

SACE TWO AUSTRALIAN CURRICULUM

CHEMISTRY

WORKBOOK
THIRD EDITION

MARIE DAZIANI
KATE MORGANTE
LUKE STARCZAK
STEPHEN TULIP



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THE AUTHORS

Marie Daziani B.Ed (Sec), B.Sc

Marie has extensive teaching experience in SACE and International Baccalaureate Chemistry across Catholic and Independent schools in South Australia. She is the Subject Coordinator of Chemistry at her current school. Marie has a passion for teaching and has thoroughly enjoyed her volunteer work with Cambodia Husk Schools in recent years.

Kate Morgante B.Sc. (Biomedical Science), B.Ed., Grad.Cert.Ed

Kate has been teaching senior Chemistry since 2009. She has extensive SACE moderation and SACE exam marking experience as well as co-editor of the SASTA Chemistry Study Guide. She has also acknowledged for her excellence in Science and STEM with the 2015 SASTA Credit Union SA Outstanding Teacher Award and the 2016 with the ATSE Teaching Excellence Award.

Luke Starczak B.Sc. (Chemistry), B.Ed.

Luke has been teaching senior Chemistry since 2012. Luke is passionate about teaching science students in engaging and relevant contexts to enable them to better engage in the curriculum. He also has extensive experience with SACE moderation and SACE exam marking as well as exam writing and contributing to a number of other publications.

Stephen Tulip M.Teach, B.Sc.(Hons) (Chemistry), B.A.

Stephen graduated from the University of Adelaide with a B.Sc. in Chemistry and a B.A. in Psychology and French. After teaching and demonstrating undergraduate Chemistry at the University of Adelaide for six years, he obtained his M.Teach from the University of South Australia. Stephen has been teaching middle and senior Science at Gleeson College in Golden Grove since 2019.

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Preface

The authors have written this book for students and educators undertaking Stage 2 Chemistry. The book has been written in the order described in the SACE Subject Outline. Each of the four chapters in this book contain a full description of the content prescribed in the subject outline, explanatory diagrams, exam-style questions, and a summary test drawing from real-world examples. A complete set of recommended solutions to all chapter questions and the summary tests have been included in the back of this book.

The questions in this workbook allow students to build confidence in their responses to the SACE Specific Features and Performance Standards. The questions vary in length and difficulty, allowing students to recall, apply, and transfer their knowledge to different contexts. Stage 1 Chemistry is assumed knowledge. The questions are in context with the intent of allowing the students to encounter different aspects of chemistry. Each chapter is supported with a 60-mark summary test, designed to emulate aspects of the external SACE assessment.

Using current and relevant Science as a Human Endeavour (SHE) contexts the authors have presented relevant aspects of the theory. The authors have presented relevant SHE contexts within questions in the summary tests in order to further emulate the external SACE assessment. The SHE topics presented offers insight into historical perspectives, local and international collaboration, limitations in chemistry, and the important links between science, technology, and society. Wherever possible, the authors have presented aspects of chemistry from both local and global perspectives. Science Inquiry Skills have been written in the relevant contexts within individual sections of the course.

As authors we hope that you develop a passion and appreciation for the course and develop an understanding of how integral chemistry is to many aspects of our society.

The authors and publisher wish you all the best for your studies in Stage 2 Chemistry.

Marie Daziani
Kate Morgante
Luke Starczak
Stephen Tulip

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Topic 1: Monitoring the environment

1.1 Global warming and climate change

Science understanding

Some gases in the atmosphere, called 'greenhouse gases', keep the Earth's atmosphere warmer than it would be without these gases. This is known as the 'greenhouse effect'.

Describe the action of the common greenhouse gases, carbon dioxide and methane, to maintain a steady temperature in the Earth's atmosphere.

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The greenhouse effect



Figure 1.1.1: Solar radiation entering Earth's atmosphere.

Solar radiation entering Earth's atmosphere consists of infrared radiation, visible light and ultraviolet radiation (UV). Solar radiation is composed largely of visible wavelengths, longer infrared wavelengths, and a smaller component of shorter ultraviolet wavelengths.

Approximately 30% of the solar radiation reaching Earth is reflected to space due to the **albedo** (reflectivity) of the Earth's surface and atmosphere. Land and sea ice, snow coverage and the clouds are all highly reflective. Approximately 22% of the solar radiation reaching Earth is absorbed by the atmosphere. A component of ultraviolet radiation is absorbed by gases present in the stratosphere, importantly by the ozone molecule. The remaining 48% of solar radiation is absorbed by the surface of the Earth, warming it (Figure 1.1.1). Of the absorbed solar radiation, approximately 17% is reradiated from the Earth at lower energies and therefore longer wavelengths. The wavelengths emitted correspond to the **thermal infrared region** (longer wavelengths at lower energy than visible light) of the electromagnetic spectrum.

Approximately 12% of this thermal radiation passes directly through the atmosphere into space, but a component of approximately 5% is absorbed by molecules in the atmosphere, collectively referred to as **greenhouse gases**. These molecules in turn reradiate the thermal radiation to other molecules in the atmosphere, into space, and back to the surface of the Earth. The effect of this is to warm the surface of the Earth and the **troposphere** (the lower layer of the atmosphere) (Figure 1.1.2).

This naturally occurring process is referred to as the **greenhouse effect**. The greenhouse effect serves to maintain a relatively stable average temperature of approximately 15°C, sustaining life on Earth.

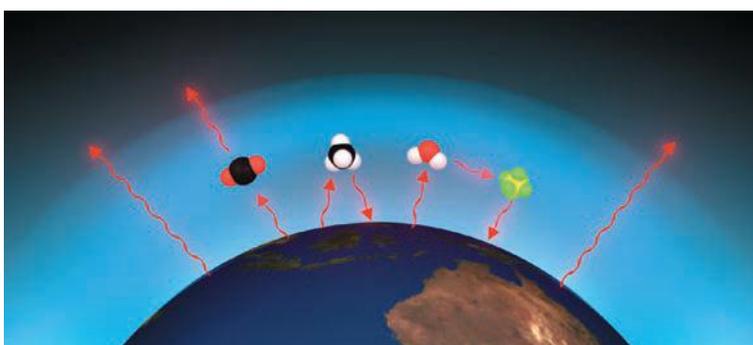


Figure 1.1.2: The natural greenhouse effect.

Greenhouse gases

Greenhouse gases absorb thermal radiation in the infrared region of the electromagnetic spectrum. Greenhouse gases originate from both natural and synthetic sources (Figure 1.1.3).

H ₂ O	CO ₂	CH ₄	N ₂ O	O ₃	SF ₆
v-shaped	linear	tetrahedral	linear	v-shaped	octahedral
water (vapour)	carbon dioxide	methane	nitrous oxide	ozone	sulfur hexafluoride (Synthetic sources only)

Figure 1.1.3: Natural and synthetic greenhouse gases.

Cycles in nature, such as the **carbon cycle**, the **water cycle** and **nitrogen cycle**, are responsible for the formation of naturally occurring greenhouse gases that enter the atmosphere. **Anthropogenic** (originating from human activity) influences have added to the concentrations of naturally occurring greenhouse gases, while also introducing synthetic greenhouse gases.

Greenhouse gas	Natural sources
water vapour	Water is present in the atmosphere as water vapour and clouds. Water moves between the soil, natural bodies of water (such as oceans and lakes), and the atmosphere via the water cycle.
carbon dioxide	Carbon dioxide is released during aerobic (presence of oxygen) respiration in animals, humans and soil-dwelling microbes, aerobic decomposition of organic matter, the combustion of natural vegetation, and volcanic activity.
methane	Methane is released during the anaerobic (absence of oxygen) decomposition of organic matter in soil. Methane is also released when sea ice, containing methane hydrates, melts.
nitrous oxide	Nitrous oxide is formed through denitrification (reduction of nitrate ions) in natural vegetation in soil and in the oceans.
ozone	Ozone occurs naturally in the stratosphere and is created and destroyed through the absorption of ultraviolet radiation in photochemical (light-absorbing) reactions.

Earth's thermal balance

On average, the temperature at the Earth's surface is approximately 32°C higher than it would be in the absence of greenhouse gases. The greenhouse effect is most strongly influenced by carbon dioxide and water vapour.

Mean surface temperature (°C) (without the greenhouse effect)	-17
Mean surface temperature (°C) (with the greenhouse effect)	15
Greenhouse warming	32

For thousands of years, the temperature of the Earth's atmosphere has been in **thermal balance**, with the amount of thermal radiation entering the atmosphere in equilibrium with the amount of thermal radiation emitted back into space (Figure 1.1.4).

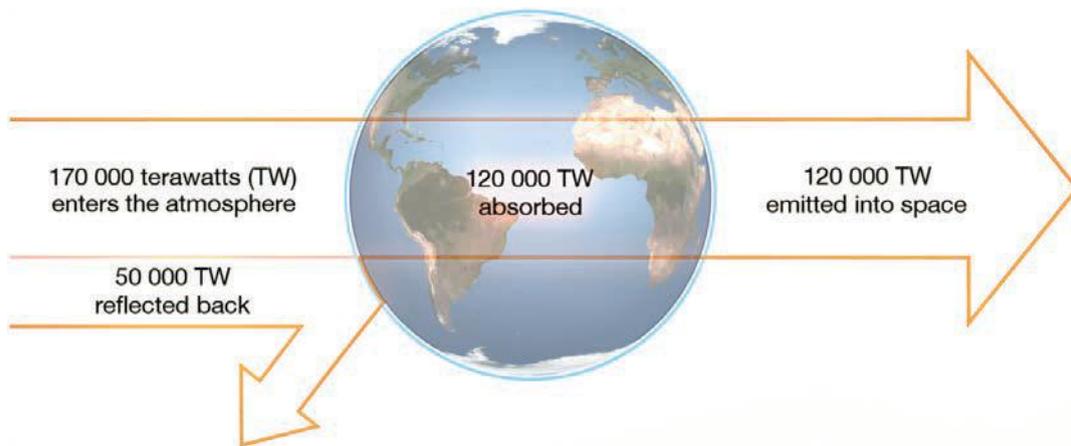


Figure 1.1.4: Thermal balance.

