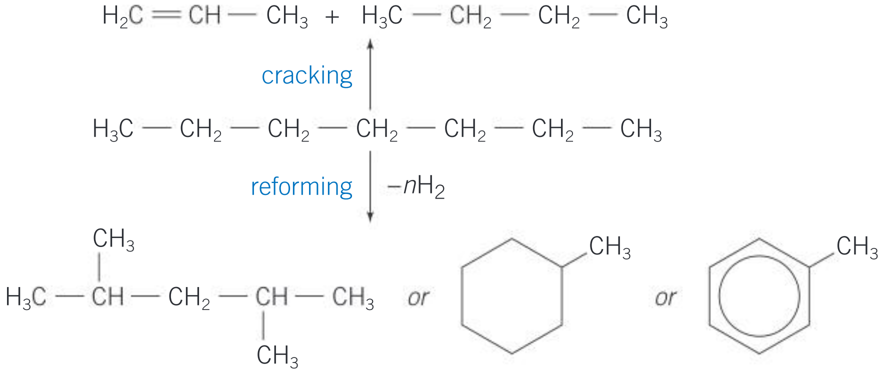
Fraction	Chain length	Uses
natural gas	C_1 and C_2	fuel for power plants and heating
refinery gas	C_3 and C_4	bottled gas
gasoline (petrol)	C_4–C_{12}	fuel for cars
naphtha	C_6–C_{14}	solvents and materials for chemical industry
kerosene	C_8–C_{16}	fuel for aircraft
diesel oil	C_{10}–C_{20}	fuel for cars and trucks
fuel oil	C_{16}–C_{24}	fuel for ships and power plants
non-distillable residue	over C_{20}	lubricating oil, paraffin wax, bitumen (asphalt)

▲ **Table C.2.1.** Natural gas and petroleum fractions

Assessment tip

You do not have to memorize the chemical composition of petroleum fractions. However, you must understand that the boiling points of hydrocarbons increase with their chain length, owing to stronger London (dispersion) forces between larger molecules.

Heavier fractions of petroleum can be converted into lighter fractions by *catalytic cracking*, which produces mixtures of alkanes and alkenes. Straight-chain alkanes can be converted into branched, cyclic and aromatic hydrocarbons by *catalytic reforming* (figure C.2.1). Both processes require high temperatures and catalysts, such as zeolites and transition metals (Pt, Pd, Re or Rh).



▲ **Figure C.2.1.** Catalytic cracking and reforming of heptane, C_7H_{16}

The *octane number* of a fuel characterizes the fuel's tendency to auto-ignite, which leads to "knocking" in a car engine. Higher-octane fuels can be compressed more and thus give better performance than fuels with lower octane numbers. Branched, cyclic and aromatic hydrocarbons have higher octane numbers than straight-chain hydrocarbons. The octane number also increases when the chain length decreases. Therefore, both cracking and reforming increase the octane number of a fuel.

Gaseous and liquid fuels can be produced from coal by *gasification* and *liquefaction*, respectively.

The choice of fuel is influenced by its availability, cost and environmental impact (table C.2.2).

Example C.2.1.

Syngas, mainly composed of CO(g) and H_2(g), can be produced by passing steam over coal or biomass in a low-oxygen environment.

a) State an equation for the production of syngas from coal.

b) The *Fischer–Tropsch process*, an indirect coal liquefaction method, uses a catalyst for converting CO(g) and H_2(g) to hydrocarbons and steam. Deduce the equation for the production of octane by this process.

c) Suggest a reason why syngas may be considered a viable alternative to crude oil.

Solution

a) $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

Note that syngas can also contain methane, as shown in the sample student answer at the end of this subtopic.

b) $8CO(g) + 17H_2(g) \rightarrow C_8H_{18}(l) + 8H_2O(l)$

c) Coal is more abundant than crude oil. Coal gasification can be carried out underground, without lifting coal to the surface. Syngas can also be produced from biomass, which is a renewable resource.

Hydrocarbons and structural isomers are discussed in topic 10.1.

Assessment tip

Double-check that the total numbers of carbon and hydrogen atoms in the products of a cracking or reforming reaction match those in the initial hydrocarbon. Do not forget to state the reaction conditions (high temperature and a catalyst).

- **Catalytic cracking** produces shorter-chain alkanes and alkenes from heavy alkanes.
- **Catalytic reforming** produces branched, cyclic and aromatic hydrocarbons from straight-chain alkanes.
- **Coal gasification** produces mixtures of hydrogen, carbon monoxide and/or methane (**syngas**) from coal and steam.
- **Coal liquefaction** produces liquid hydrocarbons from coal and steam.
- **The Fischer–Tropsch process** is an indirect method of coal liquefaction via syngas as an intermediate.
- **The octane number** characterizes the tendency of a fuel to auto-ignite.

▼ **Table C.2.2.** Advantages and disadvantages of common fuels

Fuel	Advantages	Disadvantages
natural gas*	abundant, cheap (in most countries), produces fewer particulates and less SO_x than other fossil fuels	explosive, toxic, requires complex infrastructure for storage and transportation
petroleum*	readily available in some countries, can be transported through pipes, high specific energy	limited availability in some countries, unpredictable prices, risk of oil spills
coal*	available in many countries, low cost, high specific energy	produces particulates and SO_x, contributes to smog and acid rain
biofuels	renewable, low carbon footprint, can be produced from organic waste	take up land, require fertilizers and pesticides; expensive
nuclear fuels	abundant, no direct emissions of carbon dioxide, very high specific energy and energy density, high energy transfer efficiency	high cost, health risks due to ionizing radiation, production of nuclear waste, risks of nuclear disasters, terrorism and proliferation of nuclear weapons

*Fossil fuel (finite resource, major source of greenhouse gases).

Greenhouse gases and global warming are discussed in topic C.5. Acid deposition resulting from combustion of sulfur in fuels is discussed in topic 8.5.

Carbon footprint is the net quantity of carbon dioxide produced by a particular process. Carbon footprint is commonly expressed in equivalent tonnes of carbon dioxide.

Example C.2.2.

A typical UK household uses 1100 m^3 (STP) of natural gas for heating each year. Use section 2 of the data booklet.

a) Assuming that natural gas consists of methane only, calculate the annual carbon footprint, in tonnes of carbon dioxide (1 tonne = 1000 kg), of heating a typical UK house.

b) Explain the difficulties in quantifying the total carbon footprint for a particular process.

Solution

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

$1100\ m^3 = 1.1 \times 10^6\ dm^3$

$n(CH_4) = 1.1 \times 10^6\ dm^3/22.7\ dm^3\ mol^{-1} \approx 4.8 \times 10^4\ mol$

$n(CO_2) = n(CH_4)$

$m(CO_2) = 4.8 \times 10^4\ mol \times 44.01\ g\ mol^{-1} \approx 2.1 \times 10^6\ g = 2.1$ tonnes.

b) Each process involves many steps, such as production and transportation of fuel, maintenance and repair of the equipment, and so on. Incomplete combustion of fuel may produce carbon monoxide, CO(g), which can oxidize to $CO_2(g)$ in the atmosphere. Taking into account all direct and indirect sources of carbon dioxide requires a lot of data and very complex calculations.

SAMPLE STUDENT ANSWER

Hexane, C_6H_{14}, is not a suitable fuel for internal combustion engines as it has a tendency to auto-ignite, a cause of "knocking".

a) Hexane can be converted to different organic products in a reforming process. Identify **one** of these products. [1]

b) Suggest why the product in (a) has a lesser tendency to auto-ignite than hexane. [1]

c) Coal can be heated with steam to produce synthetic gas. Formulate an equation to show the formation of methane, $CH_4(g)$, from coal, C(s), and steam, $H_2O(g)$. [1]

This answer could have achieved 2/3 marks:

a) 2-methylhexane or 3-methylhexane.

b) Because branched hydrocarbons have higher octane ratings.

c) $2C(s) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g)$

▼ These hydrocarbons contain seven carbon atoms each while hexane has only six. Some possible answers are 2- or 3-methylpentane, 2,3-dimethylbutane, cyclohexane and benzene

▲ Correct answer

▲ Correct equation. Another possible equation is:
$3C(s) + 2H_2O(g) \rightarrow CH_4(g) + 2CO(g)$

Practice problems for Topic C.2

Problem 1

Auto-ignition of hydrocarbon fuel in a car engine causes “knocking”. The tendency of a fuel to knock depends on its molecular structure.

a) Discuss how the octane number changes with the molecular structure of the alkanes.

b) Catalytic reforming and cracking reactions are used to produce more efficient fuels. Outline, using chemical equations, how the straight-chain hydrocarbon tetradecane, $C_{14}H_{30}$, can be converted to methylbenzene (toluene) in two steps.

c) Calculate the carbon footprint, in tonnes of carbon dioxide (1 tonne = 1000 kg), of burning 2.00×10^3 kg of methylbenzene.

Problem 2

Coal liquefaction often involves the intermediate production of syngas, which is a mixture of carbon monoxide, $CO(g)$, and hydrogen, $H_2(g)$.

a) Syngas can be converted to methanol, $CH_3OH(l)$, in one step. Deduce a balanced equation for this process.

b) The catalytic dehydration of methanol produces various liquid hydrocarbons. Deduce a balanced equation for the conversion of methanol to heptane, $C_7H_{16}(l)$.

c) Discuss the advantages and disadvantages of using methanol and heptane as fuels.

C.3 NUCLEAR FUSION AND FISSION

You should know:

- ✔ light nuclei can undergo fusion reactions, and heavy nuclei can undergo fission reactions;

  ^{235}U undergoes a fission chain reaction:
  $^{235}U + {}^{1}n \rightarrow {}^{236}U \rightarrow X + Y +$ neutrons;

  ^{239}Pu, used as a fuel in “breeder reactors” is produced from ^{238}U by neutron capture;
- ✔ radioactive waste may contain isotopes with long and short half-lives;
- ✔ the critical mass is the mass of nuclear fuel needed for the chain reaction to be self-sustaining;
- ✔ absorption spectra are used to determine the composition of stars.

You should be able to:

- ✔ explain fusion and fission reactions in terms of binding energy per nucleon;
- ✔ deduce nuclear equations for fusion and fission reactions;
- ✔ solve radioactive decay problems involving integral numbers of half-lives;
- ✔ discuss the storage and disposal of nuclear waste;
- ✔ explain the atomic absorption spectra of elements, including the relationships between the lines and electron transitions.

Fusion and *fission* are two types of *nuclear reactions* (table C.3.1). Both reactions can occur spontaneously when the products have higher *binding energy* per *nucleon* than the reactants. The change in binding energy per nucleon with mass number can be plotted as the binding energy curve.

The binding energy curve is shown in section 36 of the data booklet.

- A **nuclear reaction** transforms atomic nuclei into one another.
- **Fusion** produces a heavier nucleus from lighter nuclei.
- **Fission** produces lighter nuclei from a heavier nucleus.
- **Binding energy** is the energy that holds nucleons together.
- **Critical mass** is the smallest mass of fissile material that can sustain a chain reaction.
- The **half-life** ($t_{1/2}$) of a radionuclide is the time taken for its quantity to decrease by half.

	Fusion	**Fission**
Reactant(s)	two light nuclei	one heavy nucleus (and often a neutron)
Product(s)	a heavier nucleus (and sometimes other particles)	two lighter nuclei and several neutrons
Examples	${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He$ ${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$	${}^{235}_{92}U \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 2{}^{1}_{0}n$ ${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n$
Advantages	low carbon footprint; very high specific energy	
	cheap and abundant fuel, little or no radioactive waste, no risk of major accidents, higher specific energy than fission	well-known technology, reactions proceed spontaneously once the critical mass is achieved, "breeder" reactors produce more nuclear fuel than they consume
Disadvantages	produce ionizing radiation; require expensive equipment	
	requires extremely high temperatures; commercial reactors do not exist	requires a critical mass of fuel, risk of technological disasters and terror acts, long-lived nuclear waste

▲ **Table C.3.1.** Fusion and fission reactions

Atomic number (Z, number of protons in the nucleus), mass number (A, number of nucleons) and the nuclear symbol notation (${}^{A}_{Z}X$) are introduced in topic 2.1.

Nuclear equations are balanced in terms of atomic mass and charge: the sums of superscript indices (mass numbers, A) and subscript indices (atomic numbers, Z) of all elements and particles must be the same on both sides of the equation.

Example C.3.1.

Curium-240 can be synthesized by bombarding thorium-232 with carbon-12. Deduce the nuclear equation for this reaction.

Solution

The reaction produces ${}^{240}_{96}Cm$ from ${}^{232}_{90}Th$ and ${}^{12}_{6}C$. The atomic numbers are already balanced ($90 + 6 = 96$), so no charged particles will be formed. The mass numbers differ by four units ($232 + 12 - 240 = 4$), so the fusion reaction releases four neutrons:

$$ {}^{232}_{90}Th + {}^{12}_{6}C \rightarrow {}^{240}_{96}Cm + 4{}^{1}_{0}n $$

Assessment tip

Double-check that all atomic numbers match the element symbols. The two most common errors are the use of the same Z for different elements or the same element symbol for different Z.

Each radionuclide decays exponentially. Over a certain period of time, regardless of its initial value, the nuclide's activity falls by one-half. This period, known as the nuclide's *half-life* ($t_{1/2}$), can vary between nuclides from nanoseconds to billions of years.

Example C.3.2.

The amount of radioactive ${}^{225}Ac$ in a sample decays to one-eighth of its original value in 30.0 hours.

a) Deduce the half-life of ${}^{225}Ac$.

b) Determine the time, in hours, at which the activity of ${}^{225}Ac$ has fallen to 6.25% of its initial level.

Solution

a) The amount (n) of the nuclide will decrease as follows:

$$ n\ (100\%) \xrightarrow{t_{1/2}} \frac{1}{2}n\ (50\%) \xrightarrow{t_{1/2}} \frac{1}{4}n\ (25\%) \xrightarrow{t_{1/2}} \frac{1}{8}n\ (12.5\%) \xrightarrow{t_{1/2}} \frac{1}{16}n\ (6.25\%) $$

The nuclide's amount has fallen to one-eighth of its original value after three $t_{1/2}$ periods. Therefore, $t_{1/2} = \frac{30.0\ \text{h}}{3} = 10.0\ \text{h}$

b) From the above scheme, $t = 4t_{1/2} = 4 \times 10.0\ \text{h} = 40.0\ \text{h}$

Nuclear power plants generate large quantities of *high-level waste* (HLW), which contains highly radioactive nuclides with long half-lives. HLW must be stored under water for several years until its activity decreases, then vitrified or encased in steel, covered in concrete and buried deep underground in stable geological locations.

Problems involving the half-life equation and the decay constant (λ) are discussed in topic C.7.

SAMPLE STUDENT ANSWER

Carbon is produced by fusion reactions in stars.

a) Outline how the spectra of light from stars can be used to detect the presence of carbon. [1]

b) The main fusion reaction responsible for the production of carbon is:

$X + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C}$

Deduce the identity of X. [1]

c) Nuclear fusion reactors are predicted to become an important source of electrical energy in the future. State **two** advantages of nuclear fusion over nuclear fission. [2]

This answer could have achieved 2/4 marks:

a) Electrons in carbon atoms jump to higher orbitals by absorbing light of specific wavelengths. These wavelengths appear in the star's spectrum as dark lines.

b) $Z = 6 - 2 = 4$, so the element is Be. $A = 12 - 4 = 8$, so $X = {}^{8}_{4}\text{Be}$.

c) Fusion produces more energy than fission and leaves no waste.

Fusion reactions occur in stars. The composition of stars can be analysed by atomic absorption spectroscopy. The atomic spectrum of hydrogen is discussed in topic 2.2.

▲ Note that the photons are absorbed not by individual electrons but by whole carbon atoms or ions; the mark is still awarded for "dark lines" at "specific wavelengths"

▲ Correct answer

▼ The amount of energy produced depends on the quantity of the fuel; "more energy *per mass of fuel*" would be accepted, and "no waste" is too vague; "no *radioactive* waste" would be accepted.

Practice problems for Topic C.3

Problem 1

a) Uranium-235 can absorb a neutron, producing an unstable isotope. This isotope undergoes spontaneous fission, producing three neutrons, iodine-131 and another nuclide. Deduce the balanced nuclear equations for these reactions.

b) Uranium-235 has a half-life of 7.038×10^{6} years. Determine the time required for the mass of ^{235}U in a sample to decrease from 10.00 g to 1.25 g.

c) State the type of nuclear waste produced by the fission of ^{235}U in a nuclear reactor.

Problem 2

The Sun is the main source of energy used on Earth.

a) One fusion reaction occurring in the Sun is the fusion of deuterium (hydrogen-2) with tritium (hydrogen-3) to form helium-4. Deduce the balanced nuclear equation for this reaction.

b) Explain why this reaction releases energy, referring to section 36 of the data booklet.

c) State the technique used to show that the Sun is mainly composed of hydrogen and helium.

C.4 SOLAR ENERGY

You should know:

- ✔ light is absorbed by chlorophyll and other pigments with extended electron conjugation;
- ✔ photosynthesis converts light into chemical energy: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$;
- ✔ ethanol, which can be used as a fuel, is produced by the fermentation of glucose: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$;
- ✔ vegetable oils have high energy content but are too viscous to be used as fuel for cars.

You should be able to:

- ✔ identify the structural features in molecules that allow them to absorb visible light;
- ✔ deduce the equations for transesterification reactions involving simple esters and triglycerides;
- ✔ explain the reduced viscosity of methyl and ethyl esters of fatty acids;
- ✔ evaluate the advantages and disadvantages of biofuels.

The structures of chlorophyll and some pigments are given in section 35 of the data booklet.

Assessment tip

It is essential to state that the electron conjugation in coloured pigments is *extensive* or involves *many* electrons/bonds. Similarly, it is important to state that pigments absorb *visible* light (not just "light").

- **Electron conjugation** is the interaction between electrons of alternating single and multiple bonds and/or lone electron pairs adjacent to multiple bonds.
- **Biofuels** are fuels produced from plants or microorganisms.
- **Biodiesel** is a mixture of methyl or ethyl esters of fatty acids produced by transesterification of triglycerides.
- **Transesterification** is a reaction between an ester and an alcohol that produces a new ester and a new alcohol: $RCOOR^1 + R^2OH \rightarrow RCOOR^2 + R^1OH$

Chlorophyll and other pigments contain alternating single and double bonds. Electrons in these bonds become delocalized and form an extended system of *electron conjugation*. Molecules with large clouds of delocalized electrons absorb visible light and thus appear coloured. Chlorophyll initiates the process of photosynthesis, which converts solar energy into chemical energy.

Common *biofuels* are ethanol and biodiesel. Ethanol is produced by the fermentation of glucose while *biodiesel* is produced by *transesterification* of vegetable oils (*triglycerides*) with ethanol or methanol in the presence of strong acids or bases. Vegetable oils have similar energy content to common diesel but cannot be used in car engines directly due to their high viscosity.

Example C.4.1.

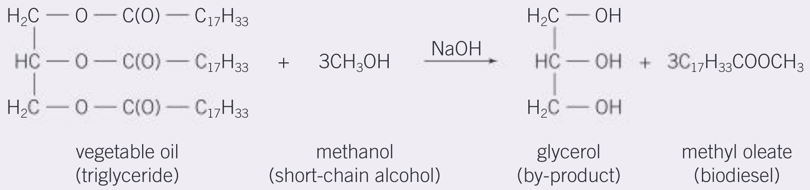
Biofuels are renewable energy sources derived mainly from plants.

a) Deduce the equation for the complete transesterification reaction between methanol and a vegetable oil containing the residues of oleic acid only.

b) Explain why the biodiesel formed in this reaction is less viscous than the original oil.

Solution

a)



A base catalyst, NaOH, is required for transesterification.

b) The molecules of methyl oleate are relatively small and flexible, so they do not pack as closely as the molecules of triglycerides and thus have weaker intermolecular interactions (London and dipole–dipole forces). Therefore, they can slip past one another more easily.

Assessment tip

When discussing viscosity, melting or boiling points, it is essential to mention the type of forces (intermolecular) and their nature (London, dipole–dipole or van der Waals).

Transesterification is a type of nucleophilic substitution (S_N) reaction, which is discussed in topic 20.1.

SAMPLE STUDENT ANSWER

Vegetable oils and diesel fuel have similar energy content but vegetable oils are not used as fuels in internal combustion engines.

a) Transesterification reactions allow waste cooking oils to be converted to biofuels. Identify a reagent and catalyst required for this conversion. [2]

b) Scientists around the world conduct research into alternatives to fossil fuels. Suggest why collaboration is important. [1]

This answer could have achieved 2/3 marks:

a) Reagent: alcohol.

Catalyst: sulfuric acid, H_2SO_4.

b) Scientists share ideas and publish their results in journals, so they don't need to do the same research twice.

▼ "alcohol" is not accepted; a more specific answer ("methanol" or "ethanol") is required

▲ Named acid is accepted; other possible answers are "NaOH" or any other strong base or acid

▲ Correct suggestion; other possible answers may refer to increased validity of experimental data, acceleration of research and economic benefits of sharing knowledge and technologies

Practice problems for Topic C.4

Problem 1

The Sun can be used as a source of energy.

a) Outline how chlorophyll absorbs visible light to enable photosynthesis to take place.

b) State the summary equation of photosynthesis.

c) Outline, using an equation, how ethanol can be produced from the product of the reaction in part (b).

Problem 2

Vegetable oils are too viscous for use as liquid fuels.

a) Describe, using an equation, how a vegetable oil can be converted to products with lower viscosity by reaction with ethanol.

b) Outline why biofuels have a lower carbon footprint than fossil fuels.

C.5 ENVIRONMENTAL IMPACT—GLOBAL WARMING

You should know:

- ✔ greenhouse gases, such as CO_2, H_2O and CH_4, absorb IR radiation causing global warming;
- ✔ particulates, such as smoke and dust, reflect sunlight and cause global dimming;
- ✔ there is a heterogeneous equilibrium between atmospheric $CO_2(g)$ and oceanic $CO_2(aq)$.

You should be able to:

- ✔ discuss the sources, relative abundance and effects of different greenhouse gases;
- ✔ explain the absorption of IR radiation by greenhouse gases at the molecular level;
- ✔ discuss the different approaches to the control of carbon dioxide emissions;
- ✔ discuss how the concentration of atmospheric $CO_2(g)$ affects the pH of oceanic water.

Carbon dioxide (CO_2), water vapour (H_2O) and methane (CH_4) are known as *greenhouse gases* (GHGs).

- The **greenhouse effect** is the warming of the Earth's surface by the IR radiation coming from the atmosphere.
- **Greenhouse gases (GHGs)** absorb IR radiation and re-radiate part of it back to Earth.
- **Global warming** is the observed rise in the Earth's surface temperature over the past century.
- **Global warming potential (GWP)** is the relative efficiency of a greenhouse gas.
- **Global dimming** is the gradual reduction in the amount of solar radiation reaching the Earth's surface over the past decades.