Science understanding

Anthropogenic increases in greenhouse gases disrupt the thermal balance of the atmosphere.

Explain the warming associated with global climate change and its consequences for the environment.

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Global warming

As concentrations of greenhouse gases have risen due to anthropogenic activities, less thermal radiation is escaping the Earth, generating a **thermal imbalance**. A new equilibrium is established with an average temperature that exceeds the current value (Figure 1.1.5). This resulting increase in temperature is referred to as **global warming**.

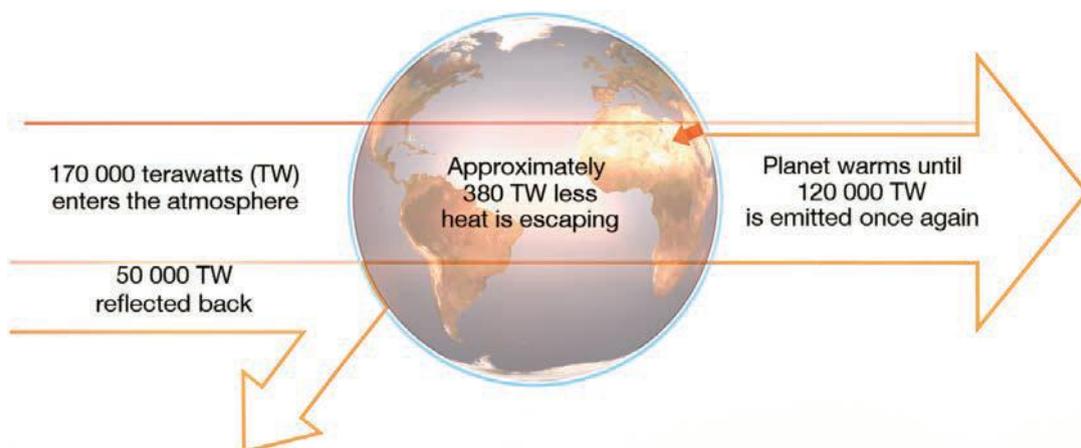


Figure 1.1.5: Thermal imbalance.

Questions

1. The impact of warming due to greenhouse gases can be seen by comparing Earth to other planets in our solar system. The details are summarised in the table below.

	Reflectivity (albedo) (%)	Mean surface temperature (without greenhouse effect) (°C)	Mean surface temperature (with greenhouse effect) (°C)	Greenhouse warming (°C)	Carbon dioxide present in the atmosphere (%w/v)
Earth	36	-17	15	32	0.040
Mars	25	-55	-50	5	95 (very thin atmosphere)
Venus	72	-42	467	509	96

- (a) Earth's atmosphere maintains temperatures that are suitable to sustain life.
- (i) **State** the mean surface temperature experienced on Earth without the greenhouse effect.
- (1 mark) **IAE3**
- (ii) **Explain** how two greenhouse gases, carbon dioxide and methane, assist in maintaining a stable temperature in the Earth's troposphere.
-
-
-
-
-
- (3 marks) **KA1**
- (b) Albedo refers to the reflectivity of the surface and atmosphere of the planet.
- Suggest** why albedo is taken into account when determining greenhouse warming.
-
-
-
- (2 marks) **KA2**
- (c) Venus has a mean surface temperature of 467°C and Mars -50°C.
- (i) **Explain**, using data in the table, why the mean surface temperature of Venus is considerably higher than that of Earth.
-
-
- (2 marks) **IAE3**
- (ii) The percentages of carbon dioxide in the atmospheres of Mars and Venus are almost equal.
- Suggest** one reason for the difference in the mean surface temperature of Mars and Venus.
-
- (1 mark) **KA2**

2. An investigation was undertaken to determine the action of carbon dioxide as a greenhouse gas.

STEP 1: Two 2 L plastic bottles were assembled, one containing air and the other a small pellet of dry ice (solid carbon dioxide), with the lids removed. A carbon dioxide sensor was inserted into each bottle to measure the concentration of carbon dioxide. The concentration of carbon dioxide present in the air in the first bottle was found to be 404 ppm. On sublimation, the dry ice produced a concentration of 826 ppm of carbon dioxide in the second bottle.

STEP 2: A temperature sensor was inserted into each bottle and the opening sealed.

STEP 3: Both bottles were placed at equal distances from a 60-watt incandescent lamp and the temperature recorded at five-minute intervals for a period of 30 minutes.

(a) From the procedure outlined,

(i) **Identify** and **discuss** the importance of the control of one factor in the investigation

.....

 (2 marks) **IAE1**

(ii) **Identify** the independent variable in the investigation.

.....
 (1 mark) **IAE1**

(iii) Hence, **state** a suitable hypothesis for the investigation.

.....

 (2 marks) **IAE1**

(iv) **Suggest** one improvement that could be made to the design to increase the validity of the procedure.

.....
 (1 mark) **IAE4**

(b) The results obtained are summarised in the table below.

Time (min)	Concentration of CO ₂	
	404 ppm	826 ppm
0	22.0	22.0
5	22.5	24.0
10	24.0	25.5
15	25.0	28.0
20	26.0	29.5
25	26.5	31.0
30	27.0	33.0

Using the data obtained,

(i) **Graph** both sets of data on the same set of axes.



(6 marks) **IAE2**

(ii) **Discuss** the conclusions that can be drawn from the data in relation to carbon dioxide as a greenhouse gas.

.

 (3 marks) **IAE3**

Anthropogenic (human) influences

The atmospheric concentrations of carbon dioxide and other greenhouse gases have shown steady increase over the past 250 years. The most significant change has been the increase recorded in atmospheric carbon dioxide.

Increased concentrations of carbon dioxide may be directly attributed to human activities. Since the industrial revolution (c. 1750), carbon deposits that had been stable for millions of years as **fossil fuels** (coal, crude oil and natural gas) have been mined, processed, consumed for energy production, and used as **feedstock** (raw material) for the chemical industry. A growing population, living in an increasingly industrialised world, has led to greater demand for natural resources and the subsequent increased release of greenhouse gases.

Greenhouse gases exist for different periods of time in the atmosphere (**atmospheric residence time**). They undergo chemical reactions to form products that result in the removal of the gases from the atmosphere. For example, carbon dioxide is used during photosynthesis or absorbed into oceans. Greenhouse gases can be compared to carbon dioxide in their relative ability to absorb thermal radiation. This value is referred to as the **global warming potential (GWP)**.

Greenhouse gas	Anthropogenic sources	Atmospheric residence (years)	Global Warming Potential
carbon dioxide	Carbon dioxide is released in considerable quantities during the combustion of fuels in the internal combustion engines of motor vehicles. Carbon dioxide is released from the combustion of fuels during electricity generation in power stations and other industry applications. Widespread deforestation and land-clearing has reduced the amount of natural vegetation available to remove carbon dioxide from the atmosphere through photosynthesis.	5 – 200	1
methane	Methane is released in mining, and during the production and use of fuels. Methane is released during digestion in ruminant animals. Atmospheric concentrations have increased due to intensive livestock farming. Rice farming releases methane due to the anaerobic conditions generated in rice fields. Landfill releases small quantities of methane from the natural anaerobic decay of organic matter.	12.4	28
nitrous oxide	Nitrous oxide is released from the use of natural and synthetic fertilisers and the cultivation of soil in agriculture. Catalytic converters in motor vehicles produce small quantities of nitrous oxide.	120	265
sulfur hexafluoride	Sulfur hexafluoride is produced synthetically for use in the electrical industry as an electrical insulator. It is also used in the industrial casting of magnesium. Sulfur hexafluoride may be released in small quantities during production, use and disposal.	3200	23500
chlorofluorocarbons (CFCs)	CFCs and HFCs have been synthetically produced for applications as aerosols and foams, refrigerants, and as insulation in electrical cabling.	45 – 1020	6310 – 11700
hydrofluorocarbons (HFCs)	They may be released in small quantities during production, use and disposal.	Days – 244	<1 – 10800

Global measurements

Atmospheric carbon dioxide concentrations have been accurately and reliably recorded by the scientific community for over 50 years.



Science as a human endeavour

Keeling's Curve

Charles Keeling of Scripps Institution of Oceanography was one of the first scientists to make regular measurements of atmospheric carbon dioxide concentrations. In 1958, Keeling began taking measurements of carbon dioxide concentration from Hawaii's Mauna Lao volcano observatory and at the South Pole. Before Keeling's measurements the scientific community had generally thought that concentrations of carbon dioxide in the atmosphere were highly variable with no significant trends apparent in recorded values.

Keeling's measurements initially revealed variation over the day and between seasons. The decay of plant matter over winter increases carbon dioxide levels; new growth of plants in spring reduces carbon dioxide levels due to increased levels of photosynthesis.

The long-term trend from measurements taken since 1958 at Mauna Lao observatory revealed a steady increase in atmospheric carbon dioxide concentrations, Keeling correlated this increase with the increased combustion of fossil fuels around the globe.

Today, carbon dioxide levels are monitored from sites all over the globe using increasingly sophisticated methods. Charles Keeling passed away in 2006. His son, Ralph Keeling, has carried on with his father's research.



The recorded concentrations of carbon dioxide from atmospheric monitoring have been combined with carbon dioxide readings obtained from ice-core samples (Figure 1.1.6). Together, these readings represent thousands of years of data.

There is strong evidence to suggest that carbon dioxide levels have increased considerably over the past 1000 years. Although there is cyclical variation over periods of tens of thousands of years, carbon dioxide concentrations in the atmosphere are currently at the highest recorded levels in human history, with values exceeding 400 ppm. This trend correlates very closely with measurements taken for average global temperature.

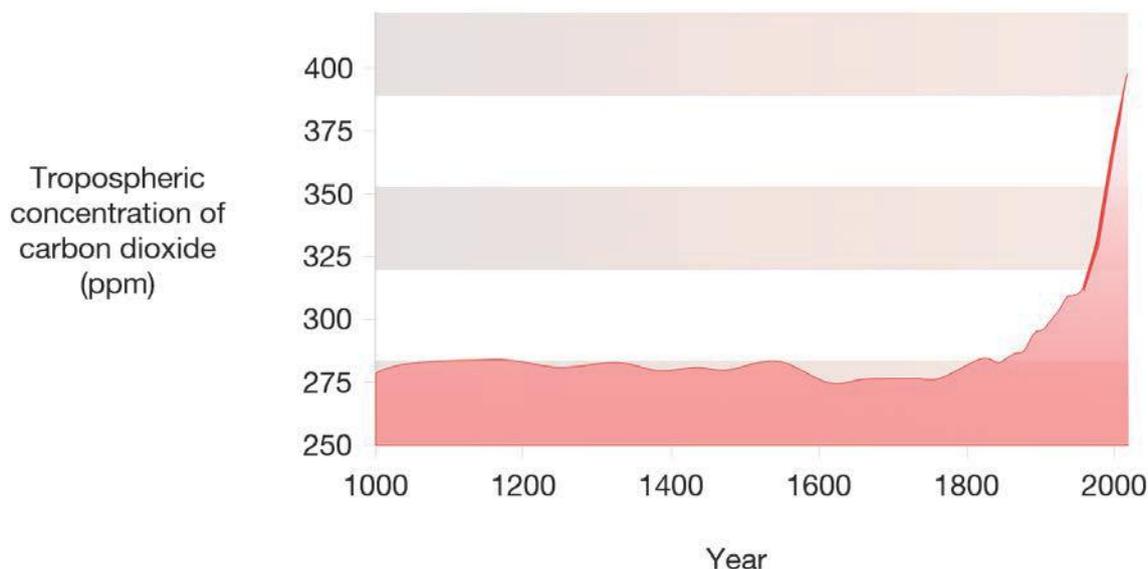


Figure 1.1.6: Variation in the tropospheric concentration of CO_2 over the past 1000 years.

Climate change

Climate can be monitored over periods of decades through the record of measurable patterns in the weather, such as temperature and rainfall. There is growing scientific evidence that the impacts of global climate change are accelerating.

Global temperature rise

Globally, temperatures have risen by approximately 0.8°C over the last 100 years. Average global surface air temperature has shown a steady increase (Figure 1.1.7).

Global feedback mechanisms have also driven further increases in temperature. For example, at higher temperatures more water vapour is present in the atmosphere due to greater evaporation, which in turn absorbs more energy while acting as a greenhouse gas, increasing temperatures in the troposphere.

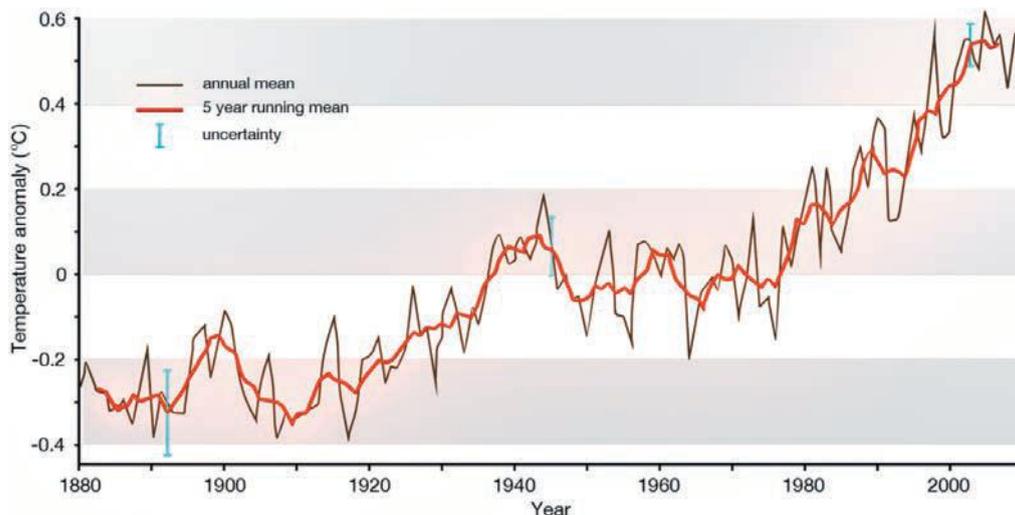


Figure 1.1.7: Global surface air temperature.

An Australian perspective

Over the past 100 years, the average surface temperature in Australia has increased by 1.0°C.

Declining arctic sea ice, shrinking ice sheets, and retreating glaciers

Melting land ice and sea ice enter the Earth’s oceans, causing a rise in sea level and altering salinity. The input of fresh water from land ice and glaciers alters the temperature and salinity (hence density) in regions of the ocean. These changes are predicted to affect the circulation of global ocean currents. Ocean currents impact upon weather and hence climate.

The loss of reflectivity has a significant impact. With a decline in ice and snow, the albedo of the Earth is reduced, resulting in a decrease in reflected solar radiation and increased global temperatures, once again altering the global climate.

Arctic sea ice has been declining at a rate of approximately 13% per decade (Figure 1.1.8).

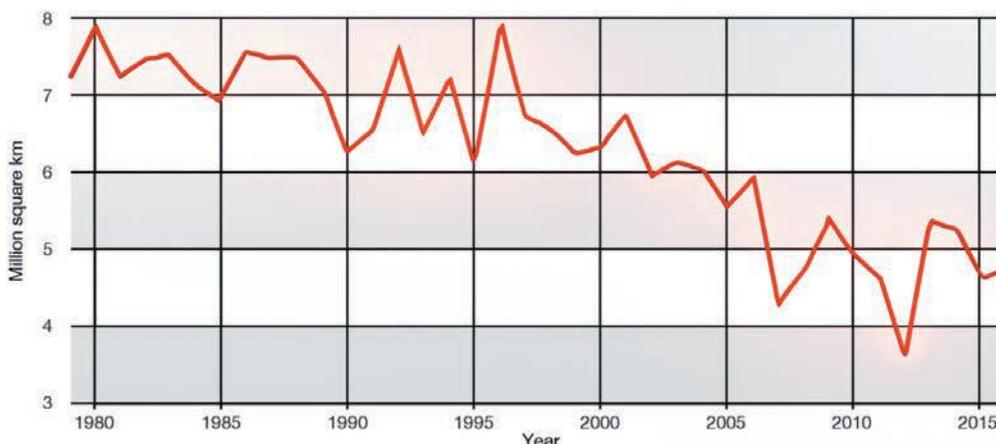


Figure 1.1.8: Arctic sea ice (1979–2017).

Similar decline has been recorded in land ice mass and the loss of glaciers (Figures 1.1.9 and 1.1.10).

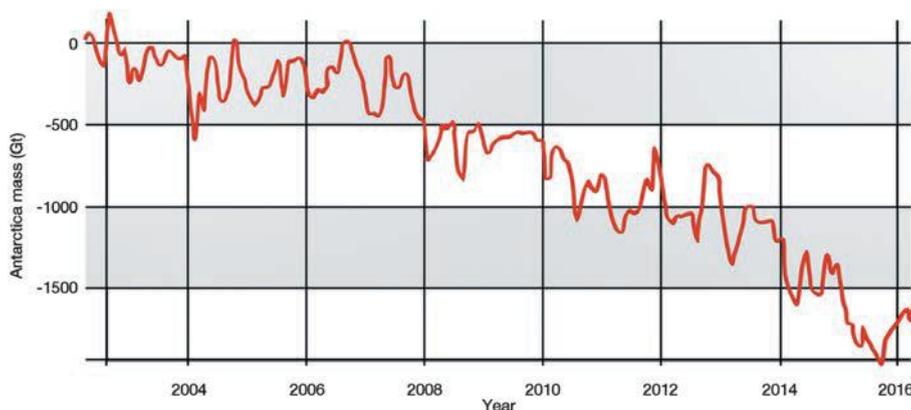


Figure 1.1.9: Ice mass measurements, Antarctica (2002–2017).

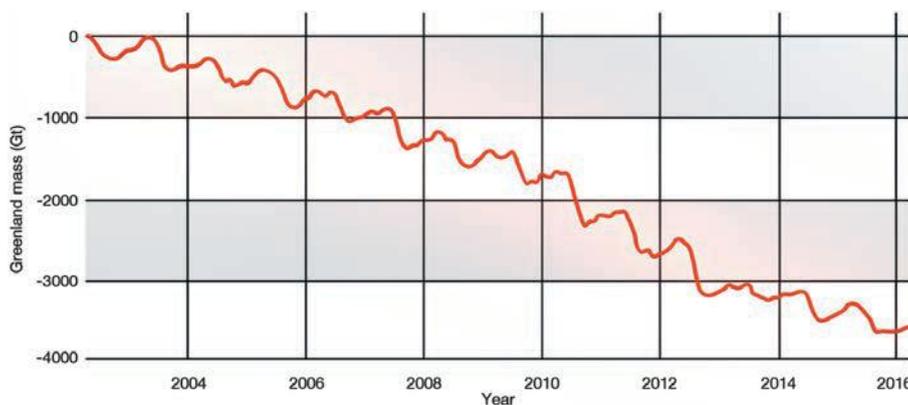


Figure 1.1.10: Ice mass measurements, Greenland (2002–2017).

Thawing permafrost (frozen soil and rock) in Greenland, Alaska and Siberia has also led to the release of methane (from methane hydrates in the ice) and other trapped greenhouse gases formed during the anaerobic decay of organic matter, contributing further to global warming.

Rising sea levels

Globally, sea levels have risen by approximately 17 cm in the last 100 years (Figure 1.1.11). As ocean temperatures increase, the water in the oceans undergoes thermal expansion increasing in volume, causing a subsequent rise in sea levels. Rising sea levels threaten low-lying coastal communities in localised regions such as the Maldives and Torres Strait Islands.