Assessment tip

You must always state that greenhouse gases *re-radiate* (first absorb and then emit) IR energy. Other terms, like "reflect", "bounce" or "trap", will not be accepted.

In contrast, particulates in the atmosphere *reflect* incoming solar radiation back into space, causing global dimming.

The electromagnetic spectrum is discussed in topic 2.2 and represented schematically in section 3 of the data booklet.

- **Carbon capture and storage (CCS)** prevents carbon emissions by storing any CO_2 produced in underground geological formations.
- **Alkaline scrubbers** absorb CO_2 by reaction with inorganic bases.
- **Carbon recycling** is the use of carbon dioxide as a feedstock for synthetic fuels.
- A **carbon sink** absorbs carbon dioxide from the atmosphere and holds it long-term.

Chemical equilibria are discussed in topics 7.1 and 8.1.

The release of GHGs to the atmosphere by human activities is associated with *global warming*. Historical data show good correlation between the concentration of atmospheric carbon dioxide and the average temperature of the Earth's surface. Details about individual GHGs are given in table C.5.1. Particulates released by human activity are reducing the amount of sunlight reaching the Earth's surface (*global dimming*).

▼ **Table C.5.1.** Major greenhouse gases*

Gas or vapour	Sources related to human activity	Concentration in atmosphere	Global warming potential	Contribution to global warming
CO_2	burning of fossil fuels, production of cement and steel, deforestation	low	high	high
H_2O	negligible	variable	low	low
CH_4	production of fossil fuels, farm animals, landfills and waste	very low	very high	moderate

*Ozone (O_3) and other minor greenhouse gases have little effect on global warming.

Example C.5.1.

Carbon dioxide, CO_2, is a greenhouse gas.

a) Explain how the greenhouse effect warms the surface of the Earth.

b) Outline how the molecules of carbon dioxide interact with infrared (IR) radiation.

Solution

a) Greenhouse gases let short-wavelength radiation from the Sun pass. This radiation warms the Earth's surface, which emits IR radiation. Greenhouse gases absorb IR radiation and re-radiate it in all directions, so some IR radiation is returned to Earth's surface and warms it further.

b) When a CO_2 molecule absorbs an IR photon, the C=O bonds bend or stretch asymmetrically, producing a net dipole moment. The excited molecule quickly emits an IR photon in a random direction and returns to the ground state with no dipole moment.

Carbon dioxide emissions can be reduced with *carbon capture and storage (CCS)* techniques, *alkaline scrubbers* and *carbon recycling*, or by switching to carbon-neutral sources of energy. Existing carbon dioxide is removed from the atmosphere by photosynthesis, which can be accelerated by planting trees and preventing deforestation.

Oceanic water acts as a *carbon sink* by absorbing carbon dioxide from the atmosphere. The solubility of carbon dioxide in water is relatively low, so $CO_2(g)$ in the atmosphere and $CO_2(aq)$ in the oceans exist in a heterogeneous equilibrium. In turn, $CO_2(aq)$ acts as a weak acid, which lowers the pH of oceanic water.

SAMPLE STUDENT ANSWER

Carbon dioxide and water vapour are greenhouse gases produced by the combustion of fossil fuels.

a) Explain the effect of the increasing concentration of atmospheric carbon dioxide on the acidity of oceans. [2]

b) Other than changes to the acidity of oceans, suggest why the production of carbon dioxide is of greater concern than the production of water vapour. [1]

This answer could have achieved 2/3 marks:

a) $CO_2(g) \rightleftharpoons CO_2(aq)$

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

High levels of $CO_2(g)$ shift both equilibria to the right, so $[H^+]$ increases and pH decreases.

b) Because the production of carbon dioxide is mainly responsible for global warming.

▲ Correct answer; note that the equilibrium sign and the states of CO_2 in the first equation are required for the mark

▼ This answer is too vague; possible answers could state that CO_2 is a more effective GHG, it has a greater GWP and its concentration in the atmosphere is increasing (unlike that of H_2O)

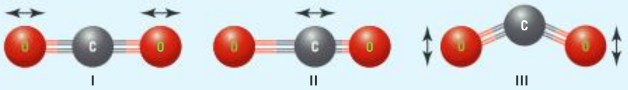
Practice problems for Topic C.5

Problem 1

A link between the combustion of fossil fuels and an increase in the temperature of the Earth's atmosphere was proposed over a century ago.

a) Suggest why it is only in recent years that specific predictions of the future effects of fossil fuel combustion have been made.

b) Carbon dioxide has three different vibrational modes (I, II and III, below).



Predict, with an explanation, which of these modes can be activated when a molecule of carbon dioxide absorbs infrared radiation.

c) Global warming affects not only the atmosphere but also the oceans. Outline, using an equation, how the rising temperature of oceanic water will affect the concentration of carbon dioxide in the atmosphere.

d) Many combustion processes release particulate matter into the atmosphere. Suggest, giving your reason, how this might affect the temperature of the Earth's surface.

C.6 ELECTROCHEMISTRY, RECHARGEABLE BATTERIES AND FUEL CELLS (AHL)

You should know:

- ✔ in a primary cell, the electrochemical reaction is not reversible, while rechargeable cells involve redox reactions that can be reversed using external source of electricity;
- ✔ a fuel cell converts the chemical energy of the fuel directly to electrical energy;
- ✔ the voltage of a cell depends on the nature of the materials used while the total energy output depends on the quantity of these materials;
- ✔ the maximum current of a cell is limited by its internal resistance, which is caused by the finite time it takes for ions to diffuse;
- ✔ microbial fuel cells (MFCs) can use carbohydrates in waste water as the fuel;
- ✔ the half-cells in a concentration cell differ only by the electrolyte concentration.

You should be able to:

- ✔ distinguish between fuel cells and primary cells;
- ✔ deduce half-equations for the electrode reactions in a fuel cell;
- ✔ discuss the advantages and disadvantages of different types of cells;
- ✔ solve problems using the Nernst equation;
- ✔ calculate the thermodynamic efficiency $\left(\frac{\Delta G}{\Delta H}\right)$ of a fuel cell;
- ✔ explain the workings of rechargeable cells and fuel cells.

Electrochemical cells convert the chemical energy of redox reactions (table C.6.1) into electrical energy.

Redox reactions and electrochemical cells are introduced in topics 9.1.

Assessment tip

You should be familiar with all reactions given in table C.6.1 and be able to explain these processes in terms of reducing and oxidizing agents, electron transfer and proton transfer.

Primary cells can be used only once, as their redox reactions are irreversible. In contrast, the redox reactions in *rechargeable cells* can be reversed using an external source of electrical energy.

Primary and rechargeable cells have limited capacity, as all chemicals are stored within the cell. *Fuel cells* can operate indefinitely but require a continuous supply of fuel and oxygen. *Microbial fuel cells (MFCs)* use microorganisms to extract fuel (carbohydrates and other organic compounds) from waste water and oxidize it under anaerobic conditions. The advantages and disadvantages of different cell types are listed in table C.6.2.

▼ **Table C.6.1.** Discharge half-equations in electrochemical cells

Cell type	**Positive electrode (cathode)**	**Negative electrode (anode)**
lead–acid cell*	$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$
NiCd cell*	$NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$	$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
Li-ion cell*	$Li^+ + e^- + CoO_2(s) \rightarrow LiCoO_2(s)$	$Li(s) \rightarrow Li^+ + e^-$
hydrogen fuel cell	*Acidic electrolyte (most common):* $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ *Basic electrolyte (less common):* $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$
direct methanol fuel cell (DMFC)		$CH_3OH(aq) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$
microbial fuel cell (MFC)		$C_6H_{12}O_6(aq) + 6H_2O(l) \rightarrow 6CO_2(g) + 24H^+(aq) + 24e^-$ or $CH_3COO^-(aq) + 2H_2O(l) \rightarrow 2CO_2(g) + 7H^+(aq) + 8e^-$

*When the cell is being recharged, all half-equations are reversed.

- A **proton exchange membrane (PEM)** is a porous polymer that separates the anode and cathode in most fuel cells; $H^+(aq)$ ions can diffuse through it, but not electrons or molecules.
- ***Geobacter*** is a genus of bacteria used in microbial fuel cells (MFCs).

▼ **Table C.6.2.** Advantages and disadvantages of different electrochemical cells*

Cell type	**Advantages**	**Disadvantages**
primary cells	cheap, ready to use, low self-discharge rate, higher capacity than rechargeable cells	can be used only once (non-rechargeable), limited shelf life, disposed of as hazardous waste
rechargeable cells	can be recharged and used many times, produce less waste than primary cells	more expensive than primary cells, must be charged before use, high self-discharge rate, limited number of uses
hydrogen and methanol fuel cells	can be used continuously (do not need to be recharged), high specific energy and thermodynamic efficiency	expensive, need constant supply of fuel, hydrogen is explosive and difficult to store/transport, methanol is toxic, methanol cells produce CO_2
microbial fuel cells	cheap, use organic waste as fuel, remove contaminants from waste water	low voltage, low power per unit mass, limited lifetime, work in narrow ranges of temperature and pH

*Portability is the common advantage of all cell types.

The Nernst equation, its constants (R and F) and standard electrode potentials are given in sections 1, 2 and 24, respectively, of the data booklet.

The *Nernst equation*, $E = E^\ominus - \frac{RT}{nF}\ln Q$, can be used to calculate the potential of a half-cell or a voltaic (electrochemical) cell under non-standard conditions. The reaction quotient, Q, must include concentrations of all aqueous species present in the cell, such as metal cations, protons (H^+) and hydroxide ions (OH^-).

Example C.6.1.

Consider the voltaic cell that uses the following redox reaction:

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

a) Calculate the standard cell potential, in V, at 298 K. Refer to section 24 of the data booklet.

b) Determine the cell potential, in V, at 298 K given that $[Zn^{2+}] = 1.00 \times 10^{-4}$ mol dm^{-3} and $[Cu^{2+}] = 1.00 \times 10^{-1}$ mol dm^{-3}. Refer to sections 1 and 2 of the data booklet.

c) Deduce, giving your reason, whether the reaction in (b) is more or less spontaneous than in the standard cell.

Solution

a) $E^\ominus(Cu^{2+}/Cu) = +0.34$ V and $E^\ominus(Zn^{2+}/Zn) = -0.76$ V (section 24 of the data booklet). Therefore, $E^\ominus_{cell} = +0.34\text{ V} - (-0.76\text{ V}) = +1.10$ V.

b) $$E_{cell} = E^\ominus_{cell} - \frac{RT}{nF}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]} = +1.10\text{ V} - \frac{8.31 \times 298}{2 \times 96500}\ln\frac{1.00 \times 10^{-4}}{1.00 \times 10^{-1}}$$

$$\approx +1.10\text{ V} + 0.0886\text{ V} \approx +1.19\text{ V}$$

Note that the solid reactants, Zn(s) and Cu(s), are not included in the reaction quotient.

c) More spontaneous, as $E_{cell} > E^\ominus_{cell}$

- A **concentration cell** consists of two half-cells with identical electrodes and electrolytes but different concentrations.
- **Thermodynamic efficiency** (η) is the ratio of the Gibbs free energy change to the enthalpy change, $\frac{\Delta G^\ominus}{\Delta H^\ominus}$.

The potential of a *concentration cell* can be determined using the Nernst equation with the method shown in example C.6.1, except that $E^\ominus_{cell} = 0$ V.

For any voltaic cell, $\Delta G^\ominus = -nFE^\ominus$ (section 1 of the data booklet), so

thermodynamic efficiency $(\eta) = \frac{\Delta G^\ominus}{\Delta H^\ominus} = -\frac{nFE^\ominus}{\Delta H^\ominus}$

Thermodynamic efficiency can never reach 100% due to heat losses to the environment and internal resistance of the cell.

Assessment tip

Fuel cells have high thermodynamic efficiency (up to 95% for hydrogen cells and up to 60% for methanol cells). This is an important advantage of fuel cells over other voltaic cells and internal combustion engines.

SAMPLE STUDENT ANSWER

Methanol fuel cells provide a portable energy source. The process can be represented by the overall equation:

$CH_3OH(aq) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

a) Deduce the half-cell equations occurring at each electrode during discharge. [2]

b) Outline the function of the proton exchange membane (PEM) in the fuel cell. [1]

c) Explain how the flow of ions allows for the operation of the fuel cell. [2]

This answer could have achieved 3/5 marks:

a) Anode (negative electrode):

$CH_3OH(aq) + H_2O(l) \rightarrow CO_2(aq) + 4H^+(aq) + 4e^-$

Cathode (positive electrode):

$O_2(aq) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

b) The PEM acts as a salt bridge by letting only $H^+(aq)$ ions move through the membrane.

c) $H^+(aq)$ ions form at one electrode and move through the PEM to the other, where they react with oxygen to form water.

▼ The first half-equation is not balanced; the correct half-equation is given in table C.6.1

▲ Correct answer

▲ Correct answer

▼ One mark is lost, as the direction of ion flow (from anode to cathode) is not stated; the rest is correct

Practice problems for Topic C.6

Problem 1

Geobacter bacteria are used in microbial fuel cells (MFCs) to oxidize aqueous ethanoate ions to carbon dioxide gas.

a) State the half-equations for the reactions at each electrode and the equation for the overall redox reaction.

b) Discuss the similarities and differences between MFCs and primary cells.

c) Identify **one** factor that affects the voltage of a cell and **a different factor** that limits the maximum current a cell can deliver.

Problem 2

A concentration cell is constructed using two copper electrodes, a salt bridge and two aqueous solutions containing 150 and 750 mmol dm^{-3} of copper(II) sulfate.

a) Deduce the functions of electrodes (anode or cathode) in each solution.

b) Using sections 1 and 2 of the data booklet, calculate the cell potential, in mV, at 298 K.

c) State **two** differences between a concentration cell and a standard voltaic cell.

C.7 NUCLEAR FUSION AND NUCLEAR FISSION (AHL)

You should know:

- ✔ the mass defect (Δm) is the difference between the mass of the nucleus and the sum of the masses of its individual nucleons;
- ✔ the nuclear binding energy (ΔE) is the energy required to separate a nucleus into nucleons;
- ✔ uranium nuclear fuel can be enriched in the required isotope by diffusion or centrifugation;
- ✔ radioactive decay is kinetically a first order process characterized by the decay constant (λ);
- ✔ ionizing radiation produces superoxide (O_2^-) and hydroxyl ($HO^\bullet$) radicals that can damage DNA and enzymes in living cells.

You should be able to:

- ✔ calculate the mass defect and binding energy of a nucleus;
- ✔ apply the Einstein equation $E = mc^2$ to determine the energy released in a nuclear reaction;
- ✔ discuss the different properties of UO_2 and UF_6 in terms of bonding and structure;
- ✔ solve problems on relative rates of effusion using Graham's law;
- ✔ solve problems involving radioactive half-life and the decay constant.

The nuclear **binding energy** (ΔE) is the energy required to separate a nucleus into protons and neutrons.

The definition of amu and the masses of elementary particles are given in sections 2 and 4, respectively, of the data booklet.

Binding energy is related to the *mass defect* (Δm) of the nucleus by the Einstein equation $E = mc^2$, as shown in example C.7.1. The energy released in a nuclear reaction is calculated in the same way, as shown in the sample student answer at the end of this subtopic.

Example C.7.1.

a) Calculate the mass defect, in kg, of a helium-4 nucleus using sections 2 and 4 of the data booklet.

b) Determine the binding energy per nucleon of a helium-4 nucleus, in kJ $nucleon^{-1}$, using your answer to part (a).

Solution

a) ^{4}He contains two protons and two neutrons.

$m(\mathrm{p}) = 1.672622 \times 10^{-27}$ kg and $m(\mathrm{n}) = 1.674927 \times 10^{-27}$ kg

$m(2\mathrm{p} + 2\mathrm{n}) = 2 \times 1.672622 \times 10^{-27}\ \mathrm{kg} + 2 \times 1.674927 \times 10^{-27}\ \mathrm{kg} \approx 6.70 \times 10^{-27}$ kg.

The mass of ^{4}He is 4 amu. 1 amu $= 1.66 \times 10^{-27}$ kg, so:

$m(^{4}\mathrm{He}) = 4 \times 1.66 \times 10^{-27}\ \mathrm{kg} = 6.64 \times 10^{-27}$ kg

$\Delta m = 6.70 \times 10^{-27}\ \mathrm{kg} - 6.64 \times 10^{-27}\ \mathrm{kg} \approx 6 \times 10^{-29}$ kg

b) According to the Einstein equation, $\Delta E = \Delta m \times c^2$, so:

$\Delta E = 6 \times 10^{-29}\ \mathrm{kg} \times (3.00 \times 10^{8}\ \mathrm{m\ s^{-1}})^2 = 5.4 \times 10^{-12}\ \mathrm{J} = 5.4 \times 10^{-9}$ kJ

There are four nucleons in ^{4}He, so the ΔE per nucleon is $5.4 \times 10^{-9}/4 \approx 1 \times 10^{-9}$ kJ nucleon^{-1}.

Naturally occurring uranium contains mostly ^{238}U with less than 1% of ^{235}U, which is insufficient for modern nuclear reactors. Therefore, nuclear fuel must be enriched with respect to ^{235}U. To do so, solid UO_2 (a common uranium mineral) is converted into gaseous UF_6 (table C.7.1), and the gas is pumped through a series of porous membranes or centrifuged. The kinetic theory predicts that all kinds of UF_6 molecules have the same average kinetic energy at any given temperature. Therefore, lighter molecules of $^{235}UF_6$ move faster than heavier molecules of $^{238}UF_6$, so the percentage of uranium-235 in the gas mixture gradually increases. According to *Graham's law*:

$$\frac{\upsilon(^{235}\mathrm{UF_6})}{\upsilon(^{238}\mathrm{UF_6})} = \sqrt{\frac{M(^{238}\mathrm{UF_6})}{M(^{235}\mathrm{UF_6})}} = \sqrt{\frac{352\ \mathrm{g\ mol^{-1}}}{349\ \mathrm{g\ mol^{-1}}}} \approx 1.004$$

▼ **Table C.7.1.** Structures and properties of uranium dioxide and hexafluoride

Compound	Molecular shape	Bonding type(s)	Crystal lattice	Melting and boiling points	Volatility
UO_2	—	ionic	giant ionic	high	low
UF_6	octahedral	covalent* and London dispersion†	simple molecular	low	high

*Intramolecular, strong; †intermolecular, weak.

Radioactive decay is kinetically a first order process that can be characterized by its *half-life* ($t_{1/2}$) and *decay constant* (λ). Both λ and $t_{1/2}$ are used in various forms of the *half-life equation*, illustrated in example C.7.2.

Example C.7.2.

Radioactive phosphorus, ^{33}P, has a half-life of 25.3 days.

a) Calculate the ^{33}P decay constant, λ, and state its unit.

b) Determine the fraction of the ^{33}P sample remaining after 70 days.

Solution

a) $\lambda = \dfrac{\ln 2}{t_{1/2}} \approx \dfrac{0.693}{25.3\ \mathrm{days}} \approx 0.0274\ \mathrm{day^{-1}}$

b) If the initial and final quantities of ^{33}P are N_0 and N, respectively, then:

$N/N_0 = e^{-\lambda t} = e^{-0.0274 \times 70} \approx 0.15$, or 15%

Note that the same answer could be obtained in one step using the half-life equation $N = N_0 \times (0.5)^{t/t_{1/2}}$:

$N/N_0 = (0.5)^{70/25.3} \approx 0.15$

Graham's law states that the rate of diffusion (υ) of a gas is inversely proportional to the square root of its molar mass.

Nuclear energy, derived from the small difference in mass between reactants and products, has advantages and disadvantages, outlined in table C.2.2.

The mathematical expression of Graham's law is given in section 1 of the data booklet.

Ionic and covalent structures are discussed in topics 4.1 and 4.3, respectively.

- The **decay constant** (λ) is related to half-life ($t_{1/2}$) as follows: $\lambda = \dfrac{\ln 2}{t_{1/2}}$.
- The **half-life equation**, $N = N_0 \times (0.5)^{t/t_{1/2}}$, allows calculation of the quantity N of a radionuclide left after time t from its original quantity N_0 and $t_{1/2}$. An alternative form of the half-life equation involves the decay constant: $N = N_0 \times e^{-\lambda t}$.

The kinetics of first order reactions is discussed in topic 16.1.

Various forms of the half-life equation are given in section 1 of the data booklet.

Radioactive decay problems involving integral numbers of half-lives and the half-life equation are discussed in topic C.3.

Nuclear decay and nuclear reactions produce ionizing radiation, which is dangerous to living organisms. Nuclear radiation has sufficient energy to break chemical bonds and produce highly reactive radicals, such as superoxide ($O_2^{\bullet-}$) and hydroxyl ($HO^{\bullet}$). These radicals initiate chain reactions that damage DNA and enzymes in living cells. High doses of ionizing radiation lead to *radiation poisoning*, which often causes nausea, headaches, vomiting and extensive damage to growing and regenerating tissues.

SAMPLE STUDENT ANSWER

a) Calculate the loss in mass, in kg, and the energy released, in J, when 0.00100 mol of ^{228}Ac decays, each nucleus losing an electron. Use section 2 of the data booklet and $E = mc^2$. [2]

$$^{228}\text{Ac} \rightarrow {}^{0}_{-1}\text{e} + {}^{228}\text{Th}$$

Particle	**^{228}Ac**	$^{0}_{-1}$e	**^{228}Th**
Mass / kg	3.78532×10^{-25}	9.10938×10^{-31}	3.78528×10^{-25}

b) Outline how nuclear ionizing radiation can damage DNA and enzymes in living cells. [1]

This answer could have achieved 1/3 marks:

a) Loss in mass: Δm (per atom) =

3.78532×10^{-25} kg − 9.109383×10^{-31} kg − 3.78528×10^{-25} kg

$\approx 3.1 \times 10^{-30}$ kg

▲ Correct loss in mass

Δm (per 0.00100 mol) =

3.1×10^{-30} kg × 0.00100 mol × 6.02×10^{23} mol^{-1}

$\approx 1.9 \times 10^{-9}$ kg

Energy released: $E = 1.9 \times 10^{-9}$ kg × $(3.00 \times 10^{8}$ m s$^{-1})^2$

$= 1.7 \times 10^{8}$ kJ $= 1.7 \times 10^{11}$ J

▼ The correct answer is 1.7×10^{8} J; this is a typical mistake—note that 1 J = 1 kg m^2 s^{-2}

b) Ionizing radiation produces superoxide and hydroxide, which alter the structure of DNA and enzymes, making them non-functional.

▼ A reference to "radicals" is required for the mark; also, "hydroxide" is an ion (HO^-); the radical name is "hydroxyl" ($HO^{\bullet}$)

Practice problems for Topic C.7

Problem 1

One of the fusion reactions occurring in the Sun is the fusion of deuterium ($^{2}_{1}$H) with tritium ($^{3}_{1}$H):

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}\text{n}$$

The masses of deuterium, tritium and helium-4 are 2.01410, 3.01605 and 4.00260 amu, respectively.

a) Using section 4 of the data booklet, calculate the mass defect, in kg, of this reaction per atom of helium-4 formed.

b) Using section 2 of the data booklet, calculate the energy, in J, released in this reaction per 1.00 g of helium-4 formed.

c) Determine the binding energy per nucleon, in kJ nucleon^{-1}, of a tritium nucleus.

d) Tritium is a radionuclide with a decay constant of 0.0563 year^{-1}. Calculate the half-life of tritium and the percentage of tritium that will decay in 45 years.