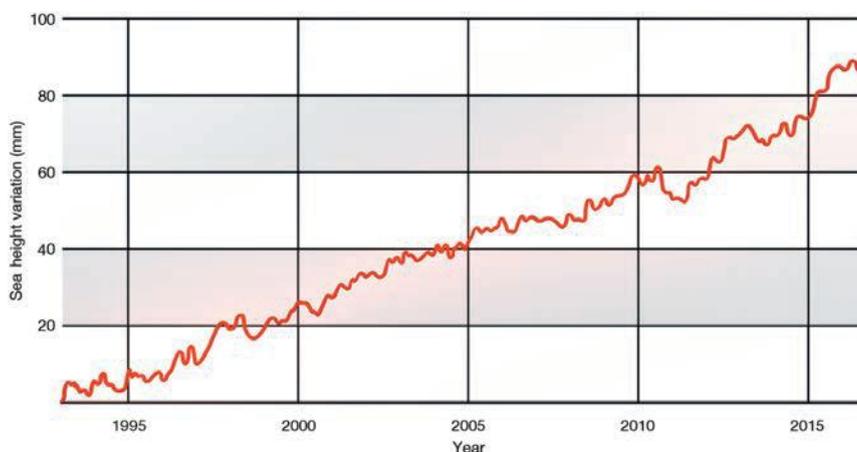


Figure 1.1.11: Satellite measurements of variation in sea height (1993–2017).

An Australian perspective

Rates of sea level rise to the north, west, and south-east of Australia have been higher than the global average.

Climate and extreme weather events

As the global climate system experiences warming, changes have occurred in both the frequency and severity of weather events. Changes to climate and severe weather events impede global crop production and alter distribution of natural vegetation. As landscapes and habitats are altered, plant and animal species must adapt or risk extinction. Climate change has led to extinction of susceptible species, resulting in permanent changes to biodiversity in ecosystems.

An Australian perspective

In Australia, the most evident change has been extreme temperature events. There have been more frequent occurrences of bushfires, increases in extreme fire weather, and longer fire seasons. There has been greater variability in trends in rainfall patterns, leading to drought and flooding. An increase in the severity of tropical cyclones (such as Cyclone Debbie in 2017) has also been noted.

Warming of oceans

Ocean temperatures and ocean heat content have steadily increased globally. The majority of the additional heat generated by the enhanced greenhouse effect is being absorbed by the world's oceans. The high specific heat capacity of water allows large quantities of energy to be absorbed. Much of the impact of the enhanced greenhouse effect on the surface of the globe has been masked by this absorption of energy.

An Australian perspective

Oceans around Australia have warmed, threatening ocean ecosystems like the Great Barrier Reef through coral bleaching and ocean acidification.



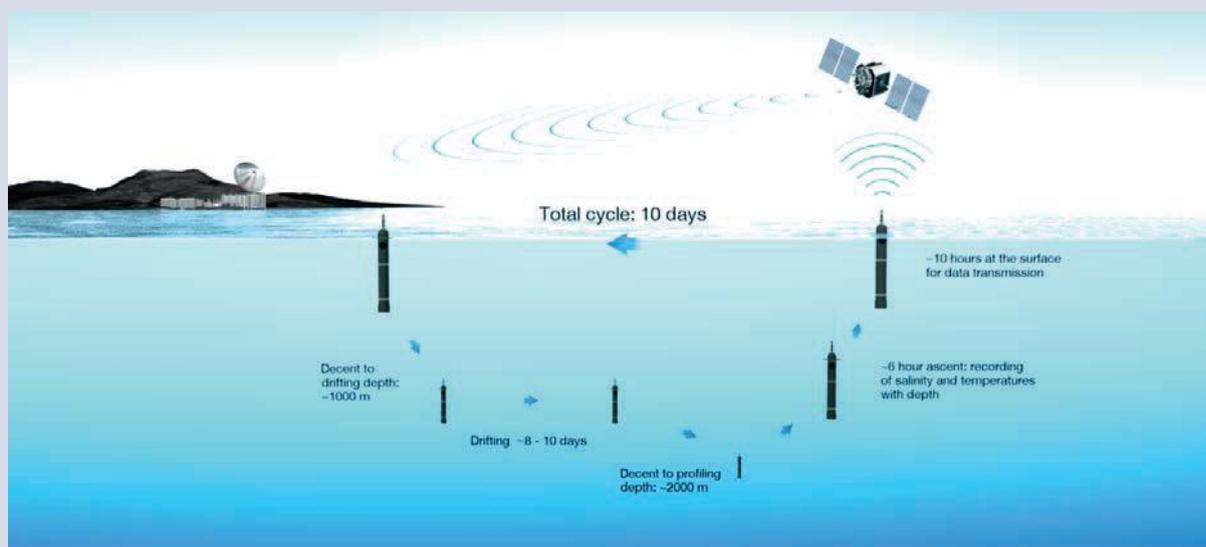
Science as a human endeavour

Argo – integrated global observation strategy

The Argo submersible program is an example of international collaboration with the support of more than 30 nations worldwide.

Argo consists of an array of more than 3800 submersible floats distributed throughout the world's oceans. The array is being used to record real-time data of ocean temperature, salinity and currents.

Submersible floats descend slowly to a depth of 2000 m and drift with the ocean currents while communicating with satellites to register global positioning and transfer data. Measurements of ocean temperature during the submersibles' descents have revealed that warming has extended to at least these recorded depths worldwide.

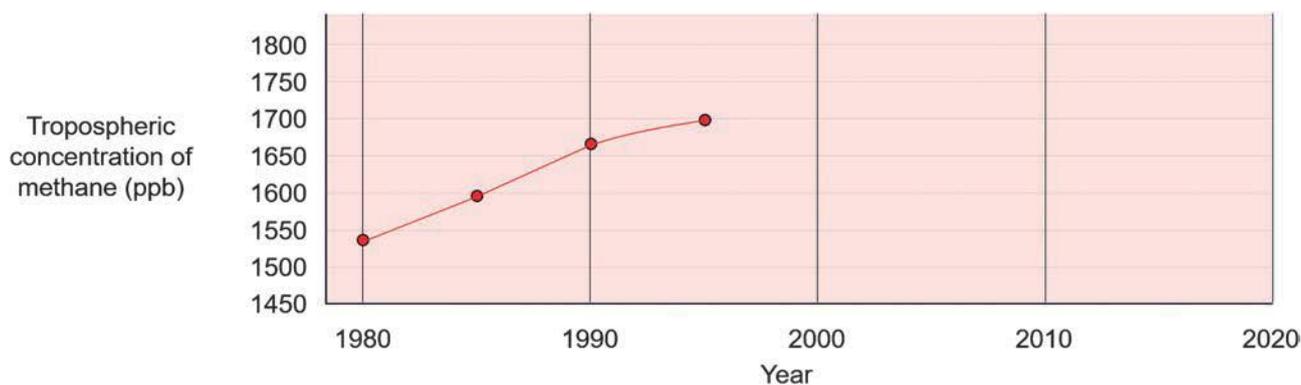


Question

3. Atmospheric methane concentrations have increased steadily over the last century.
- (a) Methane concentrations have been recorded by the CSIRO, at Cape Grim near Tasmania, since 1978. Changes in the atmospheric concentration of methane can be seen in the table and graph below.

Year	Methane concentration (ppb)
1980	1540
1985	1602
1990	1666
1995	1701
2000	1732
2005	1731
2010	1751
2015	1789

Plot the remaining data for methane.



(2 marks) KA4

- (b) Large sinkholes have appeared in regions of Siberia, where trapped methane hydrate deposits in surface ice have suddenly and violently escaped into the atmosphere.

- (i) Methane sinkholes have been appearing more frequently across regions of Siberia in recent years.

Suggest one reason why the rate of formation of methane sinkholes has increased in recent years.

.....
 (1 mark) KA2

- (ii) **Explain** how methane emissions contribute to increased temperature in the Earth's troposphere.

.....

 (3 marks) KA2

- (iii) Methane is approximately 30 times more effective than carbon dioxide as a greenhouse gas. **Suggest**, however, one reason why the contribution of methane to global warming is less significant than carbon dioxide.

.....
 (1 mark) KA2

(c) Methane is also formed from the decay of organic matter in landfill.

(i) **State** one other source of methane derived from human activities.

.....
 (1 mark) **KA1**

(ii) Methane generated in landfill may be collected in pipes below the landfill and burnt as a fuel source to produce electricity.

Discuss one advantage and one disadvantage of this process, in terms of greenhouse emissions.

.....

 (2 marks) **KA3**



Science understanding

Ocean acidification is caused by the ocean absorbing higher levels of carbon dioxide from the atmosphere. Describe and write equations to show how carbon dioxide lowers the pH of the oceans.

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Ocean acidification

A large proportion of the carbon dioxide released from anthropogenic activities is absorbed by the oceans and natural bodies of water (Figure 1.1.12)

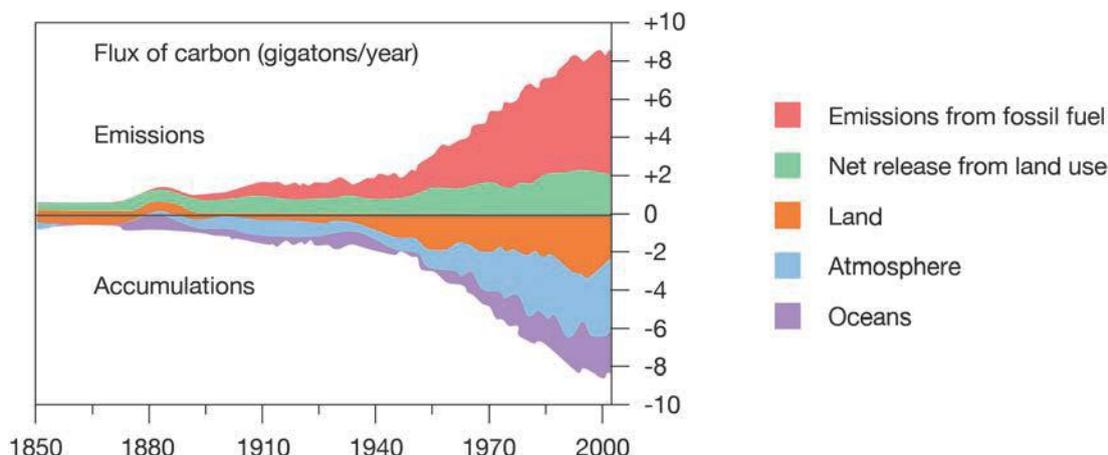
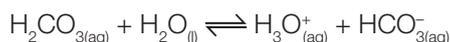


Figure 1.1.12: Carbon dioxide emissions and accumulation

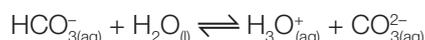
Carbon dioxide is soluble in the sea and reacts to form carbonic acid (H₂CO₃).



Carbonic acid is a weak acid and partially ionises, forming hydronium ions (H₃O⁺) and hydrogencarbonate ions (HCO₃⁻).



Hydrogencarbonate ions further ionise to form carbonate ions (CO₃²⁻). This conversion (H₂CO₃) is pH dependent.



An increase in the concentration of hydronium ions results in a decrease in the pH of the oceans.

The oceans on Earth are slightly alkaline, on average recording a pH of approximately 8.2. Human intervention has seen the pH of the oceans decrease by a value of approximately 0.1. Although this is a small change in pH, it represents a nearly 30% increase in hydronium ion concentration in the oceans.

Science understanding

Calculate the pH of solutions given the concentration of H^+ or OH^- , and vice versa.

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The ionic product of water, K_w

Water is an amphoteric substance that can both donate and accept a proton.



The resulting equilibrium, established at 25°C, results in an equal concentration of both hydronium ions (H_3O^+) and hydroxide ions (OH^-). Both ions are present at a concentration of $1.0 \times 10^{-7} \text{ mol L}^{-1}$ under these conditions.

This relationship gives rise to the following mathematical expression.

$$\begin{aligned} K_w &= [H_3O^+] \times [OH^-] \\ K_w &= (1.0 \times 10^{-7}) \times (1.0 \times 10^{-7}) \\ K_w &= 1.0 \times 10^{-14} \end{aligned}$$

When the negative logarithm is taken for each of the components in the expression, a simpler expression results.

$$\begin{aligned} pK_w &= -\log_{10} (1.0 \times 10^{-14}) = 14 \\ pH &= -\log_{10} [H_3O^+] \\ pOH &= -\log_{10} [OH^-] \\ pH + pOH &= 14 \end{aligned}$$

The concentrations of hydronium ions and hydroxide ions present in solution are extremely small. It is more convenient to express these concentrations as values on the **pH scale**.

pH is calculated from the concentration of hydronium ions present, and represents the **acidity** of an aqueous solution. **pOH** is calculated from the concentration of hydroxide ions present, and represents the **alkalinity** of an aqueous solution.

Calculations of pH and concentration of hydronium ions

To calculate the pH of a solution, the concentration of hydronium ions, $[H_3O^+]$, expressed in mol L^{-1} , is required.

$$pH = -\log_{10} [H_3O^+]$$

For a strong monoprotic acid, the concentration of hydronium ions is equivalent to the concentration of the acid.

Example

Nitric acid is generated in the atmosphere from nitrogen dioxide present in exhaust emissions. This can lead to the formation of acid rain. In one sample of acid rain, the concentration of nitric acid was determined to be $6.31 \times 10^{-5} \text{ L}^{-1}$. Calculate the pH of the sample.

	Explanation	Calculation
STEP 1	Nitric acid is a strong monoprotic acid, therefore the concentration of hydronium ions is equal to the concentration of the acid.	$[H_3O^+] = [HNO_3]$ $\therefore [H_3O^+] = 6.31 \times 10^{-5} \text{ mol L}^{-1}$
STEP 2	The value is substituted into the expression for pH.	$pH = -\log_{10} [H_3O^+]$ $pH = -\log_{10} (6.31 \times 10^{-5})$ $pH = 4.21$

To calculate the concentration of hydronium ions, $[H_3O^+]$, in solution, the pH value is substituted into a rearrangement of the pH equation.

$$[H_3O^+] = 10^{-pH}$$

Example

Acid rain in some industrialised cities has been recorded at pH values as low as 2.4.

Calculate the concentration of hydronium ions at this pH.

	Explanation	Calculation
STEP 1	The pH value is substituted into the expression.	$[H_3O^+] = 10^{-pH}$ $[H_3O^+] = 10^{-2.4}$
STEP 2	Concentration units are applied to the value.	$[H_3O^+] = 3.98 \times 10^{-3} \text{ mol L}^{-1}$

Question

4. Changes in the population and diversity of species of frogs near creeks and rivers can be used to assess the health of a waterway. Some species of frogs are able to tolerate pH values ranging from 6.5 to 4.0.

(a) (i) **Calculate** the concentration of hydronium ions, in mol L^{-1} , at a pH of 6.5 and 4.0 and hence determine the highest concentration of hydronium ions present.

(5 marks) **KA4**

(ii) **State** whether a shift in pH from 6.5 to 4.0 represents an increase or decrease in the acidity of the waterway.

..... (1 mark) **KA1**

(iii) **Explain** why a small shift in pH from 6.5 to 4.0 represents a significant shift in hydronium ion concentration.

.....

 (2 marks) **KA2**

(b) **Suggest** one human activity that could contribute to lowering the pH to a value of 4.0 in the waterway.

.....
 (1 mark) **KA1**

(c) Frog eggs are made from calcium carbonate, CaCO_3 .

Suggest why lowered pH in creeks and rivers may lead to their damage

.....
 (1 mark) **KA2**

Calculations of pOH and pH from the concentration of hydroxide ions

To calculate the pOH of a solution, the concentration of hydroxide ions, $[\text{OH}^-]$, expressed in mol L^{-1} , is required.

$$\text{pOH} = -\log_{10} [\text{OH}^-]$$

For a strong base, the concentration of the hydroxide ions is determined using the formula of the compound. The concentration of the base is multiplied by the number of hydroxide ions, $[\text{OH}^-]$, present in the formula.

To calculate the concentration of hydroxide ions in solution, the pOH value is substituted into a rearrangement of the pH equation.

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

pH is then determined using the equation for the ionic product of water, linking pH to pOH.

$$\text{pH} + \text{pOH} = 14$$

Example

Flue Gas Desulfurization (FGD) is a process used to neutralise sulfur dioxide emissions formed during the generation of electricity in coal-fired power stations. Sulfur dioxide is passed over a wet slurry of sodium hydroxide (NaOH) at a concentration of $0.0100 \text{ mol L}^{-1}$ and calcium hydroxide ($\text{Ca}(\text{OH})_2$) at a concentration of $0.0203 \text{ mol L}^{-1}$.

Calculate the pH of the sodium hydroxide and calcium hydroxide in the solution.

	Explanation	Calculation
STEP 1	Sodium hydroxide is a strong base therefore the concentration of hydroxide ions is equal to the concentration of the formula unit.	$[\text{OH}^-] = [\text{NaOH}]$ $[\text{OH}^-] = 0.0100 \text{ mol L}^{-1}$
STEP 2	The value is substituted into the expression for pOH.	$\text{pOH} = -\log_{10} [\text{OH}^-]$ $\text{pOH} = -\log_{10} (0.0100)$ $\text{pOH} = 2.00$
STEP 3	The equation linking pH to pOH is rearranged and the value for pOH subtracted from 14.	$\text{pH} = 14 - \text{pOH}$ $\text{pH} = 14 - 2.00$ $\text{pH} = 12.0$

	Explanation	Calculation
STEP 1	Calcium hydroxide is a strong base therefore the concentration of hydroxide ions is double the concentration of the formula unit.	$[\text{OH}^-] = 2 \times [\text{Ca}(\text{OH})_2]$ $\therefore [\text{OH}^-] = 2 \times 0.0203$ $[\text{OH}^-] = 0.0406 \text{ mol L}^{-1}$
STEP 2	The value is substituted into the expression for pOH.	$\text{pOH} = -\log_{10} [\text{OH}^-]$ $\text{pOH} = -\log_{10} (0.0406)$ $\text{pOH} = 1.39$
STEP 3	The equation linking pH to pOH is rearranged and the value for pOH subtracted from 14.	$\text{pH} = 14 - \text{pOH}$ $\text{pH} = 14 - 1.49$ $\text{pH} = 12.6$

Science understanding

The skeletons and shells of many marine organisms are made of calcium carbonate and are vulnerable to dissolution at low pH.

Write equations for carbonates reacting in acidic conditions.

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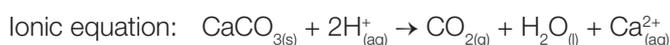
Reaction of acids and carbonates

Acids react with metal carbonates and hydrogen carbonates to form carbon dioxide, water and a salt as products. These reactions can be expressed as both **fully balanced chemical equations** and **ionic equations**.

Example

Calcium carbonate (CaCO_3) is commonly found as limestone in the sedimentary geology of marine environments. Limestone cliffs can be eroded from exposure to sulfuric acid formed in air pollution from nearby industries.

Write a fully balanced chemical equation and an ionic equation for the reaction of sulfuric acid with calcium carbonate.



pH and carbonates

Seawater is saturated (maximum concentration of solute) with calcium carbonate. Marine calcifying organisms build their shells and skeletons from calcium carbonate. A delicate **equilibrium** (the reaction occurs in both forward and backward directions) exists between carbonate and hydrogen carbonate ions in the ocean, which is affected by changes in pH (Figure 1.1.13).

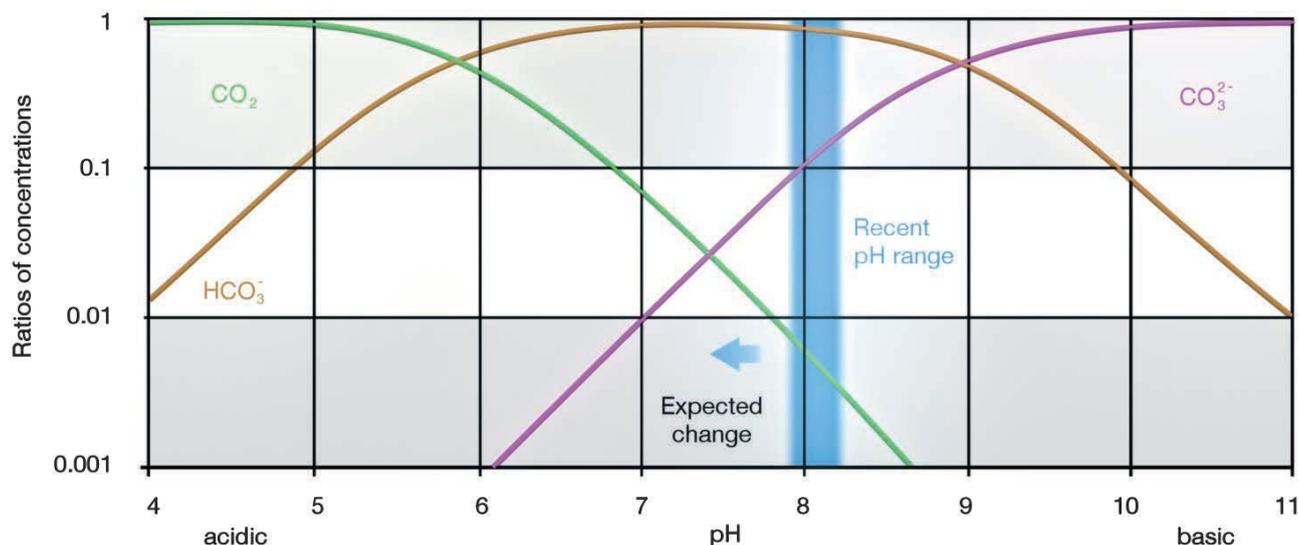


Figure 1.1.13: Chemical species present at varying ocean pH.