C.8 PHOTOVOLTAIC AND DYE-SENSITIZED SOLAR CELLS (AHL)

You should know:

- ✔ molecules with larger conjugated systems absorb light of longer wavelengths;
- ✔ the electrical conductivity of semiconductors increases with temperature while the conductivity of metals decreases;
- ✔ photovoltaic cells convert solar energy to electricity;
- ✔ dye-sensitized solar cells (DSSCs) imitate the way in which plants harness solar energy;

You should be able to:

- ✔ relate the degree of conjugation to the wavelength of light absorbed by a molecular structure;
- ✔ explain the operation of photovoltaic and dye-sensitized solar cells;
- ✔ explain how the use of dyes and nanoparticles increase the efficiency of DSSCs;
- ✔ discuss the advantages of DSSCs compared with silicon-based photovoltaic cells.

Solar energy can be converted to electricity using *solar* or *photovoltaic cells*. Traditional solar cells use silicon or other *semiconductors*, which are *doped* with small quantities of group 13 and 15 elements.

- A **semiconductor** is a material with electrical conductivity between that of a conductor and an insulator.
- **Doping** is the process of introducing specific impurities into a semiconductor to alter its electrical conductivity and other properties.
- An **electron hole**, or simply **"hole"** is a missing electron in a semiconductor crystal lattice.
- An **n-type semiconductor** has extra electrons, which carry negative charge.
- A **p-type semiconductor** has extra "holes", which in effect carry positive charge.

Example C.8.1.

Doped semiconductors have higher electrical conductivity than pure group 14 elements.

a) Describe how n-type and p-type doping of silicon is achieved and state the nature of electric charge carriers in each case.

b) Explain the operation of a silicon-based photovoltaic cell.

Solution

a) n-type: a small amount of a group 15 element, such as P, As or Sb, is added to silicon. This element has five valence electrons while silicon has only four. The extra electrons move freely around the doped semiconductor and carry the negative charge.

p-type: a small amount of a group 13 element, such as B, Al or Ga, is added to silicon. This element has three valence electrons while silicon has four. Each missing electron acts as a positively charged "hole" in the crystal structure of the doped semiconductor. These "holes" move around freely and in effect carry positive charge.

b) In the absence of light, excess electrons from n-zone migrate to p-zone and fill "holes", so the n-zone becomes positively charged while the p-zone becomes negatively charged. In light, each absorbed photon releases a valence electron, leaving a "hole" in its place. The negatively charged electron moves to the positively charged n-zone while the positively charged "hole" moves to the negatively charged p-zone due to electrostatic attraction. Such directed movement of electrons and "holes" produces electric current.

Dye-sensitized solar cells (DSSCs) use a coloured complex (dye) of a transition metal ion with an organic ligand. The ligand forms an extensive system of electron conjugation with the metal ion, which allows the dye to absorb visible light in the same way as chlorophyll does in green plants.

Electron conjugation is discussed in topic C.4.

The structure of chlorophyll is given in section 35 of the data booklet.

The efficiency of DSSCs is increased by the use of semiconducting nanoparticles of titanium dioxide, which have a very large surface area. Unlike in silicon-based solar cells, the absorption of photons and the charge separation in DSSCs occur independently (table C.8.1).

▼ **Table C.8.1.** Silicon-based and dye-sensitized solar cells (DSSCs)

	Silicon-based cells	**DSSCs**
light absorption	occur simultaneously within a semiconductor (doped silicon)	occurs in a metal-based organic dye
charge separation		involves the dye and an electrolyte (I^-/I_3^-)
charge carriers	electrons and holes	electrons and ions
advantages	wide range of working temperatures, well-known technology, long life span	cheap, easy to produce, flexible, absorb wide range of wavelengths, have high conductivity, work in low-light conditions
disadvantages	expensive, need protection from the elements, work at higher internal temperatures	low temperature stability due to use of liquid electrolyte, use transition metals and organic solvents, limited life span

SAMPLE STUDENT ANSWER

Dye-sensitized solar cells (DSSCs) convert solar energy into electrical energy.

a) Describe how a DSSC converts sunlight into electrical energy. [2]

b) Explain the role of the electrolyte solution containing iodide ions, I^-, and triiodide ions, I_3^-, in the DSSC. [2]

This answer could have achieved 3/4 marks:

a) The dye absorbs a photon and injects an electron into the TiO_2 semiconductor:

$\text{dye} + \text{photon} \rightarrow \text{dye}^+ + e^-$

TiO_2 transfers the electron to an external circuit, producing electric current.

▲ Correct answer; note that dye loses an electron and thus undergoes oxidation, while the electron is transferred by TiO_2 to the anode

b) The I^- ion returns an electron to the dye and forms a triiodide ion:

$\text{dye}^+ + I^- \rightarrow \text{dye} + I$

$2I + I^- \rightarrow I_3^-$

Then the triiodide ion receives electrons from external circuit and forms iodide ions:

$I_3^- + 2e^- \rightarrow 3I^-$

▼ Individual iodine atoms (I) do not exist in the electrolyte; it is also important to mention that the dye is reduced while iodide ions are oxidized to triiodide:

$\text{dye}^+ + e^- \rightarrow \text{dye}\ (\times 2)$

$3I^- \rightarrow I_3^- + 2e^-\ (\times 1)$

$2\text{dye}^+ + 3I^- \rightarrow 2\text{dye} + I_3^-$

▲ The last equation is correct

Practice problems for Topic C.8

Problem 1

The structures of 11-*cis*-retinal and β-carotene are given in section 35 of the data booklet. Suggest a possible wavelength of light absorbed by each molecule using section 3 of the data booklet.

Problem 2

A Grätzel dye-sensitized solar cell (DSSC) and a silicon-based photovoltaic cell both convert solar energy into electrical energy by producing a charge separation.

a) Contrast how absorption of photons and charge separation occur in each device.

b) Suggest **two** advantages of DSSCs over silicon-based photovoltaic cells.

D MEDICINAL CHEMISTRY

D.1 PHARMACEUTICAL PRODUCTS AND DRUG ACTION

You should know:

- ✔ bioavailability is the fraction of the administered dosage that reaches the systemic circulation;
- ✔ the therapeutic window is the range between the minimum effective dosage and the dosage likely to produce severe adverse effects;
- ✔ drug–receptor interactions are based on the structure of the drug and the site of activity;
- ✔ the therapeutic index is the ratio of LD_{50} to ED_{50} in animal studies or TD_{50} to ED_{50} in humans.

You should be able to:

- ✔ discuss common methods of drug administration;
- ✔ compare the effects of drug polarity and administration methods on bioavailability;
- ✔ define and explain the terms “dose”, “side effects”, “tolerance” and “addiction”;
- ✔ outline how the efficiency and safety of a drug can be determined experimentally.

Pharmaceutical drugs alter the body’s functions to prevent or cure diseases, alleviate the symptoms of health conditions, or assist in medical diagnostics. Drugs can be administered by different routes to ensure that they reach their target before they are metabolized (table D.1.1). The *bioavailability* is assumed to be 100% for intravenously injected drugs and less than 100% for drugs administered by other methods.

Method	Description	Drug type
oral	by mouth	polar, water-soluble
intravenous	injection into bloodstream	unstable or poorly absorbed
transdermal	skin patches or ointments	non-polar, lipid-soluble
rectal	suppositories or enemas	unstable in gastric acid
inhalation	breathed in	volatile or highly dispersed

▲ **Table D.1.1.** Common methods of drug administration

The physiological effects of a drug depend on its quantity (*dose*) and frequency of administration. Along with the *therapeutic effect*, drugs often have *side effects*. The *therapeutic window* of a drug is the range of *dosages* for treating the disease without causing unacceptable side effects.

- **Dose** is the mass or volume of a drug taken at one time.
- **Dosage** is the overall scheme of doses and times of administration.
- ED_{50}, LD_{50} and TD_{50} are the effective, lethal and toxic doses, respectively, for 50% of the population.
- The **therapeutic window** is the range of dosages in which the drug is effective and safe.
- The **therapeutic effect** is the intended action of a drug.
- The **therapeutic index** is the ratio of LD_{50} to ED_{50} in animal studies or TD_{50} to ED_{50} in humans.
- A **side effect** is an adverse or unintended action of a drug.

Bioavailability is the fraction of a drug that reaches the bloodstream.

Assessment tip

Do not confuse drug formulations with methods of their administration. For example, if you are asked to state the most common method of administration for over-the-counter drugs, the correct answer will be “oral”. The answers “pills”, “capsules” or “drops” will not be accepted, as they refer to drug formulations.

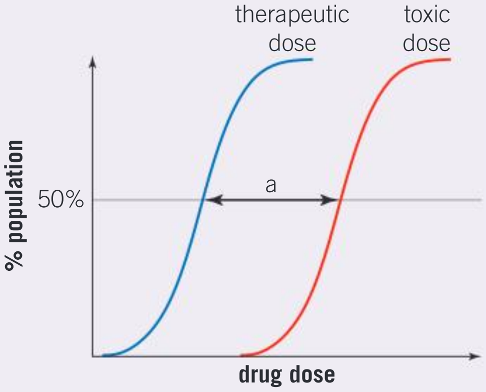
- A **placebo** is a biologically inert substance disguised as a drug.
- A **double-blind test** is a study in which neither patients nor doctors know who receives the drug and who receives a placebo.
- **Drug tolerance** is the decrease in drug efficacy after repeated administration.
- **Drug dependence** is an adaptive state of the body that causes withdrawal symptoms when the drug is discontinued.
- **Drug addiction** is the compulsive need to take the drug regardless of its adverse effects.
- **Withdrawal symptoms** are unpleasant physical and psychological effects caused by discontinued drug use.

Example D.1.1.

Dose–response curves are determined for a drug.

a) Outline the significance of range “a”.

b) Explain how the efficacy of a drug can be determined experimentally.



Solution

a) Range “a” is the therapeutic window. Within this range of doses, the drug can be used effectively and safely.

b) Volunteers are separated randomly into two similar groups of equal size. One group is given the drug, while the other receives a *placebo*. Neither the volunteers nor the researchers know who is given the drug and who receives a placebo, so this approach is known as a *double-blind test*. Any difference in therapeutic effects between the two groups is attributed to the drug action.

Tolerance, addiction and withdrawal symptoms are typical for opiates (topic D.3).

Repeated administration of a drug can lead to *tolerance* and requires progressively higher doses to achieve the desired effect. Narcotic drugs often cause *dependence* and *addiction*: the patient craves the drug and experiences *withdrawal symptoms* when use stops.

SAMPLE STUDENT ANSWER

New drugs undergo thorough clinical trials before they are approved.

a) Outline the difference between the therapeutic index in animal studies and the therapeutic index in humans. [1]

b) State the method of drug administration that gives the maximum bioavailability. [1]

This answer could have achieved 1/2 marks:

a) In animals $TI = LD_{50}/ED_{50}$ whereas in humans $TI = TD_{50}/ED_{50}$.

b) Injection.

▲ Correct answer

▼ The term “intravenous” is required for mark; “injection” can be subcutaneous (under the skin), intramuscular and so on

Practice problems for Topic D.1

Problem 1

The structure of the antiviral drug zanamivir is given in section 37 of the data booklet. This drug is poorly absorbed from the gastrointestinal tract and thus cannot be taken orally.

a) State the names of **two** different functional groups in the molecule of zanamivir.

b) Suggest, with a reason, whether zanamivir can be administered transdermally or by inhalation.

Problem 2

Effective dose (ED) is important for any drug.

a) Suggest why therapeutic index is based on ED_{50} rather than ED_{100}.

b) State **two** reasons why animal and human tests of drugs must be kept to a minimum.

Problem 3

Most pharmaceutical drugs are organic molecules.

a) State **two** common targets for drug molecules.

b) Outline how drug molecules interact with their targets.

D.2 ASPIRIN AND PENICILLIN

You should know:

- ✔ aspirin and other mild analgesics intercept the pain stimulus at the source;
- ✔ aspirin also acts as an anticoagulant, lowering the risk of heart attacks and strokes;
- ✔ penicillins contain a sterically strained beta-lactam ring in their molecules;
- ✔ penicillins prevent cross-linking of bacterial cell walls, making them permeable to water.

You should be able to:

- ✔ explain the synthesis, recrystallization and characterization of aspirin;
- ✔ describe the use of salicylic acid and its derivatives as mild analgesics;
- ✔ explain the role of the beta-lactam ring in the action of penicillins;
- ✔ discuss the effects of chemical modification of the side-chain in penicillins;
- ✔ discuss the consequences of the improper use of antibiotics.

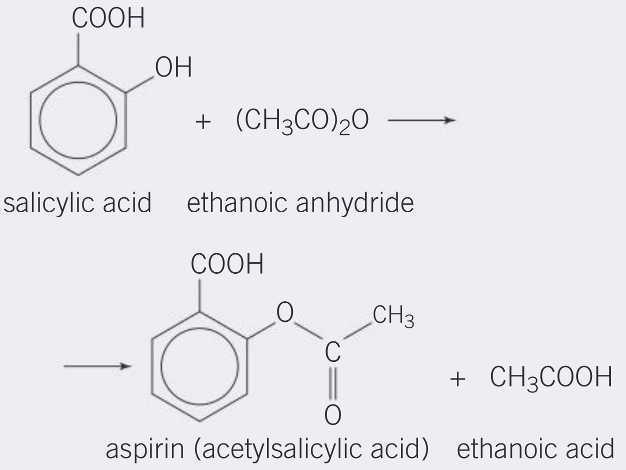
Aspirin

Aspirin is a mild *analgesic* that acts at the source of pain by inhibiting the production of prostaglandins. Low doses of aspirin also suppress blood clotting, preventing heart attacks and strokes. High doses of aspirin, especially in combination with alcohol (*synergism*), can cause stomach ulcers and bleeding.

- **Drug interaction** is the increase (**synergism**) or decrease (**antagonism**) of a drug activity when it is taken together with another substance.
- An **analgesic** is a painkiller.

Example D.2.1.

Salicycic acid is a mild analgesic. It can damage the stomach lining, so it is acylated (esterified) to produce aspirin.



Crude aspirin is isolated by filtration, recrystallized from water and dried to constant mass. The results of a typical synthesis are summarized in table D.2.1.

Compound	Molar mass / g mol^{-1}	Mass / g	Melting point / °C
salicylic acid	138.13	1.64	—
crude aspirin	180.17	1.91	116–124
recrystallized aspirin		1.72	132–135

▲ Table D.2.1. Preparation of aspirin

Literature melting point of aspirin: 136–137°C.

a) Determine the percentage yield of aspirin after recrystallization.

b) Justify the conclusion that recrystallization increased the purity of aspirin.

c) Outline how the IR spectra of salicylic acid and aspirin will differ in the region 1700–1750 cm^{-1}.

Solution

a) $m_{\text{theoretical}}(\text{aspirin}) = \dfrac{1.64\,\text{g} \times 180.17\,\text{g mol}^{-1}}{138.13\,\text{g mol}^{-1}} \approx 2.14\,\text{g}$

Yield $= (1.72\text{ g}/2.14\text{ g}) \times 100\% \approx 80.4\%$

b) The melting point of the recrystallized aspirin is closer to the literature value, and the recrystallized aspirin melts within a narrower temperature range.

c) Salicylic acid has one C=O bond, so its IR spectrum will have one strong absorption band between 1700 and 1750 cm^{-1}. Aspirin has two C=O bonds, so it will have either two strong absorption bands in that region, or one broad and even stronger band if the two individual bands overlap with each other.

Water-soluble aspirin is produced by the reaction of aspirin with sodium hydroxide:

$$CH_3C(O)OC_6H_4COOH(s) + NaOH(aq) \rightarrow CH_3C(O)OC_6H_4COONa(aq) + H_2O(l)$$

The bioavailability (topic D.1) of water-soluble aspirin is only slightly higher than that of aspirin, as it is converted back to aspirin by the reaction with stomach acid:

$$CH_3C(O)OC_6H_4COONa(aq) + HCl(aq) \rightarrow CH_3C(O)OC_6H_4COOH(s) + NaCl(aq)$$

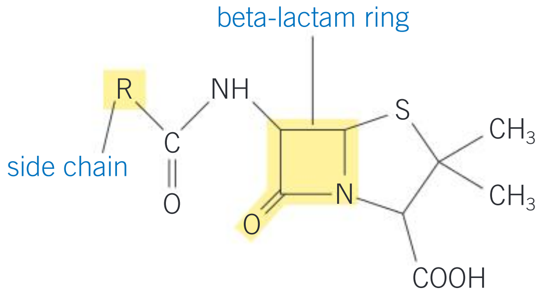
- **Antibiotics** (**antibacterials**) are drugs that kill or inhibit the growth of bacteria.
- **Resistant bacteria** are difficult to kill with antibiotics.
- **Ring strain** is the decreased stability of a cyclic molecule due to unusual bond angles.
- The **cell wall** is a structural layer outside the cell membrane in bacteria.

Assessment tip

Do not confuse *bacterial resistance* (reduced responsiveness of microorganisms to antibacterial drugs) with *tolerance* (reduced responsiveness of the patient's own body to drugs; see topic D.1) and *immunity* (the ability of the patient's body to fight infections and diseases).

Penicillins

Penicillins (figure D.2.1) are *antibiotics* produced by fungi. Penicillins contain a sterically strained β-lactam ring with bond angles of 90° instead of 109.5 and 120° for sp^3 and sp^2 hybrid atoms, respectively. This ring is responsible for the antibacterial action of penicillins, as explained in the example question below.



▲ **Figure D.2.1.** General structure of penicillins

Resistant bacteria produce the enzyme β-*lactamase* (also known as *penicillinase*), which opens the β-lactam ring and makes penicillins ineffective. When antibacterial treatment is terminated early, some bacteria survive, particularly the *resistant* ones. These pass their resistance to next generations. Overprescription of antibiotics and their use in agriculture (Topic D.6) also contribute to bacterial resistance.

The side chain in penicillins can be modified to make them less sensitive to β-lactamase and stomach acid. However, bacteria constantly mutate and eventually develop resistance to modified penicillins.

SAMPLE STUDENT ANSWER

Penicillin was one of the first antibiotics to be isolated and identified for its ability to treat bacterial infections.

a) Explain the importance of the beta-lactam ring in the antibiotic activity of penicillin. [3]

b) Identify **two** dangers of the overuse of antibiotics. [1]

This answer could have achieved 2/4 marks:

a) This ring has steric strain. In bacteria, it opens up and the resulting intermediate reacts with transpeptidase, which cross-links cell membranes. Without cross-links, weakened membranes let water in by osmosis, so bacteria burst and die.

b) Building up of resistant bacteria and making antibiotics less efficient.

▲ Correct statement about *ring strain*

▲ Correct statement about reactivity

▼ The enzyme transpeptidase cross-links *cell walls* in bacteria, not cell membranes

▼ Both statements refer to the same danger; the second danger is the destruction of beneficial bacteria

Practice problems for Topic D.2

Problem 1

A sample of aspirin was synthesized from 2.65 g of salicylic acid ($M_r = 138.13$) and 2.51 g of ethanoic anhydride ($M_r = 102.10$) with a practical yield of 72.5%.

a) Determine the limiting reactant.

b) Calculate, in grams, the theoretical and practical yields of aspirin.

c) State **three** methods that can be used to confirm the identity of aspirin.

Problem 2

Antibiotic-resistant bacterial infections can be treated using a mixture of penicillins with clavulanic acid (figure D.2.2).

▲ **Figure D.2.2.** Clavulanic acid

a) Outline what is meant by the term “ring strain”.

b) Label the carbon atom(s) in clavulanic acid that experience significant ring strain.

c) Suggest how clavulanic acid can protect penicillins from the action of β-lactamase.

D.3 OPIATES

You should know:

- ✔ strong analgesics, like morphine and codeine, block pain impulses by acting on opioid receptors in the brain and central nervous system;
- ✔ opiates are natural strong analgesics derived from the opium poppy;
- ✔ the medical and addictive effects of opiates depend on the brain’s opioid receptors;
- ✔ the ability of a drug to cross the blood–brain barrier depends on its solubility in lipids.

You should be able to:

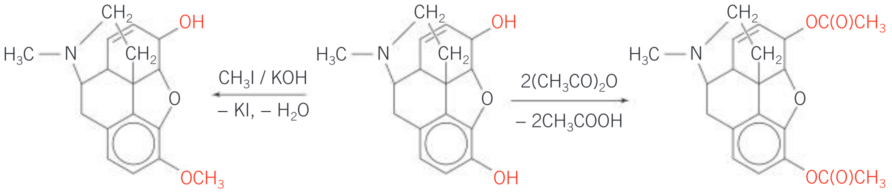
- ✔ compare the structures of morphine, codeine and diamorphine (heroin);
- ✔ explain the synthesis of codeine and diamorphine from morphine;
- ✔ describe and explain the action of strong analgesics;
- ✔ explain the greater potency of diamorphine compared with morphine;
- ✔ discuss the advantages and disadvantages of using opiates as analgesics.

Strong analgesics, such as *opiates*, prevent the transmission of pain impulses by binding to *opioid receptors* in the brain and central nervous system (CNS).

- **Opioid receptors** are proteins in the membranes of nerve cells that regulate the transmission of pain impulses.
- **Opiates** are strong analgesics derived from the opium poppy, and include morphine, codeine and diamorphine (heroin).

- The **blood–brain barrier** is a lipid-based membrane that separates the brain from the blood.

The molecule of morphine consists of several fused hydrocarbon rings with one tertiary amino, one ether and two hydroxyl groups (figure D.3.1). Codeine is synthesized from morphine by the methylation of one hydroxyl group, while diamorphine is formed by the acylation (esterification) of both hydroxyl groups.



codeine morphine diamorphine (heroin)

▲ **Figure D.3.1.** Synthesis of codeine and diamorphine

The action and potency of opiates depend on their ability to cross the lipid-based *blood–brain barrier* (BBB). This ability increases as the polarity of drug molecules decreases.

Assessment tip

Do not confuse *opiates* (morphine and its derivatives) with *opioids* (any substances that can act on opioid receptors in the brain and CNS). For example, methadone (figure D.3.2 on the next page) is an opioid but not an opiate.

Example D.3.1.

Morphine and diamorphine (heroin) are strong analgesics.

a) State **one** difference in structure between morphine and diamorphine.

b) Explain how the difference in part (a) affects the potency of these drugs.

Solution

a) Morphine has two hydroxyl groups while diamorphine has two ester (ethanoate) groups.

b) Ester groups in diamorphine are less polar than hydroxyl groups in morphine. Less polar diamorphine is more soluble in lipids, so it crosses the blood–brain barrier and reaches the opioid receptors in the brain more easily. This makes diamorphine more potent than morphine.