As pH decreases, the concentration of available carbonate ions decreases, limiting the ability of marine calcifying organisms to form shells and skeletons. Also as pH decreases, dissolution rates of calcium carbonate increase, weakening calcium carbonate structures of marine species, while also limiting the formation of new structures.

For example, ocean acidification has been found to significantly impact upon the ability of reef-building corals to form exoskeletons (outer skeletons) and reproduce. Ocean acidification has the potential to significantly affect marine ecosystems.

Question

5. Natural bodies of water, such as lakes and oceans, register differing acidity and alkalinity based upon the concentration of dissolved ions present.

(a) Rainwater entering natural bodies of water has a pH of approximately 5.6 due to dissolved carbon dioxide from the atmosphere.

(i) **State** whether this results in a pH of rainwater that is slightly acidic or alkaline.

..... (1 mark) **KA1**

(ii) **Write an equation** for the formation of carbonic acid from carbon dioxide gas dissolving in water in the atmosphere.

(2 marks) **KA4**

(b) Lake Natron in Tanzania has a pH of 10.5 due to sodium carbonate and other minerals flowing into the lake from surrounding hills.

(i) Sodium carbonate can be dissolved by acidic water running through rocks and soil.

Write an ionic equation for the reaction between sodium carbonate and acidic water.

(2 marks) **KA4**

(ii) **Calculate** the concentration of hydroxide ions, in mol L⁻¹, present in the water at a pH of 10.5.

(3 marks) **KA2**

1.2 Photochemical smog

Science understanding

Nitrogen oxides are formed in high-temperature engines and furnaces.

Write equations for the formation of nitrogen oxides NO and NO₂.

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1

Composition of the Earth's atmosphere

The **atmosphere** consists of a complex mixture of gases that form a thin layer surrounding the planet that is critical to sustaining life on Earth. Concentrations of gaseous components are variable in the atmosphere due to natural phenomena and human activity. The average chemical composition of the atmosphere is described in Figure 1.2.1.

Element	Percent by volume (%)	Concentration (ppm)
Major constituents		
nitrogen (N ₂)	78.084	780840
oxygen (O ₂)	20.946	209460
Minor constituents		
argon (Ar)	0.934	9340
carbon dioxide (CO ₂)	0.0400	400
neon (Ne)	0.00182	18.2
helium (He)	0.000524	5.24
methane (CH ₄)	0.000170	1.70
krypton (Kr)	0.000114	1.14
hydrogen (H ₂)	0.0000550	0.550
nitrous oxide (N ₂ O)	0.0000500	0.500
xenon (Xe)	0.00000900	0.0900
ozone (O ₃)	0.00000700	0.0700
nitrogen dioxide (NO ₂)	0.00000200	0.0200
Water		
water vapour (H ₂ O)	Variable between 0.00100 and 5.00	

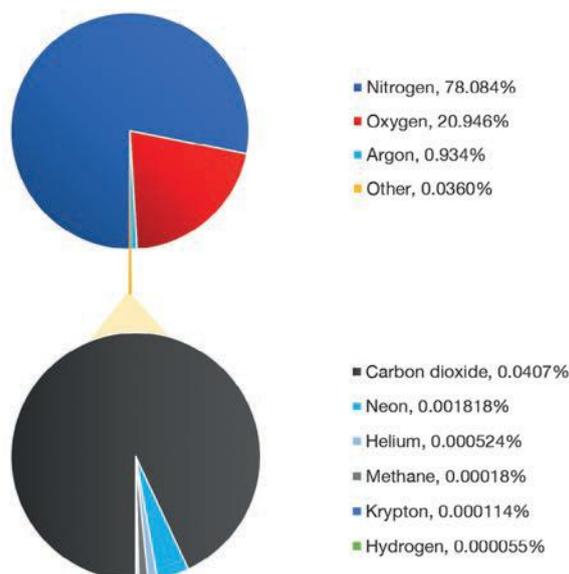


Figure 1.2.1: Average composition of the Earth's atmosphere.

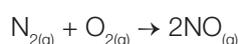
Formation of oxides of nitrogen

Nitrogen (N_2) exists in the atmosphere as a diatomic molecule, with nitrogen atoms held together by a strong covalent triple bond. A large input of energy is required to break the triple bond in the formation of new compounds, hence nitrogen is a relatively stable and inert molecule in the atmosphere.

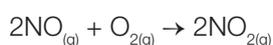
The energy required for the conversion of nitrogen to new compounds can be provided through both natural phenomena and anthropogenic activities.

Natural	Anthropogenic
Lightning	Internal combustion engines
Volcanic activity	Jet engines
Bushfires	Industrial kilns and furnaces

Sufficient energy is provided at the high temperatures encountered during these events to break the existing bonds in nitrogen and oxygen (reactants) and form nitric oxide (NO) (product).



Nitric oxide is further oxidised in the atmosphere to form nitrogen dioxide (NO_2) (product).



Science understanding

Nitrogen oxides and ozone are pollutants in the troposphere that are associated with photochemical smog.

Describe and write equations showing the role of nitrogen oxides in the formation of ozone in the troposphere.

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The troposphere

The troposphere is the lowest layer of the atmosphere (closest to the surface of the Earth; Figure 1.2.2) and its composition is most affected by human activities.

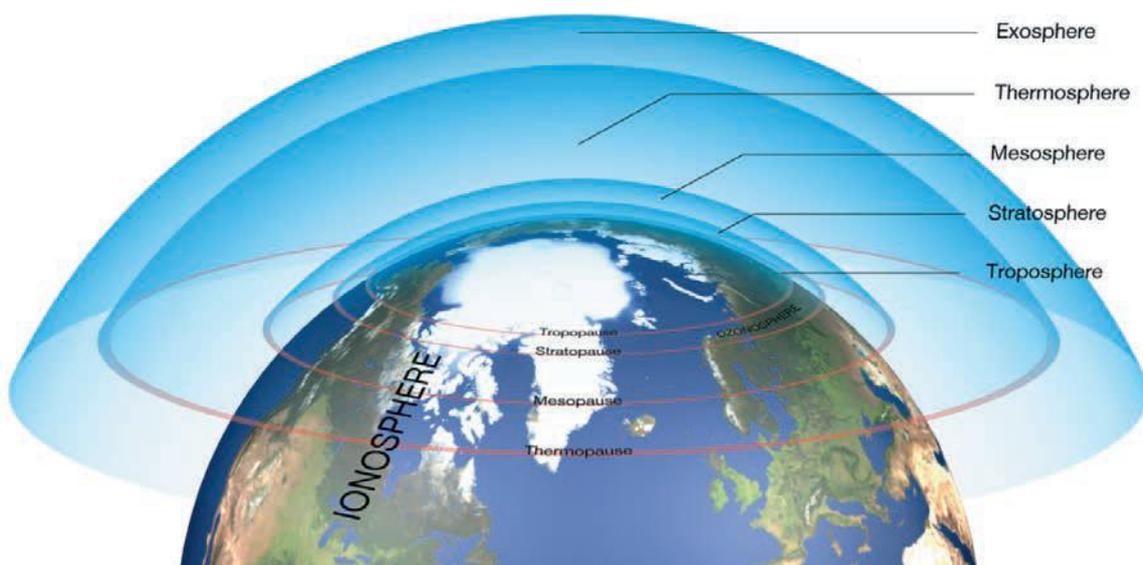


Figure 1.2.2: Layers of the atmosphere.

The troposphere contains a substantial component (75% by mass) of all the gases present in the atmosphere. It also contains nearly all the available water vapour present in the atmosphere. Human activities are responsible for releasing many pollutants directly into the troposphere.

Photochemical smog

Photochemical smog is a complex mixture of chemicals that have been output directly from the source (**primary pollutants**), or formed from the secondary reactions (many involving light and heat) between pollutants and molecules that exist in the atmosphere (**secondary pollutants**).

Photochemical smog is typically experienced in densely populated urban areas, where there is a reliance on the combustion of fossil fuels for transportation, industry, and electricity production. The following conditions are necessary for the formation of photochemical smog.

Condition	Explanation
High concentration of pollutants	Photochemical smog tends to form in densely populated areas in industrialised cities, with concentrations of pollutants changing periodically over the day.
Sunlight	Many reactions in the formation of photochemical smog are initiated by the absorption of ultraviolet radiation (UV) and heat.
Still air mass	Pollution can be dispersed or displaced depending upon prevailing weather patterns.
Temperature inversion	Warmer air containing pollutants becomes trapped between layers of cooler denser air (Figure 1.2.3).