Opiates are very potent drugs that act quickly and can relieve even the most extreme pain. However, they have many disadvantages, including tolerance, dependence and addiction. Large doses of opiates cause euphoria and stimulate sociability, so these narcotic drugs often become substances of abuse. The addiction to opiates is difficult to overcome due to severe withdrawal symptoms, which include anxiety, perspiration, cramps, diarrhea, nausea and vomiting.

Tolerance, dependence, addiction and withdrawal symptoms are discussed in topic D.1.

SAMPLE STUDENT ANSWER

The strong analgesics morphine and codeine are opiates. The structures of morphine and codeine are given in section 37 of the data booklet.

a) Outline how codeine can be synthesized from morphine. [1]

b) Explain why opiates are addictive. [2]

This answer could have achieved 2/3 marks:

a) Codeine can be made by replacing a hydroxide group in morphine with methyl.

b) Because they change the way the brain works and give a feeling of pleasure that addicts look for. Withdrawing from opiates gives bad feelings, cold sweats and cramps.

▼ "hydroxide" is not accepted for "hydroxyl"; also, the OH group is replaced with a methoxy group (OCH_3), not methyl (CH_3)

▲ Three correct points (altered brain functions, craving for euphoria and withdrawal symptoms); marks could also be scored for stating that opiates work on opioid receptors in the brain/CNS, release dopamine and alter the structure of brain cells

Practice problems for Topic D.3

Problem 1

Diamorphine (heroin) can be synthesized from morphine.

a) State the reagent needed for this synthesis and the by-product of the reaction.

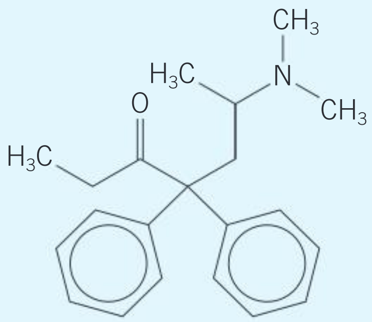
b) Compare and contrast the action of mild and strong analgesics.

Problem 2

Methadone (figure D.3.2) is a synthetic opioid.

a) State **two** similarities and **two** differences in the structures of methadone and diamorphine (heroin).

b) In contrast to diamorphine, methadone causes little or no euphoria, especially upon prolonged use. Suggest why methadone can be effective in the treatment of heroin addiction.



▲ **Figure D.3.2.** The structure of methadone

D.4 pH REGULATION OF THE STOMACH

You should know:

- ✔ antacids are weak inorganic bases that neutralize excess stomach acid;
- ✔ H_2-receptor blockers, such as ranitidine (Zantac), and proton pump inhibitors, such as omeprazole (Prilosec) and esomeprazole (Nexium), suppress the secretion of stomach acid;
- ✔ active metabolites are active forms of a drug that has been modified in the body.

You should be able to:

- ✔ construct and balance equations for the neutralization reactions between stomach acid and antacids;
- ✔ solve problems involving neutralization reactions and acid–base buffers;
- ✔ explain the action of H_2-receptor blockers and proton pump inhibitors.

Overproduction of hydrochloric acid in the stomach causes indigestion (dyspepsia), gastritis and peptic ulcers. This condition can be alleviated by neutralizing excess acid with antacids or prevented by the use of acid secretion inhibitors, such as ranitidine or omeprazole (table D.4.1).

	Antacids	**Acid secretion inhibitors**
Mechanism of action	neutralize excess acid	suppress acid secretion
Chemical nature	weak inorganic bases	organic molecules
Examples	MgO, $Al(OH)_3$, $NaHCO_3$	ranitidine, omeprazole
Advantages	low cost, immediate effect, optimal for occasional use	long duration of action, can be used prophylactically (for prevention)
Disadvantages	short duration of action, disturbed electrolyte balance	high cost, slow action, systemic side effects
Side effects	bloating, belching, kidney stones, diarrhea	headache, nausea, fatigue, dizziness, diarrhea

▲ **Table D.4.1.** Comparison of antacids and acid secretion inhibitors

Antacids are weak inorganic bases that react directly with gastric acid; for example:

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

$$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$$

- **Antacids** are weak inorganic bases that neutralize stomach acid.
- **H_2-receptor blockers** (**H_2 antagonists**) inhibit acid secretion by binding to H_2 (histamine) receptors.
- **Proton pump inhibitors** (**PPIs**) suppress the release of H^+(aq) ions into gastric juice.
- **Active metabolites** are produced in the body from a typically inactive administered drug.

Neutralization reactions are discussed in topic 8.2.

Assessment tip

Strong inorganic bases, such as NaOH, are never used as antacids because they can damage the gastrointestinal tract.

These neutralization reactions raise the pH of the stomach juice and provide quick relief from heartburn and other symptoms of indigestion.

The secretion of gastric acid can be controlled at the cellular level by two types of drugs, *H_2-receptor blockers* (the H is for histamine) such as ranitidine, and *proton pump inhibitors*, such as omeprazole and esomeprazole.

The structures of ranitidine and omeprazole are given in section 37 of the data booklet.

Example D.4.1.

Dyspepsia can be treated with ranitidine and omeprazole. Compare and contrast the action of these two drugs.

Solution

Similarities: Both drugs suppress the production of gastric acid, act on the parietal cells in the stomach lining and have long-lasting effects.

Differences: Ranitidine blocks H_2 receptors. This prevents histamine from binding to the same receptors and triggering the secretion of acid.

Omeprazole itself is inactive but produces *active metabolites* that inhibit the gastric proton pump (H^+/K^+ ATPase enzyme). This prevents the movement of protons (H^+ ions) through cell membranes into gastric juice.

Ranitidine binds to its target reversibly while the action of omeprazole is irreversible. Thus, omeprazole is more efficient and acts for longer than ranitidine.

Assessment tip

Remember that a conjugate acid must have one more proton than its conjugate base. For example, H_2CO_3 and CO_3^{2-} are *not* a conjugate acid–base pair, as they differ by two protons.

The pH of gastric juice and other biological fluids is regulated by acid–base buffers (topic 18.3). The primary biological buffer consists of aqueous carbon dioxide, $CO_2(aq)$, and hydrogencarbonate ions, $HCO_3^-(aq)$. Carbon dioxide forms unstable carbonic acid, $H_2CO_3(aq)$, that acts as the conjugate acid while hydrogencarbonate ions act as the conjugate base:

The pH of a buffer solution can be calculated using the *Henderson–Hasselbalch equation*:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

SAMPLE STUDENT ANSWER

Excess acid in the stomach can cause discomfort and more serious health issues.

a) Explain how ranitidine (Zantac) reduces stomach acid production. [2]

b) The pH is maintained in different fluids in the body by the use of buffers. Calculate the pH of a buffer solution of 0.0200 mol dm^{-3} carbonic acid, H_2CO_3, and 0.400 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$. The pK_a of carbonic acid is 6.35. [2]

This answer could have achieved 2/4 marks:

a) Ranitidine is an H_2-receptor antagonist. It lowers the production of hydrochloric acid in the gut.

b) $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[HCO_3]}{[H_2CO_3]}$

$\mathrm{pH} = 6.35 + \log\frac{0.400}{0.0200} \approx 7.65$

▲ “H_2-receptor antagonist” is a correct alternative answer

▼ A reference to parietal *cells* is required for the second mark

▲ Correct solution; note that $[HCO_3^-] \approx c(NaHCO_3)$, as $NaHCO_3$ dissociates completely into $Na^+(aq)$ and $HCO_3^-(aq)$

Practice problems for Topic D.4

Problem 1
Sodium hydrogencarbonate, $NaHCO_3$, is the active ingredient of many antacids.

a) Formulate the equation for the neutralization of stomach acid with $NaHCO_3$.

b) One tablet of a certain brand of antacid contains 800 mg of $NaHCO_3$. Calculate the amount, in mol, of gastric acid that can be neutralized with one tablet of this antacid.

c) Compare and contrast the use of antacids and omeprazole (Prilosec).

Problem 2
Calculate the pH of the buffer solution prepared by dissolving 0.400 g of solid sodium carbonate, $Na_2CO_3(s)$, in 50.0 cm^3 of 0.200 mol dm^{-3} sodium hydrogencarbonate solution, $NaHCO_3(aq)$. Assume that the volume does not change when the salt dissolves in the solution.

$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$

$pK_a = 10.35$

D.5 ANTIVIRAL MEDICATIONS

You should know:

- ✔ viruses lack cellular structure and thus are more difficult to target with drugs than bacteria;
- ✔ antivirals work by either altering genetic material or blocking enzymes within the host cell.

You should be able to:

- ✔ describe how viruses differ from bacteria;
- ✔ explain the different ways in which antiviral drugs work;
- ✔ discuss the difficulties associated with solving the AIDS problem.

In contrast to bacteria, *viruses* are not life forms and thus cannot be killed with drugs. Viruses are much smaller than bacteria, lack cellular structure, cannot feed, excrete or grow, and have no metabolism of their own. They use the biochemical machinery of host cells to multiply, which makes it difficult to target a virus without damaging healthy cells.

Antibiotics are completely ineffective against viral infections, such as colds and flu. Their use only increases bacterial resistance (topic D.2) and kills beneficial bacteria.

Antiviral drugs can work in many ways, including:

- preventing the virus from entering the host cell;
- altering the DNA of the host cell so that the virus cannot use it;
- inhibiting viral enzymes to slow down the replication and assembly of the virus;
- preventing the virus from leaving the host cell;
- stimulating the patient's immune system.

- **Viruses** are infectious agents that replicate only inside living cells.
- **Antiviral drugs** are medications used to treat viral infections.
- **Neuraminidases** are viral enzymes that help release viruses from host cells.

Example D.5.1.

Oseltamivir and zanamivir are antiviral drugs used to treat and prevent flu (influenza). Explain how these drugs work.

Solution
Both drugs inhibit the influenza virus's *neuraminidase* enzyme and thus stop the virus particles from leaving the host cell. This slows down the spread of the virus to other cells and helps the immune system to combat the infection.

Assessment tip

Do not confuse the health condition (AIDS) with the virus that causes this condition (HIV).

- **Human immunodeficiency virus (HIV)** is a retrovirus that targets the immune system.
- **Acquired immunodeficiency syndrome (AIDS)** is a health condition caused by HIV.
- **Retroviruses** are viruses that use *reverse transcriptases*.
- **Reverse transcriptase** is a viral enzyme that produces DNA from viral RNA.
- **T-cells** are a type of lymphocyte (white blood cells).

The *HIV/AIDS* pandemic is caused by a virus that targets the immune system. This condition is particularly difficult to treat because:

- the virus attacks *T-cells*, which are directly responsible for fighting infections;
- HIV has many subtypes and mutates quickly, so it is difficult to create a vaccine;
- the weakened immune system allows opportunistic infections and cancers to develop;
- *anti-retroviral* drugs are expensive and must be taken for life.

In addition to medical factors, the HIV/AIDS problem is exacerbated by sociocultural issues, such as lack of education, unprotected sex, illegal drug use and the stigma associated with HIV.

SAMPLE STUDENT ANSWER

The structures of oseltamivir (Tamiflu) and zanamivir (Relenza) are given in section 37 of the data booklet.

a) Compare and contrast the structures of oseltamivir and zanamivir, stating the names of functional groups. [2]

b) Suggest one ethical consideration faced by medical researchers when developing medications. [1]

This answer could have achieved 2/3 marks:

a) Both drugs contain ether groups.

Oseltamivir contains ester and amino groups.

b) Testing the drug on animals.

▲ Correct similarity; another common group is amido

▼ The difference is not explained clearly; the mark could be scored by stating "*only* oseltamivir" or naming the functional groups that are present only in zanamivir (carboxyl and hydroxyl)

▲ Correct answer; other possible answers are side effects of the drug, its environmental impact and potential for abuse

Practice problems for Topic D.5

Problem 1

Oseltamivir forms an active metabolite that contains a carboxyl group.

a) Deduce the name of the functional group in oseltamivir that changes into a carboxyl group in the body. Refer to section 37 of the data booklet.

b) Suggest why oseltamivir is administered to patients in its inactive form.

Problem 2

Many diseases are caused by viruses and bacteria.

a) State **two** similarities and **two** differences between viruses and bacteria.

b) One of the first antiviral drugs, rimantadine, was successfully used for treating influenza in the mid-1990s but had lost its efficacy by 2009. Suggest a possible reason for this fact.

c) Explain why poor education and the stigma associated with HIV contribute to the global HIV/AIDS pandemic.

D.6 ENVIRONMENTAL IMPACT OF SOME MEDICATIONS

You should know:

- ✔ nuclear waste is classified as high-level, intermediate-level or low-level waste by the strength of ionizing radiation and half-life;
- ✔ antibiotic resistance develops when microorganisms are exposed to antibacterials.

You should be able to:

- ✔ explain the dangers of medical nuclear waste, antibiotic waste and leftover solvents;
- ✔ discuss the basics of green (sustainable) chemistry;
- ✔ explain how green chemistry was used to develop the precursor for oseltamivir (Tamiflu).

Radioactive materials used in medical diagnostics and cancer treatment (discussed in topic D.8) produce *low-* and *intermediate-level nuclear waste* (table D.6.1). *High-level waste* is produced by nuclear reactors.

Type	Examples	Disposal
LLW	syringes, tools, tissue, gloves, protective clothing, solutions	short-term storage in shielded containers, then disposal as non-radioactive waste
ILW	Sources for radiotherapy, such as Co-60 and Cs-137	long-term storage in shielded containers or concrete chambers, then burial underground

▲ **Table D.6.1.** Medical nuclear waste

Medical nuclear waste raises the radiation levels in local ecosystems, which increases the risk of cell damage and mutations in living organisms (topics C.7 and D.8). Some radioisotopes may accumulate in living organisms and be biomagnified (topic B.6).

Antibiotic waste from hospitals and agriculture contributes to bacterial resistance (topic D.2) and reduces the diversity of microorganisms in the environment.

- **Low-level waste (LLW)** produces weak ionizing radiation for a short time.
- **Intermediate-level waste (ILW)** produces strong ionizing radiation for a short time.
- **High-level waste (HLW)** produces strong ionizing radiation for a long time.

Assessment tip

When discussing a particular type of nuclear waste, you should mention *both* the intensity of its radiation and the length of time it remains radioactive.

Example D.6.1.

Explain how the use of antibiotics in agriculture increases the proportion of resistant bacteria.

Solution

Antibiotics are given to healthy animals to prevent diseases and accelerate growth. Non-metabolized antibiotics are excreted into the environment or consumed by humans with meat and milk. Low concentrations of antibiotics kill less resistant bacteria, while more resistant bacteria survive and pass their resistance to next generations.

Many organic solvents used in the pharmaceutical industry are harmful to living organisms and the environment (table D.6.2). Chlorinated and non-chlorinated solvents must be stored and disposed of separately from each other.

Solvent type	Common hazards	Specific hazards
non-chlorinated	toxic, irritant, carcinogenic, form greenhouse gases	flammable
chlorinated		ozone-depleting, accumulate in ground water, low biodegradability, form toxic dioxins if burned

▲ **Table D.6.2.** Hazards of organic solvents

Ozone depletion, the greenhouse effect, biodegradability and formation of dioxins are discussed in topic 14.1.

- **Green chemistry** is an approach to chemistry that aims to reduce the risks to humans and the environment.
- **Supercritical fluid** is the state of a substance, typically at high pressure and temperature, where distinct liquid and gas phases do not exist.

Supercritical carbon dioxide is used in the production of taxol (topic D.7).

In *green chemistry*, the use of solvents and other hazardous substances must be minimized. For example, traditional solvents can be replaced with water or *supercritical* carbon dioxide. Other practices of green chemistry include the use of solvent-free or solid-state reactions, renewable materials, energy-saving techniques and efficient catalysis. Any waste and by-products formed in sustainable technological processes must be recycled or reused.

SAMPLE STUDENT ANSWER

Oseltamivir was commercially produced from its precursor, shikimic acid, which is a metabolite in microorganisms and plants. Outline how green chemistry was used to develop the precursor for oseltamivir in order to overcome a shortage of the drug during the flu season. [2]

This answer could have achieved 2/2 marks:

Shikimic acid was produced by biosynthesis using E. coli bacteria. The bacteria's metabolism was altered by genetic modifications, so it could convert glucose into shikimic acid. The acid was then extracted from the bacteria and purified.

▲ Correct and complete answer; alternative green techniques may involve naturally occurring cyclic esters of shikimic acid, which produce the correct stereoisomer of oseltamivir in fewer synthetic steps than shikimic acid itself

Practice problems for Topic D.6

Problem 1

The unstable isotope technetium-99m is used in medical diagnostics and is administered intravenously.

a) State **two** specific examples of medical waste generated by the use of technetium-99m.

b) State the type of medical waste from part (a) and outline its characteristics.

c) Outline **two** ethical implications of using nuclear treatments in medicine.

Problem 2

The pharmaceutical industry is one of the largest producers of waste solvents.

a) Compare and contrast the hazards of chlorinated and non-chlorinated solvents.

b) Suggest **one** green solution to the problem of organic solvent waste.

D.7 TAXOL—A CHIRAL AUXILIARY CASE STUDY (AHL)

You should know:

- ✔ taxol (paclitaxel) is an anticancer drug originally extracted from the bark of the Pacific yew but now produced semisynthetically;
- ✔ chiral auxiliaries allow synthesis of individual enantiomers of chiral molecules.

You should be able to:

- ✔ explain how taxol is obtained and used as a chemotherapeutic agent;
- ✔ describe the use of chiral auxiliaries in stereoselective synthesis;
- ✔ explain how a polarimeter is used to identify enantiomers.

The side effects of chemotherapy are similar to those of radiotherapy (topic D.8).

Taxol is a drug used in chemotherapy of several forms of cancer. When administered intravenously, taxol binds to certain proteins (tubulins) in cancerous cells and thus slows cell division. Like other anticancer drugs, taxol also damages healthy cells, which causes hair loss, nausea, fatigue and other side effects.

The *extraction* of taxol from the bark of the Pacific yew has brought this species to the brink of extinction. Now taxol is produced *semisynthetically* from 10-deacetylbaccatin, which is extracted sustainably from the needles of the European yew.

The molecule of taxol contains 11 chiral carbon atoms, all of which must have specific stereochemical configurations to maintain the drug's anticancer activity. The synthesis of specific enantiomers (stereoselective or *asymmetric synthesis*) is achieved by the use of *chiral auxiliaries*, as explained in figure D.7.1 and example D.7.1.

$$\text{S} \xrightarrow{+\text{A}^*} \text{S}—\text{A}^* \xrightarrow{\text{reagent}} \text{P}^*—\text{A}^* \xrightarrow{-\text{A}^*} \text{P}^*$$

substrate (non-chiral)	intermediate 1 (single enantiomer)	intermediate 2 (single diastereomer)	product (single enantiomer)

▲ **Figure D.7.1.** Stereoselective synthesis using a chiral auxiliary (A*)

The identity and purity of chiral compounds can be determined using a *polarimeter*. Optically active molecules rotate plane-polarized light by an angle that depends on their nature, concentration and temperature.

Example D.7.1.

Explain how a polarimeter can be used to distinguish between individual enantiomers and their racemic mixture.

Solution

A solution of the sample is placed inside the polarimeter, and a beam of plane-polarized light passed through the solution. Under identical conditions, two enantiomers of the same compound will rotate plane-polarized light by the same angle but in opposite directions. A racemic mixture will be optically inactive, as the effects of individual molecules will cancel out.

Assessment tip

You should never say that enantiomers "bend" or "reflect" plane-polarized light; the only acceptable term is "rotate".

SAMPLE STUDENT ANSWER

Taxol is produced using a chiral auxiliary. Describe how the chiral auxiliary functions to produce the desired product. [3]

This answer could have achieved 2/3 marks:

The chiral auxiliary bonds to taxol and blocks one side of its molecule.

The following reaction can no longer occur at that side, so it proceeds at the other side only and gives only one enantiomer.

After the reaction is over, the chiral auxiliary is removed and reused.

▼ The auxiliary is attached to a *precursor* of taxol, not to taxol itself

▲ The description of stereochemical induction is accepted; the mark could also be scored by stating that the existing chiral centre affects the configuration of new chiral centre(s)

▲ Correct point; note that the removal of the auxiliary gives the desired product (taxol)

- **Extraction** is a separation process in which a solute is partitioned (distributed, usually unequally) between two immiscible solvents (liquid–liquid extraction), or washed out of a solid by a solvent (solid–liquid extraction).
- **Semisynthetic compounds** are produced by chemical modification of naturally occurring materials (precursors).

Both taxol and its precursor, 10-deacetylbaccatin, can be extracted with supercritical carbon dioxide (topic D.6).

Extraction techniques are discussed in topic D.9.

The structure of taxol is given in section 37 of the data booklet.

Chirality and stereoisomerism are discussed in topic 20.3.

- **Asymmetric synthesis** produces a single enantiomer or diastereomer.
- A **chiral auxiliary** is an optically active substance that temporarily attaches to the substrate and forces the next reaction step to proceed asymmetrically.

- A **polarimeter** is an instrument that measures the angle of rotation of plane-polarized light.
- A **racemic mixture**, or **racemate**, contains equal amounts of two enantiomers of the same compound and thus is optically inactive (has a rotation angle of 0°).

Practice problems for Topic D.7

Problem 1
Taxol is an anticancer drug. Discuss **two** ethical implications of the production and use of taxol.

Problem 2
Omeprazole and esomeprazole reduce the secretion of stomach acid. Omeprazole is a racemic mixture, whereas esomeprazole is a single enantiomer of omeprazole. Outline how esomeprazole can be synthesized from a non-chiral precursor. Details of chemicals and reaction conditions are not required.

Problem 3
A mixture of enantiomers of the same compound was analysed using a polarimeter. Under certain conditions, the angle of optical rotation was found to be 6.5°. Suggest **one** conclusion about the mixture composition that can be drawn from this result.

D.8 NUCLEAR MEDICINE (AHL)

You should know:

- ✔ alpha (α), beta (β^-), gamma (γ), proton (p), neutron (n) and positron (β^+) emissions are used in medical treatment and diagnostics;
- ✔ radiotherapy can be internal or external;
- ✔ targeted alpha therapy (TAT) and boron neutron-capture therapy (BNCT) are two important techniques used in cancer treatment;
- ✔ magnetic resonance imaging (MRI) is an application of NMR technology.

You should be able to:

- ✔ discuss common side effects of radiotherapy;
- ✔ explain why technetium-99m is the most common radioisotope used in medical diagnostics;
- ✔ explain why lutetium-177 and yttrium-90 are commonly used in radiotherapy;
- ✔ balance nuclear equations involving alpha and beta particles;
- ✔ calculate the percentage of a radioactive material decayed or left after a certain period of time.

- **Ionizing radiation** consists of high-energy particles that can damage living cells.
- A **radionuclide** is an isotope that decays spontaneously and emits ionizing radiation.
- **Radiotherapy** is the treatment of diseases, such as cancer, with ionizing radiation.
- **Radiodiagnostics** is the imaging of internal organs or body parts using ionizing radiation.