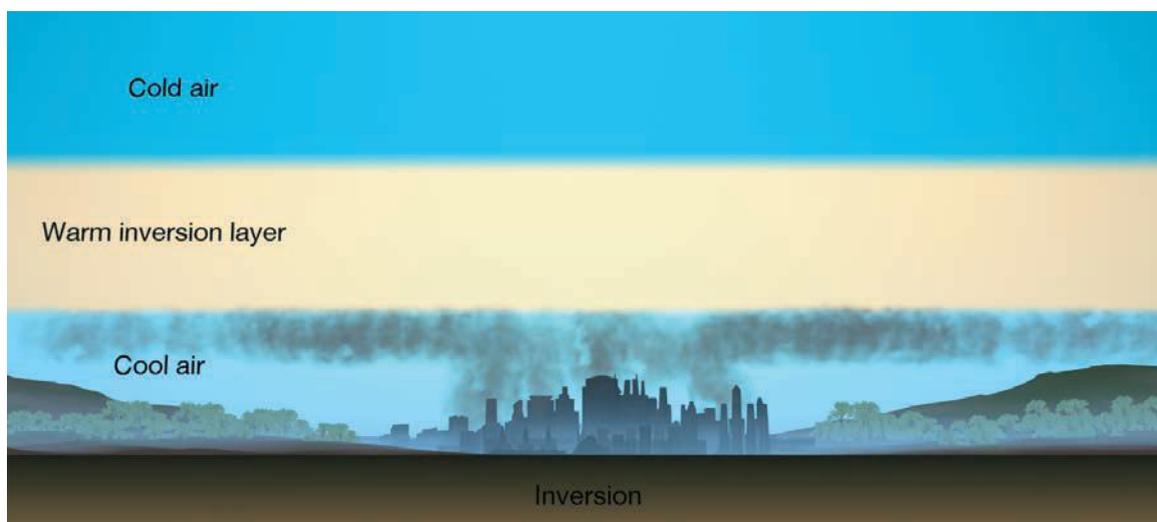
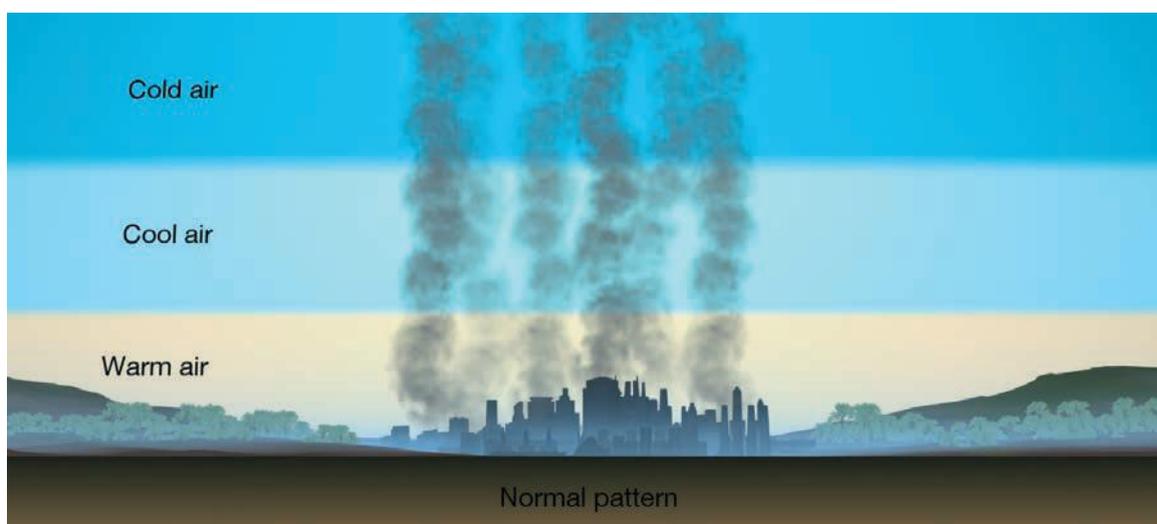


Figure 1.2.3: Temperature inversion during smog formation.

Two of the main components of photochemical smog are ozone (O_3) and nitrogen dioxide (NO_2). The brown haze associated with photochemical smog is due to the presence of nitrogen dioxide gas.

Emissions from motor vehicles are the biggest contributors to the formation of photochemical smog in urbanised areas. When stoichiometric ratios are not met during the combustion of a fuel, many undesirable products are formed. These include carbon (C), carbon monoxide (CO) and volatile organic compounds (VOCs) such as unburnt hydrocarbons.

A large component of the oxides of nitrogen (collectively referred to as NO_x) responsible for photochemical smog come directly from the exhaust emissions of motor vehicles and the high temperatures associated with the combustion of hydrocarbon fuels (petrol, diesel and natural gas) in internal combustion engines.

In densely populated urban areas with heavy traffic flow, transport patterns lead to peak times for emission of primary pollutants and subsequent formation of secondary pollutants (Figure 1.2.4).

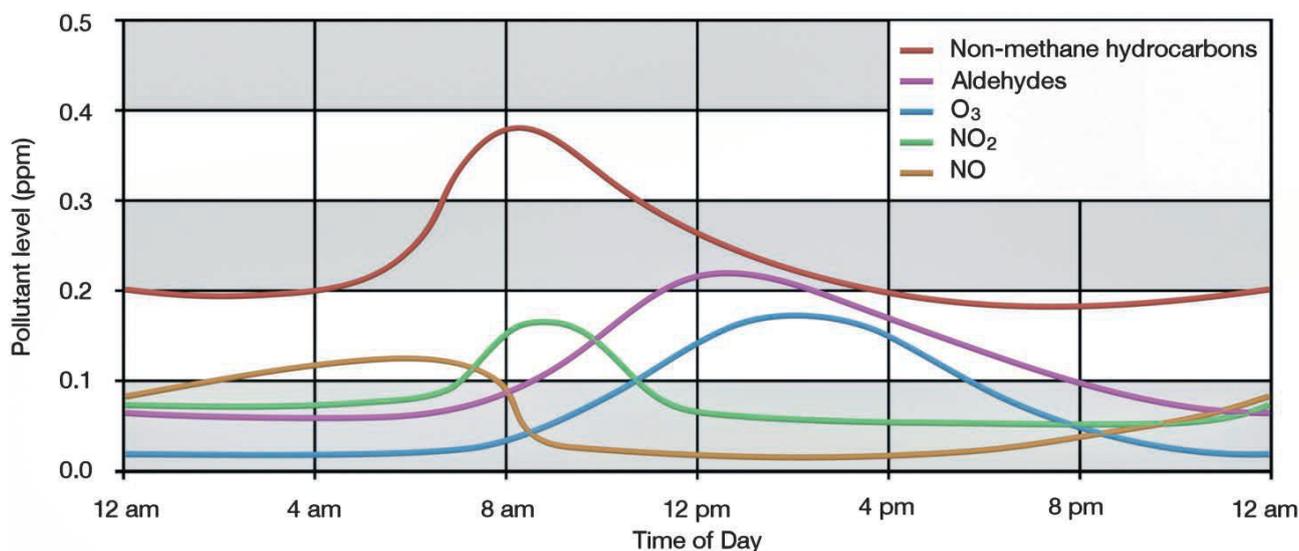
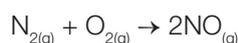


Figure 1.2.4: Pollutant levels over the day in urban cities.

Energy is released when fuel is combusted inside an internal combustion engine. The heat released from the combustion of fuel provides the energy needed to initiate the reaction of nitrogen and oxygen.



Concentrations of nitric oxide peak early in the morning as they are released directly from the exhaust systems of motor vehicles.

Nitric oxide is oxidised during or after exhaust is emitted from a motor vehicle, to form nitrogen dioxide.



Nitrogen dioxide concentrations therefore peak after nitric oxide levels.

At noon (12pm), when ultraviolet radiation concentrations are elevated, nitrogen dioxide photodissociates in the presence of ultraviolet radiation (UV) to form nitric oxide and a highly reactive oxygen radical (O).



The oxygen radical rapidly combines with an oxygen molecule to form ground level (tropospheric) ozone. Therefore, ozone concentrations peak after midday.



Increased concentrations of ozone and the oxides of nitrogen have implications for the natural and built environment.

Question

6. The flight paths, altitudes and burn rates of fuels for aircraft on global flights have been studied in an attempt to reduce their contribution to the formation of nitrogen oxides in the upper troposphere.

(a) Elemental nitrogen is an abundant element in the troposphere. It exists as a diatomic molecule, N₂.

(i) **State** the type of bonding present in the nitrogen molecule.

..... (1 mark) KA1

(ii) **Draw** a diagram to show the bonding and shape of N₂.

(2 marks) KA4

(b) When fuel undergoes combustion in aircraft engines, oxides of nitrogen are produced.

Explain, with the aid of two equations, how nitrogen oxides are produced from aircraft engines.

.....
.....
.....
.....
.....
.....
.....
.....

(4 marks) KA1

(c) Nitrogen dioxide gas (NO₂) is emitted in the exhaust stream of aircraft in flight. Nitrogen dioxide undergoes photodissociation after its emission into the atmosphere.

(i) **State** the type of chemical reaction in which energy is absorbed.

..... (1 mark) KA1

(ii) **Describe**, with the aid of an equation, how the photodissociation of nitrogen dioxide can lead to the formation of ozone.

.....
.....
.....
.....
.....

(3 marks) KA1

(d) Mathematical modelling of fuel burn-rates, altitudes, flight distance, and the extent of intercontinental crossings were analysed in terms of the production of nitrogen oxides, NO_x.

(i) **Suggest** why flight paths are considered in terms of the production of NO_x.

..... (1 mark) KA3

(ii) Modelling of alternative flight paths and altitudes provided evidence of lower emissions for the oxides of nitrogen in some cases, but also higher emissions of carbon dioxide.

Discuss one environmental problem associated with increased carbon dioxide concentrations in the troposphere

.....
.....
.....
.....
.....

(3 marks) KA2

Science understanding

Describe the harmful effects of nitrogen oxides and ozone in the troposphere.

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Effects of photochemical smog

Elevated concentrations of ozone and the oxides of nitrogen present during the formation of photochemical smog can have detrimental effects on humans, animals, plants and synthetic materials, including some polymers.

Humans and animals

Photochemical smog is harmful to humans and animals due to exposure to ozone, oxides of nitrogen and other reactive species. Exposure to elevated concentrations of these pollutants can have severe health effects.

Smog causes eye irritation, as pollutants react in the fluid secreted to lubricate the eyes. Oxides of nitrogen make the fluid more acidic due to the formation of acids such as nitric acid.

Pollutants present in photochemical smog cause respiratory distress. In particular, ozone in photochemical smog irritates and damages respiratory tissue during inhalation. Ozone damages tissues lining the lungs, thus reducing the rate of diffusion of oxygen to the lungs over time. The young, elderly, and those susceptible to asthma, bronchitis and allergies are more severely affected by exposure to increased concentrations of ozone (Figure 1.2.5).