Ionizing radiation is widely used in medicine (table D.8.1). Small quantities of *radionuclides* can be administered to the patient intravenously for producing images of internal organs or treating dispersed cancers. Large quantities of radionuclides are used as external radiation sources for treating localized cancers.

Name	Particle	Symbol	Source	Medical use
alpha	helium-4 nucleus	α, $^{4}_{2}He$	^{223}Ra, ^{225}Ac	internal *radiotherapy* of dispersed (spread) cancers
beta	electron	β^-, $^{0}_{-1}e^-$	^{90}Y, ^{177}Lu	
gamma	high-energy photon	γ, $^{0}_{0}\gamma$	^{60}Co	external radiotherapy
			^{99m}Tc	*radiodiagnostics*

▲ **Table D.8.1.** Common types of ionizing radiation

Dispersed or metastatic cancers can be treated with *targeted alpha therapy* (*TAT*), in which an α-emitter (^{223}Ra or ^{225}Ac) is delivered directly to cancer cells by a carrier drug or protein (a *radiopharmaceutical*). Alpha particles have strong ionizing power but low penetration, so they destroy cancer cells without causing much damage to surrounding tissues.

Smaller tumours are treated with β-emitters, such as ^{90}Y and ^{177}Lu, which are delivered to cancer cells by carrier drugs or injected into arteries that supply blood to affected areas. Beta-particles (electrons) have lower ionizing power than alpha particles, so they are less damaging to healthy cells. In addition, ^{177}Lu produces just enough gamma radiation for cancer imaging.

Assessment tip

The three key points of TAT are the use of carrier drugs and the high ionizing power and short range of α-radiation.

The treatment of cancer with ^{90}Y and ^{177}Lu is similar to TAT except that β-radiation has lower ionizing power.

Boron neutron-capture therapy (*BNCT*) involves the use of boron-containing drugs that are selectively absorbed by cancer cells. The affected area is then irradiated with neutrons, which are absorbed by boron atoms and make them radioactive. These atoms emit α-particles that destroy cancer cells.

Assessment tip

Remember that BNCT is a combination of external and internal radiotherapy: an external source of neutrons creates radionuclides from non-radioactive boron atoms inside the patient's body.

Ionizing radiation damages both cancer and healthy cells. Tissues that are growing or regenerating, such as hair follicles, reproductive organs, skin and bone marrow, are particularly sensitive to this damage. As a result, the side effects of radiotherapy include hair loss, sterility, skin irritation, nausea, fatigue and secondary cancers.

Technetium-99m (^{99m}Tc) is the most widely used radioisotope in medical diagnostics. It has a short half-life (see below) and emits soft gamma radiation, which causes relatively little harm to the patient and can be detected by traditional X-ray equipment, making it a good *radiotracer*. Technetium readily forms compounds with biologically active molecules, so it can be easily delivered to specific organs or tissues.

Assessment tip

Do not confuse ^{99m}Tc (metastable nuclide) with ^{99}Tc (ground-state nuclide). These two radionuclides have different half-lives and undergo different types of decay.

Nuclear equations are balanced in terms of atomic mass and charge (table D.8.2). The sums of superscript indices (mass numbers, *A*) and subscript indices (atomic numbers, *Z*) of all elements and particles must be the same on both sides of the equation.

Mass number, atomic number and nuclear symbol notation, $^{A}_{Z}$X, are discussed in topic 2.1.

Decay type	Change in mass number (*A*)	Change in atomic number (*Z*)	Example
alpha (α)	−4	−2	$^{223}_{88}\text{Ra} \rightarrow {}^{219}_{86}\text{Rn} + {}^{4}_{2}\text{He}$
beta (β⁻)	0	+1	$^{177}_{71}\text{Lu} \rightarrow {}^{177}_{72}\text{Hf} + {}^{0}_{-1}\text{e}^{-}$
gamma (γ)	0	0	$^{99m}_{43}\text{Tc} \rightarrow {}^{99}_{43}\text{Tc} + {}^{0}_{0}\gamma$

▲ **Table D.8.2.** Nuclear decay equations

Assessment tip

Double-check that all atomic numbers match the element names. The two most common errors are the use of the same *Z* for different elements or the same element symbol for different *Z*.

The *half-life* ($t_{1/2}$) of a radionuclide is the time taken for its quantity to decrease by half. For example, if ^{99m}Tc has a half-life of 6 h, its amount will drop to 50% of its initial value after the first 6 h, to 25% after another 6 h (total 12 h), to 12.5% after another 6 h (total 18 h), and so on.

- **Half-life** ($t_{1/2}$) is the time taken for a radionuclide to decay by half.

The half-life equation, $N_t = N_0 \times (0.5)^{t/t_{1/2}}$, relates the quantity N_t of a radionuclide left after the period of time *t* using its original quantity N_0 and half-life $t_{1/2}$.

Example D.8.1.

The half-life of lutetium-177 is 6.65 days.

a) Calculate the percentage of the original sample remaining after 15 days.

b) Calculate the time, in days, taken for 90% of the original sample to decay.

Solution

a) Using the *half-life equation*, $N_t = 100\% \times (0.5)^{15/6.65} \approx 21\%$

b) If 90% of the sample decays, 10% will remain.

$$10\% = 100\% \times (0.5)^{t/6.65}$$

$$0.1 = (0.5)^{t/6.65}$$

$$\log(0.1) = \log(0.5) \times \frac{t}{6.65}$$

$$-1 \approx \frac{t}{6.65} \times (-0.301)$$

$$t \approx 22.1 \text{ days.}$$

Assessment tip

You do not need to use the decay constant (λ) unless it is mentioned in the question. All decay problems can be solved using the half-life equation, which is given in section 1 of the data booklet. The decay constant is discussed in topic C.7.

NMR spectroscopy is discussed in topics 11.3, 21.1 and D.9.

Magnetic resonance imaging (*MRI*) uses the same principle as NMR spectroscopy. The patient is placed inside a powerful magnet and scanned with radio waves. The protons (^1H nuclei) in the patient's body absorb and emit radio waves, which are detected and processed to create 3D images of the patient's internal organs. In contrast to ionizing radiation, radio waves have low frequency, so MRI poses no risk to the patient.

SAMPLE STUDENT ANSWER

Technetium-99m is the most widely used medical radioisotope. It is made onsite in medical facilities from isotopes of molybdenum.

a) Deduce equations for the following nuclear reactions:

i) Molybdenum-98 absorbs a neutron. [1]

ii) The isotope produced in (a)(i) decays into technetium-99m. [1]

b) Molybdenum-99 has a half-life of 66 hours, while technetium-99m has a half-life of 6 hours. Outline why technetium-99m is made on-site. [1]

c) Outline two reasons, other than its half-life, why technetium-99m is so useful in medical diagnosis. [2]

This answer could have achieved 2/5 marks:

a) (i) $^{98}_{42}Mo + ^{1}_{0}n \rightarrow ^{99}_{42}Mo$

(ii) $^{99}_{42}Mo \rightarrow ^{99m}_{42}Tc + ^{0}_{-1}e^-$

b) Because Tc-99m has very short half-life.

c) Because it produces gamma rays and does not harm the patient. It also decays quickly, so has no long-term effect.

▲ Correct equation for neutron absorption

▼ The atomic number of technetium is 43, not 42

▼ A reference to delivery time is needed for mark (e.g., "if it's made off-site, most of it would decay in transit")

▲ The reference to γ-radiation is accepted

▼ Any ionizing radiation is a health risk; "decays quickly" is related to half-life, which is not allowed in the question; the second reason is the diverse chemistry of technetium, which allows it to be used in various radiopharmaceuticals

Practice problems for Topic D.8

Problem 1

Yttrium-90 and actinium-225 are used in radiotherapy.

a) Formulate the nuclear equations for the decay of these radionuclides.

b) Compare and contrast the use of yttrium-90 and actinium-225 in the treatment of leukaemia and other dispersed cancers.

c) Discuss **two** ethical implications of using nuclear treatments in medicine.

Problem 2

Iodine-131 is used in the radioimaging and treatment of thyroid cancer. It decays into an unstable nuclide, $^{131}_{54}Xe^*$, which immediately emits a gamma quantum and forms a stable isotope.

a) Formulate the nuclear equations for the decay of iodine-131 and $^{131}_{54}Xe^*$.

b) Suggest which of the two radiation types produced in (a) is used for the radioimaging and which one for the treatment of thyroid cancer.

c) The half-life of iodine-131 is 8.02 days. Calculate the time, in days, taken for 99% of the original sample of this radionuclide to decay.

D.9 DRUG DETECTION AND ANALYSIS (AHL)

You should know:

- ✔ organic structures such as medical drugs can be identified by IR, ^{1}H NMR and mass spectroscopy;
- ✔ steroids can be detected by gas chromatography and mass spectrometry;
- ✔ the presence of alcohol in breath can be detected by a breathalyser that uses a fuel cell or acidified potassium dichromate;
- ✔ organic compounds can be separated or isolated by extraction and fractional distillation.

You should be able to:

- ✔ predict IR and ^{1}H NMR spectra of organic molecules;
- ✔ interpret IR, ^{1}H NMR and MS data to determine an organic structure ;
- ✔ describe the process of detection of steroids;
- ✔ explain how alcohol is detected in breath;
- ✔ explain the relationship between organic structure and solubility;
- ✔ describe the processes of extraction and purification of organic compounds.

Drugs are organic molecules that can be identified and characterized by various analytical techniques (table D.9.1). Common spectroscopic data are given in sections 26 (IR), 27 (^{1}H NMR) and 28 (MS) of the data booklet.

Analytical techniques are also discussed in topics 11.3 and 21.1 (IR, NMR, MS and X-ray) and D.2 (IR). Organic functional groups are discussed in topic 10.1.

Technique	Data type	Example
IR spectroscopy	chemical bonds	strong absorption of C=O at 1700–1750 cm^{-1}
^{1}H NMR spectroscopy	hydrogen environments	singlet of $CH_3C(O)$ in aspirin at 2.0–2.5 ppm
mass spectroscopy (MS)	mass to charge (*m/z*) ratio	$M^{+\cdot}$ of testosterone at *m/z* 288
X-ray crystallography	bond lengths and angles	3D structure of a protein
melting point (m.p.)	identity and purity of a substance	m.p. of morphine is 255°C

▲ **Table D.9.1.** Common analytical techniques

Example D.9.1.

The structure of the opioid drug methadone is given in figure D.3.2.

a) Suggest **one** absorption, other than those of C–H bonds, that would be present in the IR spectrum of methadone. Refer to section 26 of the data booklet.

b) State the number of different hydrogen environments in the molecule of methadone (ignore the benzene rings).

c) Predict the chemical shifts and splitting patterns for the ^{1}H NMR signals produced by the $CH_3CH_2C(O)$ fragment. Refer to section 27 of the data booklet.

d) State the m/z values for the molecular ion and any **two** other signals in the mass spectrum of methadone. Refer to section 27 of the data booklet.

e) Suggest **two** techniques, other than IR, NMR and MS, that can be used to verify the identity of methadone.

Solution

a) A strong absorption of C=O in ketones at 1700–1750 cm^{-1}.

b) Six, including three different CH_3, two different CH_2 and one CH. Note that the two CH_3 groups at nitrogen will produce one signal, as all six protons in these groups are in the same chemical environment.

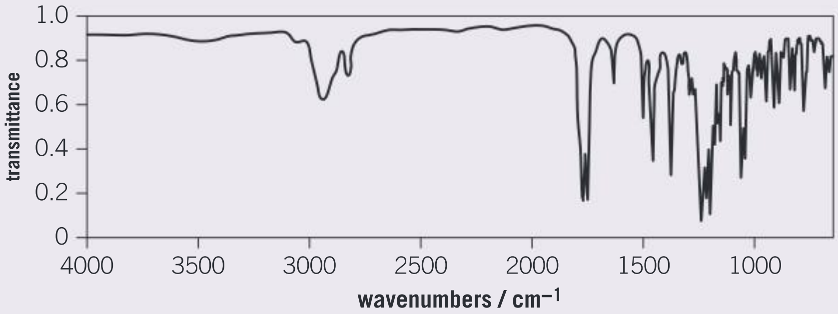
c) A triplet of CH_3 at 0.9–1.0 ppm and a quartet of CH_2 at 2.2–2.7 ppm. Note that the CH_2 group is adjacent to C=O, so its chemical shift corresponds to that of R–C(O)–**C**$\mathbf{H_2}$– in section 27.

d) Molecular ion ($M^{+\cdot}$): $m/z = 309$. Other possible signals will have m/z of 15 (CH_3^+), 29 ($CH_3CH_2^+$), 77 ($C_6H_5^+$), their remainder fragments and so on.

e) Chromatography (GC, HPLC, TLC or paper) and X-ray crystallography. The identity of methadone can also be confirmed by measuring its melting point.

Example D.9.2.

The IR spectrum of an unknown opiate is shown below.



Deduce, giving two reasons, whether the unknown opiate is morphine, diamorphine or codeine. Refer to figure D.3.1 and section 26 of the data booklet.

Solution

Both morphine and codeine contain hydroxyl groups (figure D.3.1), so their IR spectra must show a strong and broad absorption of the O–H bond at 3200–3600 cm^{-1}. Diamorphine has no hydroxyl groups but contains two ester groups, so its IR spectrum must show two strong absorptions (or one, if they overlap) of C=O bonds at 1700–1750 cm^{-1}. The IR spectrum of the unknown opiate shows two absorptions at about 1750 cm^{-1} and none at 3200–3600 cm^{-1}, so it is diamorphine.

Anabolic steroids have medical uses but are also abused in sports. Steroids can be detected by a combination of gas chromatography and mass spectrometry (GC/MS). A sample of blood or urine is vaporized and injected into a column containing a liquid or solid stationary phase, which is constantly flushed with a gaseous mobile phase. The individual compounds in the sample have different volatilities and affinities for the stationary phase, so they move through the column at different speeds and separate into individual bands. The MS of each band is checked for specific m/z peaks, such as molecular ions of banned substances, or compared with computer databases of known drugs.

The presence of alcohol (ethanol) in breath can be detected by a *breathalyser*. In all common types of breathalyser, gaseous ethanol is oxidized to ethanoic acid:

$$C_2H_5OH(g) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$$

The reduction half-equation depends on the breathalyser type (table D.9.2). The intensity of the colour change or electric current is proportional to the concentration of alcohol.

The reactions of alcohols with potassium dichromate are discussed in topic 10.2.

Breathalyser type	Reduction process	Observation
redox (acidified potassium dichromate)	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	colour change from orange to green
fuel cell	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	electric current

▲ Table D.9.2. Alcohol detection using a breathalyser

Liquid–liquid extraction involves the partition of substances between two immiscible solvents, one of which is usually water. Polar substances stay in the aqueous layer because they form intermolecular hydrogen bonds with water. Non-polar substances stay in the organic layer because of London (dispersion) forces. A typical extraction is described in the sample student answer on page 229.

Mixtures of volatile liquids can be separated by *fractional distillation*. The liquid with the lowest boiling point will evaporate from the boiling mixture faster than other compounds. The vapour of this liquid will move up the distillation column while other liquids will condense and fall back into the flask. At the top of the column, the vapour will pass through a water-cooled condenser, liquefy and flow into the receiver flask, producing the first fraction. Other components of the mixture will form subsequent fractions, which can be collected in different flasks.

Raoult's law states that the partial pressure (p) of a volatile substance A is proportional to the mole fraction (x) of A in the mixture and the vapour pressure (p_0) of pure A at the same temperature:

$$p(\mathrm{A}) = x(\mathrm{A}) \cdot p_0(\mathrm{A})$$

As the mixture moves up the distillation column, it becomes enriched with the most volatile component A. An increase in x(A) raises p(A) and lowers the partial pressures of all other components, so the vapour at the top of the column contains almost pure A.

Assessment tip

Fractional distillation differs from simple distillation in that it uses a long fractionating column. In *simple distillation*, the vapours of all volatile compounds pass directly into the condenser and thus are not separated into fractions.

SAMPLE STUDENT ANSWER

Some mild analgesics contain a solid mixture of acidic aspirin and a non-acidic organic chemical of similar polarity to aspirin. Discuss how acid-base properties and the process of solvent extraction can be used to separate aspirin from the mixture. [3]

This answer could have achieved 2/3 marks:

1) Shake the mixture with water and hexane in a separating funnel.

2) Acidic aspirin will dissolve in water whereas the impurity will dissolve in hexane.

3) Run off the water layer into one flask and the hexane layer into another flask.

4) Evaporate the water and collect the aspirin

▲ Good choice of two immiscible solvents

▼ Both molecules have similar polarity, so the separation will not occur as described; first a base, such as NaOH, must be used to convert aspirin into a water-soluble salt

▲ Correct point about separating the layers

▼ To obtain the aspirin, the salt must be converted back to aspirin by adding an acid, such as HCl

▲ Correct point about evaporating the solvent (the third mark is missed as the acid–base properties are not used)

Practice problems for Topic D.9

Problem 1

The reaction of salicylic acid with ethanoic anhydride is given in example D.2.1.

a) Suggest **two** absorbances, other than the absorbances due to the ring structure and C–H bonds, that would be present in the infrared (IR) spectrum of salicylic acid.

b) Compare and contrast the ^{1}H NMR spectra of salicylic acid and aspirin. Ignore the signals produced by the benzene rings in these compounds.

c) State **two** techniques, other than IR and ^{1}H NMR spectroscopy, which could be used to distinguish salicylic acid and aspirin.

Problem 2

The use of performance-enhancing drugs presents a challenge in the world of competitive sports.

a) Outline how anabolic steroids can be detected by gas chromatography and mass spectrometry.

b) Two common anabolic steroids are testosterone ($C_{18}H_{28}O_2$) and nandrolone ($C_{18}H_{26}O_2$). The mass spectrum of a biological sample contains five strong signals with m/z = 79, 91, 110, 215 and 274. Determine, with a reason, which of these steroids is likely to be present in the sample.

INTERNAL ASSESSMENT

The IB Diploma Programme Chemistry Internal Assessment (IA) is an individual investigation. You choose a research question, design and carry out an investigation to answer that question and then write a report on it, with your teacher's supervision and guidance.

The IA is worth 20% of your final grade. Like all IAs for diploma subjects, it is graded against a set of criteria. If you fully understand these criteria, you can maximize your success.

Mark criteria

Assessment tip

Know the mark criteria.

Your investigation is marked using the six criteria below, out of a total of 24 marks. The criteria and the maximum number of marks available for each criterion are shown in table 1.

Criterion	Maximum mark
Personal engagement	2
Exploration	6
Analysis	6
Evaluation	6
Communication	4
Total	**24**

▲ **Table 1.** Mark criteria for the IA

Every May and November the IB publishes a subject report for Chemistry. In that report there is advice from the Chief Moderator on how best to maximize your success. Reading the most recent subject report before you embark on your investigation is very helpful.

Choice of research question

The most important factor to consider when choosing the research question is that you can collect data to answer the question in the lab or by the use of a database. An interesting research question that yields little data, or insufficiently useful data, will score very poorly. The ideal plan of action will see you research and try out several ideas before you embark on a full investigation.

A good research question will be in the category of determining how an independent variable that is continuously measurable (such as concentration, mole fraction or temperature) affects a dependent variable that can be measured precisely using techniques commonly available in a school laboratory (such as temperature, gas volume or change in mass, or titration data for acid–base or redox reactions).

▼ **Bad question**
Investigating enthalpies of combustion

▲ **Good question**
How does isomerism affect the enthalpy of combustion values of pentanol and its isomers?

Avoid simple brand analyses of food, cleaning or pharmaceutical products, as any trends that are identified are often business decisions rather than the outcome of solely scientific principles. If you want to study commercial products, you have to link some component of the product composition (which you can experimentally determine or read from the packaging) to a chemical or physical property of the product.

If we look at the mark criteria in table 2 one by one, we can see that the most marks are available for exploration, data analysis and evaluation – that is why it is so important that the investigation yields good data. Start by looking at topics you have already studied in class so that you understand the theoretical background to your investigation. Generally, you will collect primary data yourself, however this isn't the only possibility. Measurements may be carried out with basic equipment or with high-tech data-logger probes.

If you do not identify a suitable independent variable and only focus on comparative assays (comparing one product to another), or if you do not generate usable data because you try to develop your own measurement technique and it turns out to be ineffective (such as using digital photography to quantify colour), your investigation will be limited and less successful.

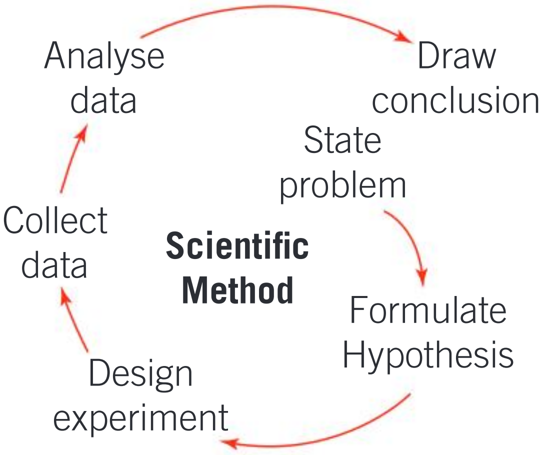
It is a good idea to apply a known technique to an interesting real-world situation. Use your time to carry out trials at plenty of values of the independent variable (at least five), including repeated measurements, rather than confining yourself to one or two trials.

Assessment tip

Research and try out your ideas to make sure you can generate sufficient useful data before you embark on a full investigation.

If you use secondary data (or data from models and simulations) instead of collecting primary data in the lab, you will need more than one source of data so that the variance between sources can be evaluated. In that case, error analysis and evaluation will be more successful.

Once a research question has been chosen it is important that your report addresses each of the criteria. You should apply the scientific method to ensure that you are able to answer your research question.



Personal engagement

This criterion assesses your engagement with the exploration and how you have made it your own. Personal engagement can be demonstrated by evidence of your personal interests or, perhaps more importantly, independent thinking, creativity, or initiative in the design, implementation or presentation of your investigation. This criterion consists of two parts: personal significance and personal input.

Personal significance

Your research question should be one you want to answer. Avoid an undemanding research question with an outcome that is obvious before any data collection, such as determining how the mass of alcohol combusted affects the heat energy evolved, or how the time a current is passed during electrolysis affects the mass of an electrode. However, if you could change the question to be more demanding, and to be one that you are genuinely interested in, you will do well.

Personal input

The second part of the criterion is about personal input and initiative; these will be demonstrated by the contents of your report. Don't just copy a method from a book or the internet without adapting it for your investigation. Ensure that the method works, and if it does not, modify it and explain how and why you modified it in your report.

Assessment tip

Communicate your interest in your investigation.

Pose a question to which you do not already know the answer.

Do not use a known method without making any modifications to it. In addition to this, explain why you are using the method you have chosen.

Exploration

This criterion is about establishing a scientific context, stating a clear and focused research question and using appropriate concepts and techniques in your method. It also assesses your awareness of safety, environmental and ethical considerations.

Make sure your research question is focused and precisely expressed. For example: "To what extent is simple distillation a suitable process for purifying ethanol mixtures?" is not a good question, as we do not know the criteria for "suitable". The criteria could be, for example, cost, safety, energy demand or degree of separation.

After stating the research question you need to include suitable background information, which should focus on the specifics of your chosen research question and methodology. Describe the context for your question and existing knowledge. Include balanced chemical equations for the key reactions associated with the investigation.

The background information is followed by a statement of the variables and how they will be controlled. The format in table 2 may be helpful for clarifying your thinking and ensuring you have mentioned everything.

Independent variable	*state the type and range*	
Dependent variable	*what will be measured (be precise)*	
Controlled variable	**Reason for controlling variable**	**Control method**

▲ **Table 2.** Planning around variables

You should plan in advance how many measurements you will need to take for a valid conclusion, and your method must permit sufficient repeats to ensure that each measurement is valid. Choose apparatus that will enable you to collect reliable data, for example by using graduated pipettes and measuring cylinders to measure volume rather than beakers.

Include a section for the apparatus and materials, and be specific.

▼ **Poor description of apparatus**
measuring cylinders

▲ **Good description of apparatus**
3 × 25.0 cm^3 ± 0.5 cm^3 measuring cylinders

Make sure that your method is written in sufficient detail for any reader to repeat the investigation and estimate the associated uncertainties. It is a good idea to describe in a paragraph the process of developing your methodology. This narrative will help explain the amount of data you are collecting and give insight into your decision-making, which is part of the evidence for the "personal engagement" criterion.

After the method section, you should add in a short section about the safety, ethical and environmental issues relevant to your methodology. This might be quite basic, such as noting the need for gloves and safety glasses, but could also include safe and environmentally appropriate disposal of reagents.

Assessment tip

Make sure you include:

- ✔ the research question
- ✔ background information
- ✔ variables
- ✔ apparatus
- ✔ method
- ✔ safety considerations.

Collect sufficient data over a meaningful range, with adequate repeats, and use the most precise apparatus you have access to.

Analysis

The analysis criterion is about providing evidence that you have selected, recorded, processed and interpreted the data in ways that are relevant to the research question and can support the conclusion you reach.

You need to record enough data about the independent and dependent variables to enable meaningful processing and interpretation. You also have to record qualitative observations. If you use photos, make sure that that these are supporting and not replacing written qualitative data. Also record the wider data that can provide necessary context for the evaluation of the procedure, such as measurements of controlled variables. For example, in a study of reaction rates, take the temperature of your reaction mixture, as opposed to room temperature; in an electrolysis investigation, measure the actual current rather than simply assuming that current is directly proportional to the voltage setting on a power pack, and measure the voltage too.

Remember, you need to include the raw data. If you only report processed data, such as added volume of a titrant, or averages from repeated measurements, you will limit your achievement.

Processing does not have to be complicated. You can simply average the data on the dependent variable and then plot it against the independent variable in a graph to see the nature of the relationship. Other good data-processing approaches are quantitative determinations based on titrations and calorimetry calculations. You should show a sample calculation, but you do not need to include the calculations for all your data.

For graphical analysis, remember that bar charts are of limited analytical use and are only used if you have discontinuous variables. If you are measuring rates of reaction, you need to use the tangent to the curve of the concentration–time graph at the start to determine the initial rate rather than just establishing the average rate.

Once you have collected the data, include the associated uncertainty in a table. You need to interpret and evaluate the uncertainty in the data and the size of any discrepancy between your results and those in the literature (if they exist).This gives an indication of how accurate your data is.

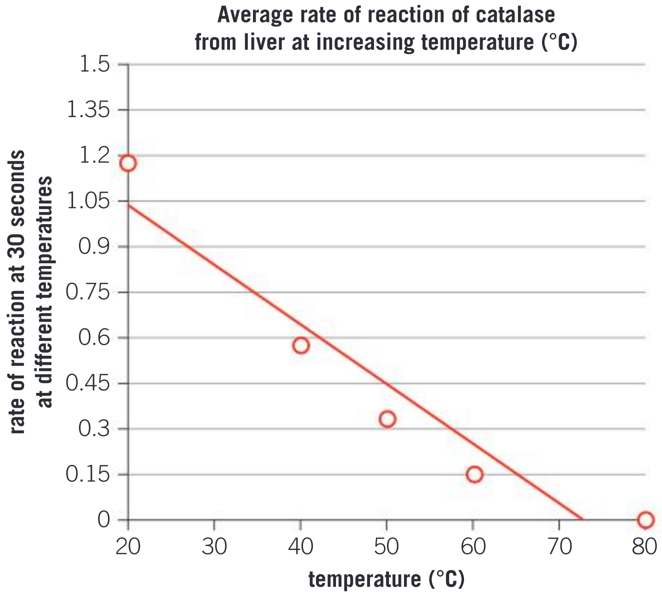
If you are familiar with statistical analysis, you can consider the impact of measurement uncertainty on your results using the following techniques:

- propagate the errors through numerical calculations (described in topic 11.1)
- calculate the standard deviation (if you have a sufficiently large data set)
- draw a line of best fit on your graph
- consider including error bars and/or the maximum or minimum slopes that can be drawn with the data you have, based on the range of values at each data point (topic 11.2).

When you interpret the data, you need to consider whether there are any outliers. Completing several trials will make it easier for you to decide which results are inconsistent. If you can, it would be good to compare the data from different data sources (secondary data examples) to evaluate reproducibility. If you are using data from a database, you need to show that you have done some research into the uncertainties associated with these data and applied it.

In all of this section you need to keep an eye on both significant figures and decimal places (topics 1.2 and 11.1) – they need to be consistent.

Look at the example of the graph below, and its successes and drawbacks. What else might you consider to improve the graph?



Assessment tip

Present the raw data as well as processed data.

Include qualitative and quantitative data.

Show uncertainties with raw data and propagate those uncertainties in your calculations.

Make sure that significant figures and decimal places are consistent.

Evaluation

This criterion assesses the evidence provided in your report of your evaluation of the investigation and your results with regard to the research question and the accepted scientific context.

Evaluation is a demanding reflective criterion. Drawing a conclusion that is consistent with the data is the most straightforward, but correctly describing or justifying your conclusion through relevant comparisons to the accepted scientific context is more difficult. But you can do this by comparing your experimentally determined quantities to available literature values and/or checking whether any trends and relationships that you identify are in line with accepted theory, possibly by referring to background information. You can also use the techniques learnt in topic 11.1 to calculate the percentage error of your result.

The next part of the criterion asks you to identify limitations and suggest improvements. You should address systematic and random errors in detail within your specific investigation. Include a discussion of the likely effect of systematic errors; for example, for an exothermic reaction, heat loss to the surroundings will lead to a calculated enthalpy change smaller than the true value.

▲ **Good aspects**
- Graph has a title
- Axes have labels
- Data points are clearly marked
- Scale of graph is appropriate

▼ **Bad aspects**
- Units missing on the *y*-axis
- Line of best fit is straight, but the data indicates that a curve would be a better fit

Do not be tempted to suggest things that are unnecessary, such as more repeats if you have sufficient results that agree. Remember to review the content of topic 11 when you are completing this section of your report.

Lastly, if you can see a good extension to your investigation, include it here.

You may find it useful to present the evaluation of your experiment in the form of a table, as shown in table 3:

Error or difficulty
There was a time lag between the addition of potassium iodate and the colour change of the tin(II) solution. Although some solutions produced immediate colour change, at some concentrations such as 0.5 mol dm^{-3} HCl, it often took two minutes before the solution would show any colour change. This made it difficult to predict exactly when the end point of the titration occurred.
Influence on result (increase or decrease in the value)
As it was difficult to identify the exact end-point of the titration, excess potassium iodate was often added. This resulted in a larger volume of potassium iodate and therefore an increase in the mass of tin(II) calculated.
Possible modification to reduce impact
Another method could have included recording the time it takes for the reaction to completely change colour after iodate is added. However, this would not be effective for all trials as some underwent immediate colour change.

▲ **Table 3.** Part of an evaluation

Assessment tip

Make sure you have a basis to your conclusion which you then compare with a literature value or a scientific theory.

Identify whether errors are random or systematic.

Suggested improvements should address the errors identified.

Communication

The communication criterion assesses whether your investigation is presented and reported in a way that supports effective communication of the focus, process and outcomes.

In general this will be the easiest criterion for you to do well in. Ensure that your report is written clearly, has an appropriate structure and coherently presents the information. Include sufficient detail in the description of the methodology, and at least one worked example of a calculation (if need be) so that the examiner can understand how you processed your data. It is important to include citations and references for anything that has come from another source.

Your report should be concise: you must stay within the 12-page limit, so do not include too much general background information, but focus on the research question. Do not waste space by including unnecessary pictures of chemicals and equipment: for example, a photograph of a normal titration set-up. Do not include an appendix, as the examiner does not have to read it.

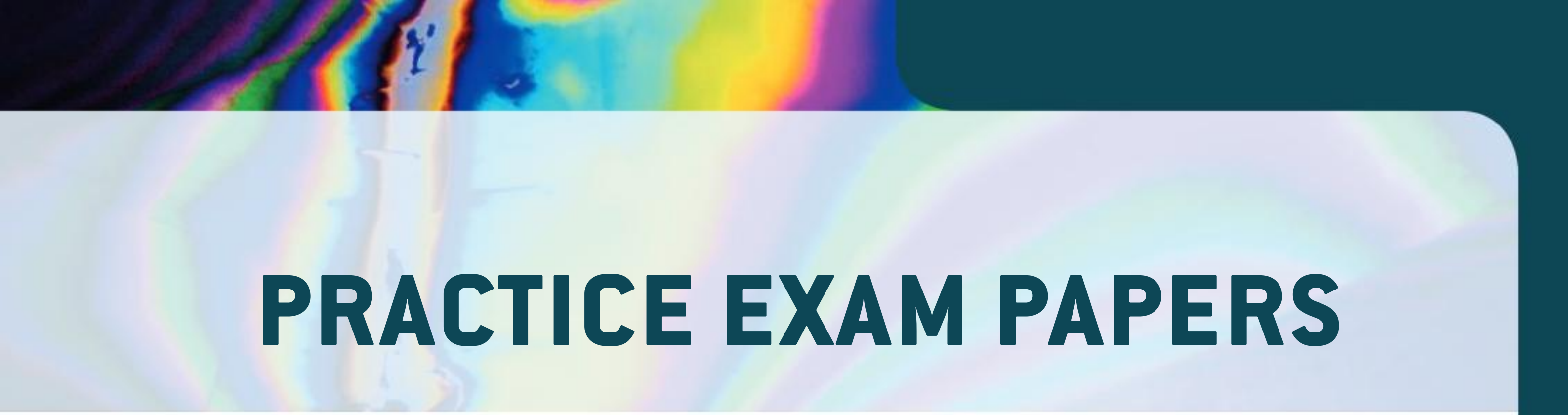
Check that you have labelled graph axes, included units in data tables and used the appropriate number of decimal places and significant figures.

Assessment tip

Stick to the 12-page limit and have a clear structure.

Make sure that your terminology is correct and consistent.

Label axes on graphs, and include units on graphs and tables.



PRACTICE EXAM PAPERS

At this point, you will have re-familiarized yourself with the content from the topics and options of the IB Chemistry syllabus. Additionally, you will have picked up some key techniques and skills to refine your exam approach. It is now time to put these skills to the test; in this section you will find practice examination papers, **1**, **2** and **3**, with the same structure as the external assessment you will complete at the end of the DP course. Answers to these papers are available at **www.oxfordsecondary.com/ib-prepared-support**

Paper 1

SL: 45 minutes

HL: 1 hour

Instructions to candidates

- For each question, choose the answer you consider to be the best and indicate your choice on the answer sheet (provided at **www.oxfordsecondary.com/ib-prepared-support**).
- A clean copy of the **periodic table** is required for this paper. No other reference materials can be used during the examination.
- The maximum mark for the SL examination paper is **[30 marks]**.
- The maximum mark for the HL examination paper is **[40 marks]**.

SL candidates: answer questions 1–30 ***only***.

HL candidates: answer questions 1–20 and 31–50.

1. Which change of state is endothermic?

A. $Cu(l) \rightarrow Cu(s)$
B. $H_2O(g) \rightarrow H_2O(l)$
C. $CO_2(g) \rightarrow CO_2(s)$
D. $NH_3(l) \rightarrow NH_3(g)$

2. In which mixture is hydrochloric acid the limiting reactant?

A. 0.10 mol HCl + 0.10 mol NaOH
B. 0.20 mol HCl + 0.10 mol NaOH
C. 0.10 mol HCl + 0.10 mol $Ca(OH)_2$
D. 0.20 mol HCl + 0.10 mol $Ca(OH)_2$

3. In which set do all the species contain more neutrons than electrons?

A. ^{11}C, ^{19}F, ^{23}Na
B. ^{12}C, $^{19}F^-$, $^{23}Na^+$
C. $^{13}C^{4+}$, ^{19}F, ^{23}Na
D. $^{14}C^{4-}$, $^{19}F^-$, $^{23}Na^+$

4. Which trends are correct across period 2 (from Li to F)?

I. Atomic radius decreases
II. Melting point decreases
III. First ionization energy increases

A. I and II only
B. I and III only
C. II and III only
D. I, II and III

5. Which oxide, when added to water, produces the solution with the lowest pH?

A. Al_2O_3
B. Na_2O
C. P_4O_{10}
D. MgO

6. Which compound has the shortest C–N bond?

A. CH_3CN
B. CH_3NH_2
C. $(CH_3)_2NH$
D. $(CH_3)_3N$

7. Which statements are correct for metals?

I. They conduct electricity because they have free moving electrons.
II. They consist of a close-packed lattice of cations with delocalized electrons.
III. They are malleable because the layers of ions can slide over each other.

A. I and II only
B. I and III only
C. II and III only
D. I, II and III

8. When 15.0 cm^3 of a 2.00 mol dm^{-3} NaOH(aq) solution is mixed with 15.0 cm^3 of a 2.00 mol dm^{-3} HCl(aq) solution at a certain temperature, the temperature rises by ΔT degrees. Which expression gives the enthalpy of neutralization in kJ mol^{-1}? (Assume that the density of the mixture is 1.00 g cm^{-3} and its specific heat capacity is 4.18 kJ kg^{-1} K^{-1}.)

A. $-\dfrac{15.0 \times 4.18 \times \Delta T}{30.0 \times 2.00}$

B. $-\dfrac{15.0 \times 4.18 \times \Delta T}{15.0 \times 2.00}$

C. $-\dfrac{30.0 \times 4.18 \times \Delta T}{30.0 \times 2.00}$

D. $-\dfrac{30.0 \times 4.18 \times \Delta T}{15.0 \times 2.00}$

9. Which equation represents the enthalpy of the H–Cl bond in hydrogen chloride?

A. $H^+(aq) + Cl^-(aq) \rightarrow HCl(aq)$
B. $H(g) + Cl(g) \rightarrow HCl(g)$
C. $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
D. $HCl(g) \rightarrow 0.5H_2(g) + 0.5Cl_2(g)$

10. Chloride ions, $Cl^-(aq)$, catalyse the corrosion of aluminium metal in sea water.
$2Al(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s) + 3H_2(g)$
Why do chloride ions affect the reaction?

A. Decrease the activation energy
B. Increase the activation energy
C. Decrease the enthalpy change
D. Increase the enthalpy change

11. Which methods can be used to monitor the progress of the reaction in the previous question?

I. Change in volume of gas evolved
II. Change in mass of aluminium metal
III. Change in colour of the reaction mixture

A. I and II only
B. I and III only
C. II and III only
D. I, II and III

12. The equilibrium constant for the reaction $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ is K.
What is the equilibrium constant for the reaction $CO_2(g) \rightleftharpoons CO(g) + 0.5O_2(g)$?

A. K
B. $0.5K$
C. $\sqrt{K}$
D. $0.5\sqrt{K}$

13. Which 1.0 mol dm^{-3} solution has the highest pH?

A. Ammonium nitrate
B. Nitric acid
C. Potassium nitrate
D. Ammonia

14. Which of the following gases causes acid deposition?

A. O_3
B. NO
C. CO
D. CO_2

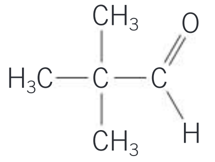
15. What is the oxidation half-equation in the reaction below?
$Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$

A. $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$
B. $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$
C. $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
D. $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

16. Which statement is correct for a voltaic but **not** for an electrolytic cell?

A. Anode is the negative electrode.
B. Reduction occurs at the cathode.
C. The overall redox reaction in the cell is non-spontaneous.
D. Electrons flow through the external circuit.

17. What is the IUPAC name of the compound below?



A. 2,2-dimethylpropanal
B. 2,2,2-trimethylethanal
C. 2,2-dimethylpropan-1-one
D. 2,2-dimethyl-1-oxopropane

18. Which conditions are used to convert ethanol to ethanoic acid?

A. Excess ethanol and distillation
B. Excess ethanol and reflux
C. Excess oxidizing agent and distillation
D. Excess oxidizing agent and reflux

19. A student used a coffee-cup calorimeter to determine the standard enthalpy of neutralization. Which type of error is likely to occur and how will it affect the quality of the measurements?

A. Random error and low precision
B. Systematic error and low accuracy
C. Random error and low accuracy
D. Systematic error and low precision

20. Which information about a molecule is provided by its ^1H NMR spectrum?

A. Number of hydrogen atoms
B. Number of C–H bonds
C. Number of hydrogen environments
D. Vibration frequency of C–H bonds

Questions 21–30 are for SL candidates ***only****.*

HL candidates: proceed to question 31.

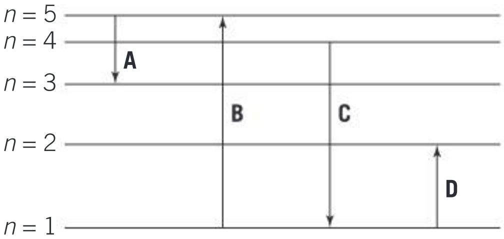
21. Why do real gases do not obey the ideal gas law at high pressures?

A. Gas molecules occupy a certain volume.
B. The gas volume increases because of cohesive forces.
C. At high pressures gases have higher temperatures than at lower pressures.
D. Increased pressure increases the frequency of collisions between gas molecules.

22. 20.0 cm^3 of a 5.00 mol dm^{-3} aqueous potassium hydroxide, KOH(aq), was added to a volumetric flask, and the volume was made up to 0.500 dm^3 with water. What is the concentration, in mol dm^{-3}, of potassium hydroxide in the final solution?

A. 0.0500 mol dm^{-3}
B. 0.200 mol dm^{-3}
C. 0.500 mol dm^{-3}
D. 2.00 mol dm^{-3}

23. Which electron transition emits radiation of the shortest wavelength?



24. Which compound contains both ionic and covalent bonds?

A. H_2O
B. NH_4Cl
C. HCOOH
D. CaO

25. Which substance has a giant covalent structure?

	Melting point / °C	Solubility in water	Electrical conductivity in the molten state
A.	−39	low	good
B.	17	high	poor
C.	734	high	good
D.	1687	low	poor

26. The enthalpy changes for two reactions are given below.

$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H^{\ominus} = x$ kJ
$NO_2(g) \rightarrow NO(g) + 0.5O_2(g) \quad \Delta H^{\ominus} = y$ kJ

What is the enthalpy change for the following reaction?

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

A. $x - 2y$
B. $x + 2y$
C. $y - 2x$
D. $2y - x$

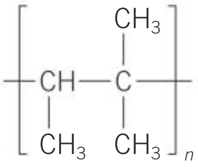
27. Which element has the same oxidation state in both species?

A. N in N_2H_4 and NO_2
B. H in CaH_2 and $Ca(OH)_2$
C. N in N_2O_5 and NO_3^-
D. O in H_2O_2 and NaOH

28. Which pair of compounds are structural isomers?

A. $CH_3CH_2CH_2Br$ and $BrCH_2CH_2CH_3$
B. $CH_3CH_2CH_2OH$ and $CH_3CH_2OCH_2CH_3$
C. $(CH_3)_2CHNH_2$ and $CH_3CH(NH_2)CH_3$
D. $(CH_3)_2C{=}O$ and CH_3CH_2CHO

29. Which monomer was used to form the polymer with the following repeating unit?



A. $CH_3CH{=}CHCH_2CH_3$
B. $CH_3CH{=}C(CH_3)_2$
C. $CH_2{=}CHCH(CH_3)_2$
D. $CH_3CH_2CH(CH_3)_2$

30. What is the index of hydrogen deficiency (IHD) of perfluoroethene, C_2F_4?

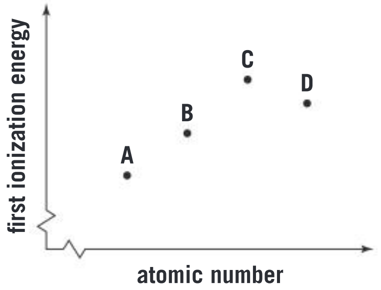
A. 1
B. 2
C. 3
D. 4

The following questions are for HL candidates ***only****.*

31. The complete combustion of 0.25 dm^3 of a gaseous hydrocarbon produces 0.75 dm^3 of carbon dioxide gas and 1.00 dm^3 of water vapour. What is the molecular formula of the hydrocarbon? (All volumes are measured at the same temperature and pressure.)

A. C_3H_4
B. C_3H_8
C. C_4H_6
D. C_6H_8

32. The diagram shows the first ionization energies of four consecutive elements in a period. Which element is in Group 15?



33. $[Ni(CN)_6]^{4-}$ is orange, while $[Ni(NH_3)_6]^{2+}$ is blue. Which statement is correct?

A. $[Ni(NH_3)_6]^{2+}$ absorbs blue light.
B. The different colours are due to the different oxidation states of nickel in these complexes.
C. The different colours are due to the different charges on the complexes.
D. The different ligands cause different splitting in the 3d orbitals.

34. Which of the following series shows **increasing** hydrogen bonding with water?

A. Ethane < ethanal < ethanol < ethanoic acid
B. Ethane < ethanol < ethanal < ethanoic acid
C. Ethanal < ethane < ethanoic acid < ethanol
D. Ethanoic acid < ethanol < ethanal < ethane

35. How many sigma (σ) and pi (π) bonds are present in the molecule of 3-oxobutanenitrile, $CH_3C(O)CH_2CN$?

A. 10 σ and 3 π
B. 3 σ and 10 π
C. 8 σ and 5 π
D. 5 σ and 8 π

36. Which of the following is correct?

	Atom	Number of electron domains	Molecular geometry	Hybridization
A.	C in C_2H_4	3	trigonal planar	sp^2
B.	C in CO_2	4	linear	sp
C.	N in NH_4^+	4	octahedral	sp^3
D.	N in NH_3	3	trigonal pyramidal	sp^2

37. Which equation represents the lattice enthalpy of calcium oxide?

A. $CaO(s) \rightarrow Ca(g) + O(g)$
B. $CaO(s) \rightarrow Ca(s) + 0.5O_2(g)$
C. $2CaO(s) \rightarrow 2Ca(s) + O_2(g)$
D. $CaO(s) \rightarrow Ca^{2+}(g) + O^{2-}(g)$

38. The combustion of ethanol is an exothermic process:

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

What is correct for this reaction?

	ΔH°	ΔS°	Spontaneous?
A.	< 0	< 0	yes
B.	< 0	> 0	yes
C.	> 0	< 0	no
D.	> 0	> 0	no

39. The reaction $2X(g) + Y(g) \rightarrow 2Z(g)$ is first order in each of the reactants. By which factor will the rate of this reaction decrease when the concentrations of X and Y are both decreased by a factor of 4?

A. 4
B. 8
C. 16
D. 64

40. Which statements are correct for an Arrhenius plot of ln *k* against $1/T$?

I. The activation energy, E_a, can be found from the gradient.
II. The rate constant, *k*, can be found from the intercept on the *x*-axis.
III. The frequency factor, *A*, can be found from the intercept on the *y*-axis.

A. I and II only
B. I and III only
C. II and III only
D. I, II and III

41. Which variable affects the equilibrium constant, K_c?

A. Catalyst
B. Temperature
C. Concentration of reactants
D. Concentration of products

42. Which statement is correct?

A. Lewis acids are proton donors
B. Lewis acids are nucleophiles
C. Nucleophiles are Lewis bases
D. A species cannot act as both a Lewis base and a Brønsted–Lowry base

43. Which combination of acid and base is most likely to have a pH of 5.5 at the equivalence point in a titration?

A. Hydrochloric acid and potassium hydroxide
B. Hydrochloric acid and ammonia
C. Ethanoic acid and potassium hydroxide
D. Ethanoic acid and ammonia

44. What are the signs of $E^{\ominus}_{\text{cell}}$ and $\Delta G^{\ominus}$ for a non-spontaneous redox reaction occurring in an electrolytic cell?

A. $E^{\ominus}_{\text{cell}} > 0, \Delta G^{\ominus} > 0$
B. $E^{\ominus}_{\text{cell}} > 0, \Delta G^{\ominus} < 0$
C. $E^{\ominus}_{\text{cell}} < 0, \Delta G^{\ominus} > 0$
D. $E^{\ominus}_{\text{cell}} < 0, \Delta G^{\ominus} < 0$

45. What are the major products of the electrolysis of a concentrated aqueous calcium bromide, $CaBr_2(aq)$?

A. Calcium and bromine
B. Hydrogen and bromine
C. Calcium and oxygen
D. Hydrogen and oxygen

46. What describes the reaction of a primary halogenoalkane with a dilute aqueous sodium hydroxide?

	Reaction type	Bond fission in halogenoalkane
A.	addition	homolytic
B.	addition	heterolytic
C.	substitution	homolytic
D.	substitution	heterolytic

47. In which pair can both compounds be reduced by lithium aluminium hydride, $LiAlH_4$?

A. Ethanoic acid and ethanol
B. Propanal and propanone
C. Propan-1-ol and propane
D. Ethanal and ethene

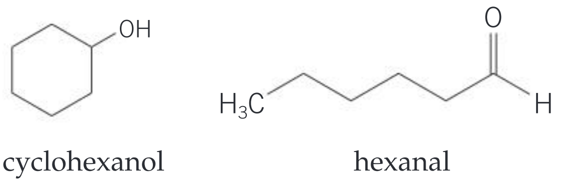
48. Which order of synthetic steps will transform ethane into ethanoic acid?

A. Radical substitution, nucleophilic substitution, oxidation
B. Nucleophilic substitution, radical substitution, oxidation
C. Radical substitution, oxidation, nucleophilic substitution
D. Oxidation, radical substitution, nucleophilic substitution

49. Which molecule is chiral?

A. Propan-1-ol
B. Propan-2-ol
C. Pentan-2-ol
D. Pentan-3-ol

50. Which experimental data can be used to distinguish between the two compounds below?



A. Colour change in reaction with acidified potassium dichromate
B. The *m/z* value of the molecular ion
C. Percentage composition
D. IR spectrum

Paper 2

SL: 1 hour 15 minutes

HL: 2 hours 15 minutes

Instructions to candidates

- Answers must be written within the answers boxes (answer sheets are provided at **www.oxfordsecondary.com/ib-prepared-support**).
- A calculator is required for this paper.
- A clean copy of the **chemistry data booklet** is required for this paper.
- The maximum mark for the SL examination paper is **[50 marks]**.
- The maximum mark for the HL examination paper is **[95 marks].**

SL candidates: answer questions 1–4 ***only****.*

HL candidates: answer ***all*** *questions.*

1. The properties of elements and their compounds vary across periods.

(a) Outline, using chemical equations, how the acid–base properties of oxides of period 3 elements change from magnesium to sulfur. [3]

(b) Deduce the full electron configurations for the atoms of magnesium, Mg, and sulfur, S. [2]

(c) Explain, with reference to part (b), the differences in the first ionization energy, IE_1, and the electron affinity, E_{ea}, of these two elements. Use section 8 of the data booklet. [2]

(d) A student prepared a sample of magnesium sulfide, MgS(s), by heating 0.500 g of magnesium metal, Mg(s), with equal mass of elemental sulfur, S(s).

(i) Calculate the theoretical yield, in g, of magnesium sulfide. Use section 6 of the data booklet. [3]

(ii) Assuming that one of the reactants was used up completely, determine the mass percentage composition of the final mixture. [2]

(e) The student added the mixture from part (d) to excess hydrochloric acid, HCl(aq).

$MgS(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2S(g)$

(i) State **two** changes observed by the student. [2]

(ii) Suggest why this experiment must be carried out in a fume cupboard. [1]

(f) Outline why the electrical conductivity of molten magnesium sulfide, MgS(l), is over 10^{10} times higher than that of the solid compound, MgS(s). [2]

2. Iodine(I) bromide, IBr, is an interhalogen compound. Under standard conditions, it is a volatile solid that melts at 42°C and boils at 116°C.

(a) Deduce, with a reference to electronegativity, the type of chemical bonding between iodine and bromine in IBr. Use sections 8 and 29 of the data booklet. [2]

(b) Predict, with a reason, the type of crystal structure in IBr(s). [1]

(c) Identify **two** types of forces that hold together the structural units of IBr(s). [1]

(d) At high temperatures, iodine(I) bromide decomposes into molecular iodine and bromine: $2IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$ $\Delta H^{\ominus} = +11.7$ kJ

(i) State the effects, if any, of the following changes in temperature (T) and pressure (p) on the position of equilibrium, giving a reason in each case. [2]

T	p	Effect	Reason
decreases	constant		
constant	increases		

(ii) Sketch and annotate the potential energy profile for the decomposition of IBr(g), indicating the enthalpy change, ΔH, and the activation energy, E_a, of the forward reaction. [2]

(e) Iodine(I) bromide can be titrated with sodium thiosulfate, $Na_2S_2O_3(aq)$:

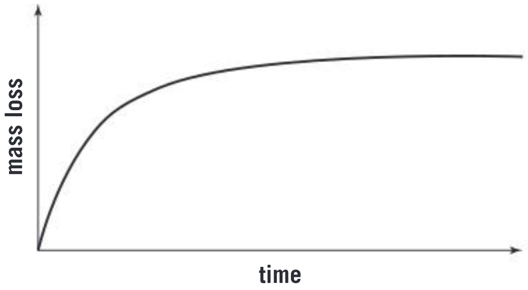
$IBr(s) + 2Na_2S_2O_3(aq) \rightarrow NaI(aq) + NaBr(aq) + Na_2S_4O_6(aq)$

(i) Identify the oxidizing and reducing agents in this reaction. [1]

(ii) Determine the volume of 0.100 mol dm^{-3} solution of $Na_2S_2O_3(aq)$ that will react completely with 3.10 g of IBr(s). Use section 6 of the data booklet. [3]

3. Two students investigated the properties of *magnesite*, a mineral composed of magnesium carbonate, $MgCO_3(s)$.

(a) The first student added a large crystal of magnesite to excess dilute sulfuric acid, $H_2SO_4(aq)$, in a conical flask, plugged the flask with a loose piece of cotton wool, placed the flask on a digital balance and recorded the mass changes at regular intervals. The graph below outlines the results of his experiment.



(i) Formulate an equation for the reaction of magnesite with sulfuric acid. [1]

(ii) Outline, with a reference to kinetic theory, why the rate of this reaction decreases with time. [2]

(iii) Sketch, on the graph on the answer sheet, the expected results if the experiment were carried out at a higher temperature, keeping all other variables unchanged. [1]

(b) The second student wanted to determine the enthalpy change, ΔH, for the thermal decomposition of magnesite.

$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ $\Delta H = ?$

To do so, she prepared two samples of powdered magnesite with a mass of 2.00 g each, placed the first sample into a coffee-cup calorimeter containing dilute sulfuric acid and recorded the temperature change using a glass thermometer. After that, she heated the second sample until the decomposition was complete, allowed the residue to cool down and placed it into the same calorimeter filled with fresh acid solution. The results of her experiments are summarized below.

	Experiment 1	Experiment 2
Initial temperature/°C	21.4 ± 0.1	21.5 ± 0.1
Final temperature/°C	23.2 ± 0.1	29.6 ± 0.1
Volume of dilute $H_2SO_4(aq)/cm^3$	100 ± 1	100 ± 1

(i) Calculate the relative uncertainty in the temperature change obtained in the **first** experiment. [1]

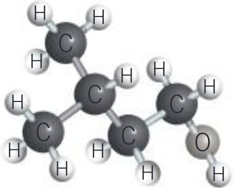
(ii) Calculate the amount of heat, in kJ, produced in each experiment. Use sections 1 and 2 of the data booklet. [2]

(iii) Determine the enthalpy change, in kJ mol^{-1}, for the decomposition of magnesite. [3]

(iv) State **one** factor that could reduce the accuracy of the value obtained in part (iii) and **one** factor that could affect the precision of that value. [2]

(v) Suggest **one** improvement to this experiment and state whether it would increase the accuracy or precision of the measurement. [1]

4. A 3-D model of an oxygen-containing organic compound is shown below.



(a) Deduce the IUPAC name of this compound. [1]

(b) State the reagents and reaction conditions that are required to convert this compound to a carboxylic acid. [2]

(c) Formulate an equation for the reaction of the carboxylic acid from part (b) with methanol. [2]

(d) State the conjugate base for the carboxylic acid from part (b). [1]

(e) Outline **one** experimental technique that can be used to estimate the strength of the carboxylic acid from part (b). [2]

The following questions are for HL candidates ***only***.

5. This question is about iodine(I) bromide, IBr, which first appeared in question 2.

(a) (i) State the K_c expression for the equation given in part (d) of question 2. [1]

(ii) Calculate the K_c value for this reaction at 135 °C if the standard Gibbs free energy, ΔG°, for the decomposition of IBr(g) into $I_2(g)$ and $Br_2(g)$ at that temperature is $+7.2$ kJ mol^{-1}. Use section 1 of the data booklet. [2]

(b) At low temperatures, IBr reacts with excess bromine to produce iodine(III) bromide, IBr_3:

$IBr(s) + Br_2(l) \rightleftharpoons IBr_3(s)$

(i) Draw the Lewis (electron dot) structure for IBr_3. [1]

(ii) Apply the VSEPR theory to deduce the electron domain geometry and the molecular geometry of IBr_3. [2]

(iii) Predict, with a reason, the approximate values of bond angles in IBr_3. [1]

(c) In the absence of water, IBr reacts with iron(III) bromide, $FeBr_3$, as follows:

$IBr + FeBr_3 \rightleftharpoons I^+ + [FeBr_4]^-$

Describe this reaction in terms of acid–base theories and state the roles of each of the two reactants. [2]

(c) Iodine(I) bromide also reacts with alkenes.

(i) Deduce the structural formula of the **main** organic product in the reaction of IBr with propene. [1]

(ii) State the hybridization of the central carbon atom in propene and in the organic product from part (i). [1]

6. This question continues the discussion of magnesite, $MgCO_3(s)$, which first appeared in question 3.

(a) The first student investigated the effects of concentration and temperature on the reaction of magnesite with dilute sulfuric acid. The experimental results are summarized below.

Experiment	***T* / °C**	**$c(H_2SO_4)$ / mol dm^{-1}**	**Initial rate / mol dm^{-1} s^{-1}**
1	21.4	0.250	1.65×10^{-4}
2	21.4	0.500	3.36×10^{-4}
3	35.2	0.250	5.22×10^{-4}

(i) Outline how the initial rate of the reaction could be determined from the graph given in part (a) of question 3. [1]

(ii) Deduce the reaction order with respect to $H^+(aq)$ ions. [1]

(iii) Calculate the activation energy, E_a, in kJ mol^{-1}, for the reaction using sections 1 and 2 of the data booklet. [2]

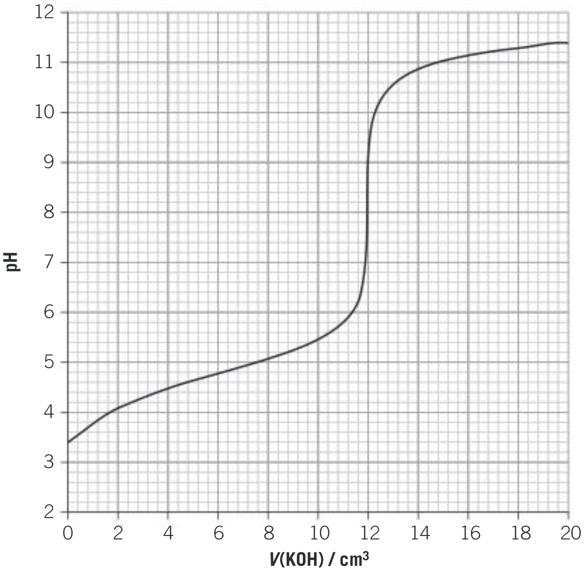
(iv) The student used the same mass of magnesite and the same volume of dilute sulfuric acid in all experiments. Suggest **one** other variable, besides temperature and concentration, which the student should have controlled in the experiment to ensure a fair comparison of the reaction rates. [1]

(b) The standard entropy values for $MgCO_3(s)$ and $MgO(s)$ are 65.7 and 27.0 J K^{-1} mol^{-1}, respectively. Calculate the standard entropy change, ΔS°, in J K^{-1} mol^{-1}, for the decomposition of $MgCO_3(s)$ to $MgO(s)$ and $CO_2(g)$. Use section 12 of the data booklet. [1]

(c) Using section 1 of the data booklet and your answers to questions 3(b)(iii) and 6(b), determine the temperature, in °C, above which the decomposition of magnesite becomes favourable.
(If you did not get answers to 3(b)(iii) and 6(b), use 100 kJ mol^{-1} and 200 J K^{-1} mol^{-1}, respectively, although these are not the correct answers.) [3]

(d) Explain the difference in the lattice enthalpy values for magnesium oxide, $MgO(s)$, and calcium oxide, $CaO(s)$. Use section 18 of the data booklet. [2]

7. A solution containing 5.52 mg of an unknown monoprotic acid was titrated with 0.0100 mol dm^{-3} KOH(aq). The resulting pH curve is shown below.



(a) Calculate the pH of the standard solution used in this titration. [1]

(b) Suggest a suitable acid–base indicator for this titration. Use section 22 of the data booklet. [1]

(c) Calculate the amount, in mol, of KOH(aq) used at the equivalence point. [1]

(d) Calculate the molar mass of the acid. [1]

(e) Determine the pK_a of the acid from the titration curve. [1]

(f) Deduce the full structural formula of the acid if it contains one carbon atom. [1]

8. Titanium, Ti, is the second transition element of the fourth period.

(a) Outline how the first ionization energy, IE_1, of titanium can be determined from its line spectrum. Refer to section 2 of the data booklet. [1]

(b) Two complex ions formed by titanium are $[Ti(H_2O)_6]^{3+}$ and $[TiF_6]^{2-}$.

(i) Deduce the oxidation state of titanium in each of these ions. [1]

(ii) Suggest, with a reason, which of these ions is coloured. [1]

(iii) The coloured ion strongly absorbs visible light at $\lambda = 580\ cm^{-1}$. Using section 17 of the data booklet, predict the colour of that ion. [1]

9. Consider a voltaic cell that consists of a silver half-cell, $Ag(s)/Ag^+(aq)$, and a nickel half-cell, $Ni(s)/Ni^{2+}(aq)$.

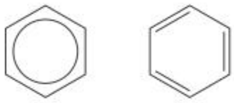
(a) Formulate an equation for the spontaneous reaction that occurs when the circuit is completed. [1]

(b) State the one-line cell diagram notation for this cell. [1]

(c) Determine the standard cell potential, in V, for the cell. Refer to section 24 of the data booklet. [1]

(d) Predict, giving a reason, the change in cell potential when the concentration of nickel(II) ions increases. [2]

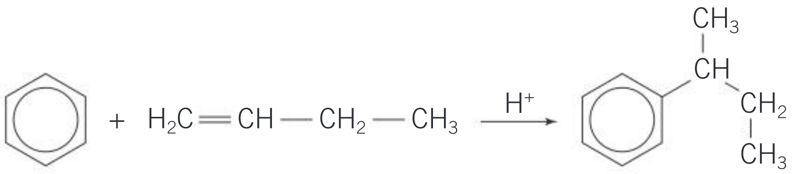
10. The structure of benzene, C_6H_6, can be represented in several ways.



(a) Discuss **two** examples of the physical evidence that support structure **A** and contradict structure **B**. [2]

(b) Formulate an equation for the reaction that produces nitrobenzene from benzene, and state the reaction conditions. [2]

(c) In the presence of an acid catalyst, benzene reacts with but-1-ene as follows:



(i) The reaction product can exist as two enantiomers. Draw three-dimensional representations of these enantiomers. [1]

(ii) Deduce the number of signals and their integration ratio in the ^1H NMR spectrum of the reaction product (ignore the signals of the aromatic ring). [2]

(iii) Suggest a reagent (an individual substance or mixture) that can be used to distinguish the reaction product from but-1-ene. [1]

Paper 3

SL: 1 hour

HL: 1 hour 15 minutes

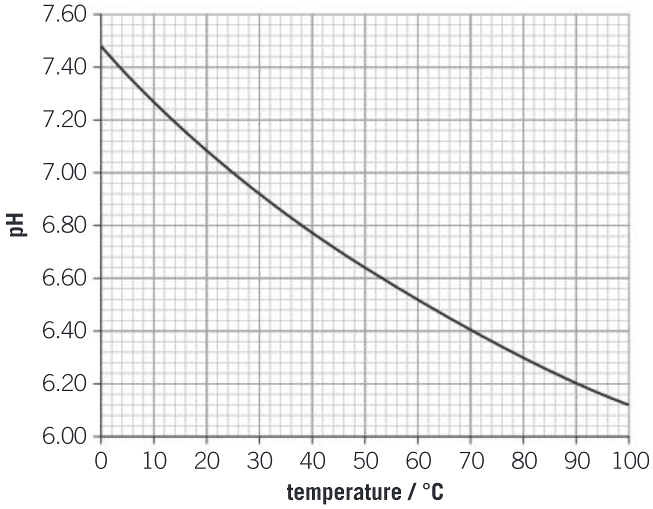
Instructions to candidates

- Answers must be written within the answers boxes (answer sheets are provided at **www.oxfordsecondary.com/ib-prepared-support**).
- A calculator is required for this paper.
- A clean copy of the **chemistry data booklet** is required for this paper.
- The maximum mark for the SL examination paper is **[35 marks]**.
- The maximum mark for the HL examination paper is **[45 marks]**.

Section A

*SL and HL candidates: answer **all** questions.*

1. The pH of pure water varies with temperature, as shown below.



(a) Determine the pH of pure water at 32 °C. [1]

(b) Calculate the K_w value at 32 °C using your answer from part (a). [2]

(c) Sketch a curve to show how the K_w varies with temperature. [2]

(d) State the equation for the dissociation of water. [1]

(e) Outline how the sign of ΔH° for the equation in part (d) can be deduced from the sketched curve in part (c). [1]

2. Two groups of students investigated how the concentration of hydrochloric acid, HCl(aq), affects the initial rate of the following reaction:

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

Each group prepared 50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid and 50.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid.

The first group added 1.00 g of zinc powder to each of the two solutions and recorded the time taken for all zinc to dissolve.

The second group added 10.0 g of zinc granules to each of the two solutions and recorded the time taken for bubbles to stop forming.

(a) Neither method actually gives the initial rate. Describe an experiment that would allow the initial rate to be determined. [2]

(b) Deduce, giving a reason, which of the two methods would be least affected by random errors in the measured mass of zinc metal. [1]

(c) State **one** characteristic that can vary between the samples of zinc powder of exactly the same mass. [1]

(d) Outline how the characteristic from part (c) may affect the reaction rate. [1]

(e) The second group repeated the experiment with 1.00 mol dm^{-3} hydrochloric acid several times and obtained the following data:

Trial	**Time / s**
1	150.2
2	186.7
3	144.3
average	160.4 ± 0.1

Justify whether it is appropriate to record the uncertainty of the average time as ±0.1 s. [1]

(f) Doubling the concentration of hydrochloric acid doubles the reaction rate. Estimate the average reaction time obtained by the second group for the 2.00 mol dm^{-3} hydrochloric acid. [1]

(g) All students from the second group performed the trials in turns. Each student first dropped the zinc granules into the acid and then picked up the stopwatch to start it. State, giving a reason, whether this approach introduced a random or systematic error to the calculated average value of the reaction time. [1]

Section B

Answer **all** of the questions from **one** of the options.

Option A: Materials

*SL candidates: answer questions 3–5 **only**.*

HL candidates: answer questions 3–7.

3. Zirconium(IV) oxide, ZrO_2, also known as *zirconia*, is used to make ceramic knives and composite materials for dental crowns.

(a) Distinguish between ceramics and composites. [1]

(b) Determine the type of bonding present in $ZrO_2(s)$, showing your method. Use sections 8 and 29 of the data booklet. [1]

(c) The production of zirconium metal is an expensive process that involves a reaction of zirconium(IV) chloride, $ZrCl_4$, with magnesium metal. Suggest why zirconium metal cannot be produced from its oxide by the reaction with common reducing agents, such as coke (carbon) or hydrogen gas. [1]

(d) Organic complexes of zirconium are used as homogeneous catalysts in the production of polypropene. Compare and contrast the mechanisms of action of homogeneous and heterogeneous catalysts. [3]

(e) Traces of zirconium in a sample of polypropene can be detected by inductively coupled plasma mass spectroscopy (ICP-MS).

(i) Outline the nature of the plasma state. [1]

(ii) Explain how plasma is produced in ICP-MS. [2]

4. Polypropene is an addition polymer.

(a) Draw the isotactic form of polypropene showing **three** repeating units. [1]
(b) Outline how the properties of polypropene can be modified by the addition of plasticizers. [2]
(c) State **two** environmental concerns of the production and use of polypropene. [1]
(d) The resin identification code (RIC) of polypropene is 2. Suggest why plastics with different RICs should be recycled separately. [1]

5. Nematic liquid crystals and nanoscale materials are used in liquid crystal displays (LCDs) to control the brightness of each pixel in the image.

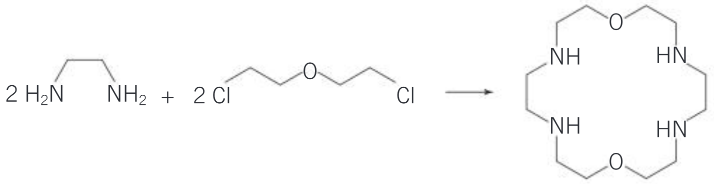
(a) State the overall shape of a nematic molecule. [1]
(b) A typical nematic phase is formed by polar molecules with long hydrocarbon chains. Explain why these two properties are important for the liquid crystals used in LCDs. [2]
(c) Carbon nanotubes, which can be produced by the HiPCO process, are one of the components of transparent electrodes in LCDs. Identify the catalyst and conditions used in the HiPCO process. [2]
(d) Suggest **one** concern of using nanoscale materials in consumer electronics. [1]

The following questions are for HL candidates ***only***.

6. Zirconium metal is a Type 1 superconductor while zirconium(IV) oxide is a component of Type 2 superconductors.

(a) Compare and contrast the composition and properties of Type 1 and Type 2 superconductors. [3]
(b) X-ray diffraction study shows that a unit cell of zirconium metal contains six atoms and has a volume of 0.1394 nm^3. Using section 6 of the data booklet, calculate the density of zirconium metal, in $g\ cm^{-3}$, correct to **three** significant figures. [2]

7. A reaction of ethane-1,2-diamine with bis(2-chloroethyl) ether produces a mixture of condensation products, one of which is shown below.



(a) Identify the inorganic by-product of this reaction. [1]
(b) Estimate the atom economy of the condensation process. Assume that the reaction yield is 100%. [1]
(c) The condensation products of this reaction can act as chelating agents. Explain why chelate ligands are more effective in removing heavy metal ions from solution than monodentate ligands. [3]

Option B: Biochemistry

SL candidates: answer questions 8–11 ***only***.

HL candidates: answer questions 8–13.

8. Glucose, $C_6H_{12}O_6$, is the most common monosaccharide in living organisms.

(a) State the equation for the cellular respiration of glucose. [1]
(b) Deduce the full structural formula of the disaccharide formed by the condensation of two cyclic α-glucose molecules. Refer to section 34 of the data booklet. [2]
(c) Outline the difference between condensation and hydrolysis reactions. [1]
(d) A polymer of glucose, starch, is a constituent of many plastics, especially those used for packaging. Discuss **one** advantage and **one** disadvantage of starch-based packaging materials. [2]

9. The structures of common amino acids are given in section 33 of the data booklet.

(a) Deduce the structural formula of the tripeptide His-Glu-Pro. [2]
(b) State the conditions required for breaking down this tripeptide into individual amino acids. [1]
(c) A mixture of histidine, glutamic acid and proline was placed in the centre of a plate covered in polyacrylamide gel at pH = 6.0. On the copy of the diagram on the answer sheet, sketch and label the relative positions of these amino acids after the potential difference was applied to the opposite sides of the plate. [2]

10. *Rumenic acid* is the common name of a fatty acid found in many dairy products. The molar mass of rumenic acid is 280.50 g mol^{-1}.

(a) A solution of 0.250 g of rumenic acid in a non-polar solvent reacts completely with 17.8 cm^3 of a 0.100 mol dm^{-3} solution of iodine, I_2. Determine the number of carbon–carbon double bonds in the molecule of this acid. [3]
(b) Suggest the molecular formula of rumenic acid if it contains 18 carbon atoms. [1]
(c) The molecular formula of sucrose is $C_{12}H_{22}O_{11}$. Suggest why sucrose releases less energy per gram than rumenic acid. [1]
(d) The structure of another fatty acid, stearic acid, is shown in section 34 of the data booklet. Explain why stearic acid has a higher melting point than rumenic acid. [2]

11. Molecular chlorine, Cl_2, is commonly used for killing bacteria in drinking water. Excess chlorine can be removed from water by a reducing agent, such as sulfur dioxide, SO_2, or ascorbic acid, $C_6H_8O_6$:

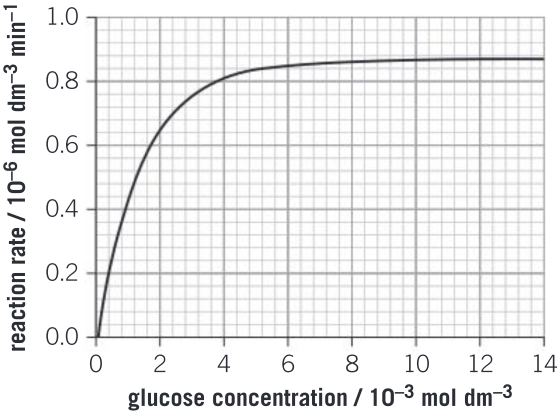
$$SO_2(aq) + Cl_2(aq) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2HCl(aq)$$
$$C_6H_8O_6(aq) + Cl_2(aq) \rightarrow C_6H_6O_6(aq) + 2HCl(aq)$$

The structure of ascorbic acid (vitamin C) is shown in section 35 of the data booklet.

(a) Outline, why ascorbic acid is soluble in water. [1]
(b) Suggest, why ascorbic acid is considered to be a "green" alternative to sulfur dioxide. [1]

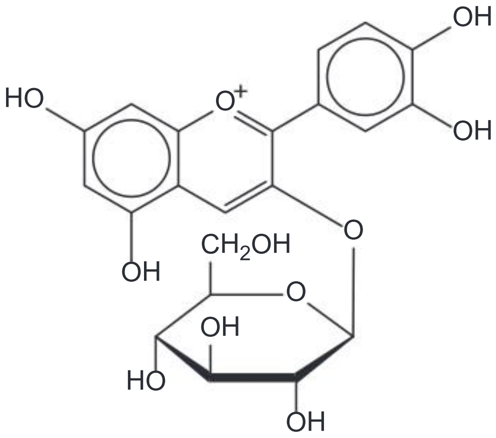
The following questions are for HL candidates ***only****.*

12. Glucose can be converted to glucose-6-phosphate by the enzyme hexokinase. The Michaelis–Menten plot for this reaction is shown below.

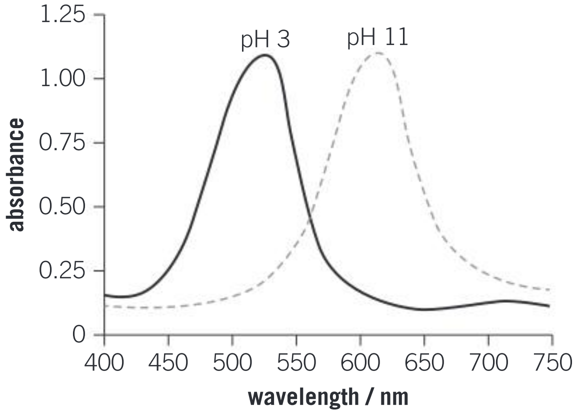


(a) Determine the K_m value of hexokinase and state its units. [1]
(b) Outline what is meant by product inhibition as it applies specifically to this reaction. [1]
(c) The product inhibition of hexokinase does not affect its K_m value. Deduce the type of binding site for the inhibitor. [1]
(d) An RNA involved in the synthesis of hexokinase contains the nucleotide fragment –GAUAACGUA–. Deduce the nucleotide sequence in the DNA template that was used for making this fragment. [1]
(e) State **two** differences between RNA and DNA. [1]

13. Red cabbage juice is rich in biological pigments, anthocyanins, which can be used as acid–base indicators. The structure of a typical anthocyanin is shown below.



(a) Label with asterisks (*) all chiral carbon atoms in the molecule of this anthocyanin. [1]
(b) Outline why biological pigments absorb visible light. [1]
(c) A student used a UV-vis spectrophotometer to record the visible spectra of red cabbage juice at two different pH. The results are shown at the top of the following page.



Deduce, with a reference to section 17 of the data booklet, the colours of red cabbage juice at pH = 3 and pH = 13. [2]

(d) Another biological pigment, retinal, is involved in vision. State the configurational change in the molecule of retinal when it absorbs a photon. [1]

Option C: Energy

SL candidates: answer questions 14–17 ***only***.

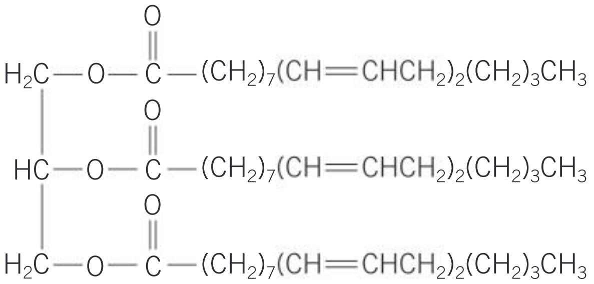
HL candidates: answer questions 14–20.

14. Ethanol, C_2H_5OH, can be used as a source of energy directly or converted to other fuels.

(a) Calculate the specific energy of ethanol, in MJ kg^{-1}, using sections 1, 6 and 13 of the data booklet. [2]

(b) Gasoline (petrol) has a specific energy of 47 MJ kg^{-1}. Using your answer to part (a), comment on the usefulness of ethanol for powering a moving vehicle. If you did not work out an answer for part (a), use 28 MJ kg^{-1}, although this is not the correct value. [1]

(c) Vegetable oils contain various triglycerides, one of which is shown below.



(i) Outline, why vegetable oils must be converted to biodiesel for use in internal combustion engines. [1]

(ii) Deduce the structural formula of the biodiesel formed from the above triglyceride and ethanol. [1]

(iii) State the reaction type and the catalyst required for the conversion in part (ii). [2]

(iv) Apart from the energy density, discuss **one** advantage and **one** disadvantage of biofuels compared to fossil fuels. [2]

(d) "Knocking" in a car engine can be prevented by increasing the octane number of the fuel. Outline, including an equation with structural formulas, how heptane, C_7H_{16}, could be converted to a hydrocarbon with a higher octane number. [2]

15. Fusion and fission transform nuclides into one another.

(a) Compare and contrast fusion and fission in terms of binding energy and the types of nuclei involved. [2]

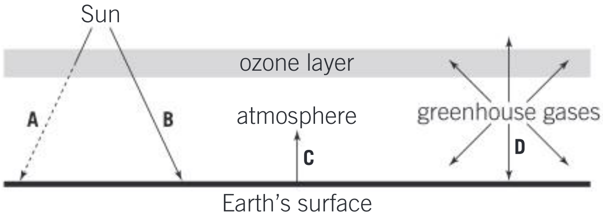
(b) Element No. 104, rutherfordium, was first synthesised by bombarding plutonium-242 with another nuclide, ${}^{A}_{Z}\mathrm{X}$:

$${}^{242}_{94}\mathrm{Pu} + {}^{A}_{Z}\mathrm{X} \rightarrow {}^{259}_{104}\mathrm{Rf} + 5\,{}^{1}_{0}\mathrm{n}$$

Deduce the identity of ${}^{A}_{Z}\mathrm{X}$. [2]

(c) The quantity of rutherfordium-259 in a sample decreases to one eighth (1/8) of its original value in 9.6 s. Estimate the half-life of this radionuclide. [1]

16. The diagram below shows how the ozone layer and greenhouse gases interfere with the radiation emitted by the Sun and the Earth's surface.



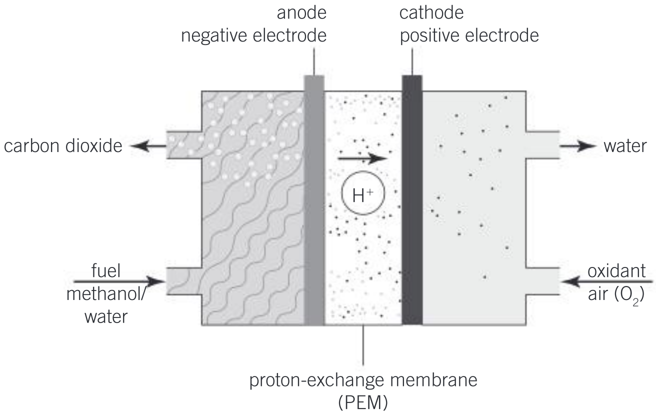
State the radiation type (IR, visible or UV) represented by each of the letters **A**, **B**, **C** and **D** on the diagram. [2]

17. Outline the effect of increasing concentrations of atmospheric carbon dioxide on the pH of the oceans, including an equation in your answer. [2]

*The following questions are for HL candidates **only**.*

18. Fuel cells and rechargeable batteries use redox reactions for producing electrical energy.

(a) A schematic diagram of a direct methanol fuel cell (DMFC) is shown below.



Deduce the half-equations for the reactions at each electrode of this cell. [2]

(b) Suggest **one** advantage and **one** disadvantage of a DMFC over a lead–acid battery as an energy source in a motor vehicle. [2]

19. Nuclear fuel must be enriched with uranium-235 to be used in nuclear reactors. The enrichment process involves uranium hexafluoride, UF_6, which is synthesised from uranium dioxide, UO_2.

(a) Explain, with a reference to molecular structure, why uranium hexafluoride vaporises at 57 °C under normal pressure while the boiling point of uranium dioxide is over 3500 °C. [2]

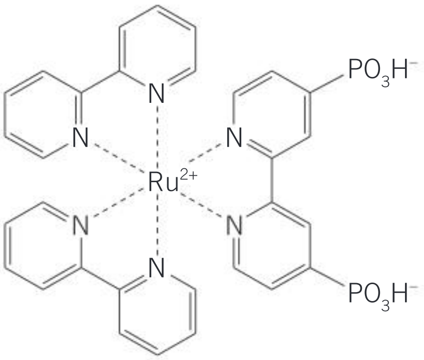
(b) The fission of uranium-235 usually occurs when the nucleus of this isotope absorbs a neutron, for example:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{137}_{55}Cs + ^{96}_{37}Rb + 3\,^{1}_{0}n$$

Using the table below and section 4 of the data booklet, calculate the mass defect, in kg, when 1.00 mol of uranium-235 undergoes fission according to this equation. [1]

Nuclide	$^{235}_{92}U$	$^{137}_{55}Cs$	$^{96}_{37}Rb$
Mass / amu	235.04393	136.90709	95.93427

20. Dye-Sensitized Solar Cells (DSSCs) use organic dyes that mimic the first step of photosynthesis. The structure of one dye used in DSSCs is shown below.



(a) Identify **two** ways in which the structure of this dye resembles that of chlorophyll. Refer to section 35 of the data booklet. [2]

(b) Many dyes used in DSSCs have deep brown or black colours. Suggest how such colours may affect the efficiency of the dye in absorbing solar radiation. [1]

Option D: Medicinal chemistry

*SL candidates: answer questions 21–25 **only**.*

HL candidates: answer questions 21–28.

21. Mild and strong analgesics provide pain relief using different mechanisms of action. The structures of several analgesics are given in section 37 of the data booklet.

(a) Describe how mild analgesics function. [2]

(b) The mild analgesic aspirin is only slightly soluble in water. Outline, using an equation, how aspirin can be converted to a more water-soluble derivative. [2]

(c) Opiates, such as morphine and codeine, are strong analgesics.
   (i) Outline the action of opiates as pain killers. [1]
   (ii) Identify a reagent that can be used to prepare codeine from morphine. [1]
   (iii) State, with a reason, whether morphine or codeine will pass more readily through the blood-brain barrier. [1]
   (iv) Suggest, why codeine is available without prescription in many countries whilst morphine is administered under strict medical supervision. [1]

22. Molecules of many antibacterial drugs contain a beta-lactam ring. Outline the importance of this ring in the action of penicillin, using section 37 of the data booklet. [2]

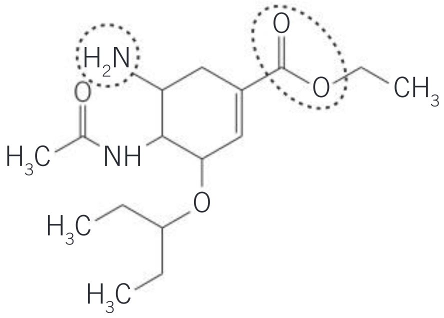
23. The blood pH is maintained within a narrow range by acid–base buffers.

(a) Calculate the pH of the hydrogencarbonate buffer containing 24.0 mmol dm^{-3} $HCO_3^-(aq)$ and 2.14 mmol dm^{-3} $CO_2(aq)$ if $pK_a(CO_2) = 6.34$. Refer to section 1 of the data booklet. [1]

(b) Suggest how a large dose of aspirin may affect the pH of the patient's blood. [1]

24. Ranitidine (Zantac) and omeprazole (Prilosec) are used for preventing the overproduction of hydrochloric acid in the stomach. Identify the site of action of each drug in the body. [2]

25. Oseltamivir (Tamiflu) is used to treat and prevent influenza. The structure of oseltamivir is shown below.



(a) Identify the **two** functional groups circled in the structure of oseltamivir. [2]

(b) The production of oseltamivir involves the use of many dangerous chemicals, including chlorinated organic compounds. Suggest **two** environmental problems associated with chlorinated organic waste. [2]

(c) Explain why influenza cannot be treated with antibacterial drugs, such as penicillin. [2]

The following questions are for HL candidates ***only***.

26. The structure of oseltamivir is shown in the previous question.

(a) Label with asterisks (*) all chiral centres in this structure. [1]

(b) Identify an apparatus that can be used to distinguish between enantiomers of oseltamivir. [1]

(c) Predict the number of signals in ^{1}H NMR spectrum of oseltamivir. [1]

(d) State **one** spectroscopic technique, other than NMR, that could be used to confirm the identity of oseltamivir. [1]

27. Targeted Alpha Therapy (TAT) is an efficient method of treating cancer.

(a) One radioisotope used in TAT is lead-212. It is produced by alpha-decay of another radioisotope, $^{A}_{Z}X$. Formulate the equation for this process. [2]

(b) The half-life of lead-212 is 10.6 hours. Calculate the percentage of this radioisotope that will decay in 48.0 hours. [2]

28. The blood alcohol content (BAC) can be estimated by measuring the level of alcohol in a breath sample. Formulate half-equations for the reactions at the anode (negative electrode) and the cathode (positive electrode) in a fuel cell breathalyser. [2]

Index

Key terms are in **bold.**

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Authors

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Brian Murphy
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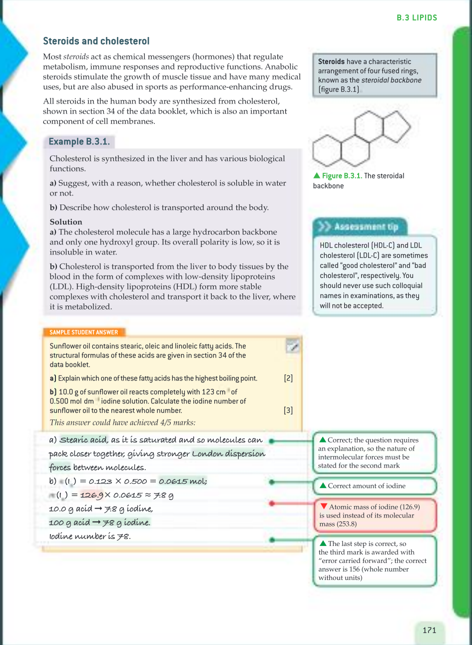
FOR FIRST ASSESSMENT IN 2016

Key syllabus material is explained alongside **key definitions**

Assessment tips **offer guidance** and warn against common errors

Assessment questions and **sample student responses** provide practice opportunities and useful feedback



B.3 LIPIDS

Steroids and cholesterol

Most *steroids* act as chemical messengers (hormones) that regulate metabolism, immune responses and reproductive functions. Anabolic steroids stimulate the growth of muscle tissue and have many medical uses, but are also abused in sports as performance-enhancing drugs.

All steroids in the human body are synthesized from cholesterol, shown in section 34 of the data booklet, which is also an important component of cell membranes.

Steroids have a characteristic arrangement of four fused rings, known as the *steroidal backbone* (figure B.3.1)

▲ Figure B.3.1. The steroidal backbone

Example B.3.1.

Cholesterol is synthesized in the liver and has various biological functions.

a) Suggest, with a reason, whether cholesterol is soluble in water or not.

b) Describe how cholesterol is transported around the body.

Solution

a) The cholesterol molecule has a large hydrocarbon backbone and only one hydroxyl group. Its overall polarity is low, so it is insoluble in water.

b) Cholesterol is transported from the liver to body tissues by the blood in the form of complexes with low-density lipoproteins (LDL). High-density lipoproteins (HDL) form more stable complexes with cholesterol and transport it back to the liver, where it is metabolized.

Assessment tip

HDL cholesterol (HDL-C) and LDL cholesterol (LDL-C) are sometimes called "good cholesterol" and "bad cholesterol", respectively. You should never use such colloquial names in examinations, as they will not be accepted.

SAMPLE STUDENT ANSWER

Sunflower oil contains stearic, oleic and linoleic fatty acids. The structural formulas of these acids are given in section 34 of the data booklet.

a) Explain which one of these fatty acids has the highest boiling point. [2]

b) 10.0 g of sunflower oil reacts completely with 123 cm^3 of 0.500 mol dm^{-3} iodine solution. Calculate the iodine number of sunflower oil to the nearest whole number. [3]

This answer could have achieved 4/5 marks:

a) Stearic acid, as it is saturated and so molecules can pack closer together, giving stronger London dispersion forces between molecules.

b) $n(I_2) = 0.123 \times 0.500 = 0.0615$ mol;
$m(I_2) = 126.9 \times 0.0615 \approx 7.8$ g
10.0 g acid → 7.8 g iodine,
100 g acid → 78 g iodine.
Iodine number is 78.

▲ Correct; the question requires an explanation, so the nature of intermolecular forces must be stated for the second mark

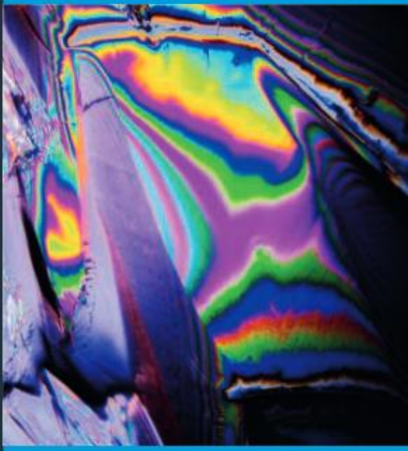
▲ Correct amount of iodine

▼ Atomic mass of iodine (126.9) is used instead of its molecular mass (253.8)

▲ The last step is correct, so the third mark is awarded with "error carried forward"; the correct answer is 156 (whole number without units)

171

What's on the cover?
Microcrystals of tartaric acid in polarized light



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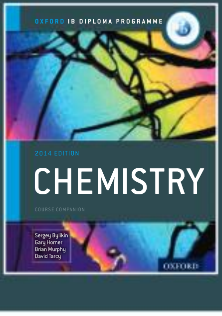

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