Figure 1.2.5: Photochemical smog in Shanghai.

Plants and vegetation

During photosynthesis, atmospheric gases (including carbon dioxide and ozone) enter gas-exchange pores (stoma) on the surface of leaves.

Exposure to high levels of ozone cause stomata on the leaves of plants to close, limiting the exchange of gases required for photosynthesis. Ozone entering plant cells also undergoes a range of reactions as a strong oxidant, further disrupting photosynthesis and other cell reactions. As a result, plant growth is limited and plants are left more susceptible to disease and extreme weather conditions, such as drought (Figure 1.2.6).

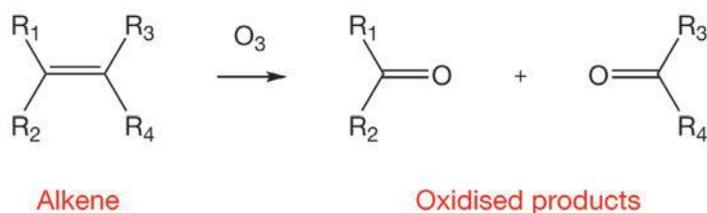


Figure 1.2.6: Leaves exposed to ozone.

Polymers

Ozone can damage **elastomers** (elastic polymers), making these materials more brittle and susceptible to cracking under stress.

Ozone causes degradation of the polymer chains. The carbon-carbon double bonds (C=C) in unsaturated polymers readily undergo reaction with ozone, and saturated polymers undergo slow oxidation.



Ozone breaks cross-links that are comprised of carbon-carbon double bonds, decreasing their frequency in the polymer and causing a reduction in elasticity (Figure 1.2.7). Ozone cleaves the polymer chains where carbon-carbon double bonds exist, producing smaller molecules and thus reducing the strength of interactions due to dispersion forces. As a strong oxidant, ozone also causes changes in the chemical composition of the polymers, resulting in weaker interactions between polymer chains.



Figure 1.2.7: Car tyres (synthetic polymer) cracking due to ozone exposure.

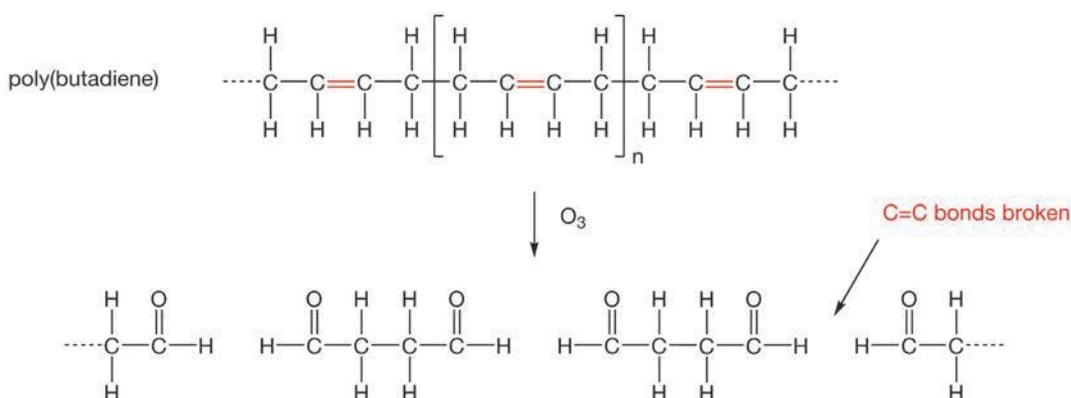


Figure 1.2.8: Degradation of the synthetic polymer chain in poly(butadiene).

Questions

7. Many athletes in highly populated cities are choosing to train indoors due to increased concentrations of photochemical smog and air pollution.
- (a) An Air Quality index, such as the one below, has been developed for schools in the Los Angeles area that are exposed to high levels of ozone from photochemical smog. Recommendations for varying levels of physical activity have been made based on the concentration of ozone in ppm.

	0–50 ppm	51–100 ppm	101–150 ppm	151–200 ppm	201–300 ppm
Activity	Low	Moderate	Unhealthy for sensitive groups	Unhealthy	Extremely unhealthy
Recess (15 minutes)	No restrictions	No restrictions	Make indoor space available for individuals with asthma or respiratory problems	Make indoor space available for any individual experiencing respiratory problems	Restrict all outdoor activities to light exercise
Physical education (1 hour)	No restrictions	Limit intense activity for sensitive groups	Make indoor space available for individuals with asthma or respiratory problems	Make indoor space available for any individual experiencing respiratory problems	Restrict all outdoor activities to light exercise not exceeding 1 hour
Sports training (2–4 hours)	No restrictions	Limit intense activity for sensitive groups	Individuals with asthma, respiratory or cardiovascular disease should medically manage the condition and include rest breaks	Activities over 2 hours should be decreased in intensity and duration and include frequent rest breaks	Sustained rigorous exercise for more than 1 hour must be rescheduled or moved indoors

- (i) **Suggest** one reason why increased physical activity leads to greater exposure to ozone.
-
 (1 mark) **KA1**
- (ii) With reference to the table, **discuss** the conclusions that can be drawn about exposure to ozone from photochemical smog.
-

 (2 marks) **KA3**
- (b) Exposure to ozone leads to respiratory irritation and impaired performance during physical exercise. Oxides of sulfur cause respiratory irritation when they combine with moisture in the lungs to form acids.
- (i) **Write an equation** for the formation of sulfuric acid in the lungs from sulfur trioxide, SO₃.
-
 (2 marks) **KA4**
- (ii) **State** the effect of the ionisation of sulfuric acid on the pH of the moisture in the lungs.
- (1 mark) **KA1**

(ii) VOCs and nitrogen dioxide, NO_2 , are responsible for the formation of ozone in the lower atmosphere.

Write equations to show the formation of ozone from nitrogen dioxide.

(4 marks) **KA4**

(b) High-voltage electrical discharges (from the use of photocopiers and laser printers) result in ozone formation. Small quantities of ozone are released by these office machines; health concerns have been expressed about these machines being placed in poorly ventilated areas.

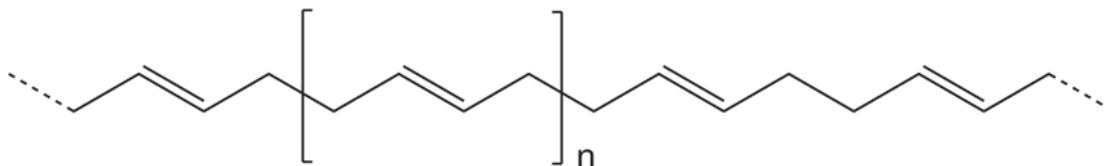
(i) **State** why ventilation is required.

.....
 (1 mark) **KA1**

(ii) **State** one harmful effect on humans from exposure to high concentrations of ozone.

.....
 (1 mark) **KA1**

(c) Photocopier components such as rollers are made from synthetic rubber. The structure of the synthetic rubber polybutadiene is shown below.



(i) **State** whether or not this polymer has been formed from an addition reaction.

..... (1 mark) **KA1**

(ii) **Draw** the monomer of polybutadiene.

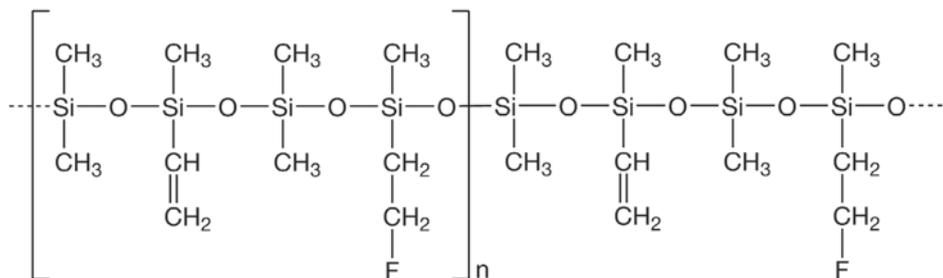
(2 marks) **KA4**

(iii) **Describe** one disadvantage of exposing synthetic rubber to ozone.

.....

 (2 marks) **KA2**

- (iv) Silicone rollers can also be used in photocopiers. The structure of a silicone-based polymer is shown below.



Suggest one reason why this polymer would be preferable to synthetic rubber for use in a photocopier.

.....
 (1 mark) **KA2**

Science understanding

Describe and write equations showing how catalytic converters reduce the quantities of nitrogen oxides generated by motor vehicles

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Catalytic converters

Catalytic converters were introduced into the exhaust system of motor vehicles to reduce the impact of pollutants released as exhaust emissions. When operating temperatures have been achieved and air to fuel stoichiometric ratios are maintained within a suitable range, catalytic converters are able to convert a number of the precursor compounds of photochemical smog to less harmful products.

Science as a human endeavour

Catalytic converters

The catalytic converter was first invented by the French mechanical engineer, Eugene Houdry, who was living in America in the 1950s. He was concerned with the findings of early studies in Los Angeles that linked air pollution to exhaust emissions from motor vehicles and industry. Houdry founded the company Oxy-Catalyst to develop catalytic converters for industry and, later, motor vehicles.

Two-way catalytic converters were used in the 1970s with increased awareness of pollutants and interest in their methods of reduction. These were phased out in 1981 when three-way converters were introduced. Three-way converters continue to be used in motor vehicles today.

The platinum-group metals, used as the catalysts in modern three-way catalytic converters, are rare and expensive. Nanotechnology is being applied to disperse nano-sized particles of these precious metals onto the porous bed of the converter. As the surface area to volume ratio is greatly increased, the rate of surface-catalysed reactions increases. This limits the quantity of precious metal required by the converter. This allows an effective converter to be produced at a lower cost.



Three-way catalytic converters

Current three-way catalytic converters typically consist of a porous ceramic (cordierite) block with parallel channels along the length to allow for the flow of exhaust emissions. The porous ceramic block is coated with a thin layer of highly porous alumina (aluminium oxide), with very small amounts of the precious platinum-group metals (platinum, palladium and rhodium) bonded to the surface in the alumina coating at varying percentages (Figure 1.2.10).

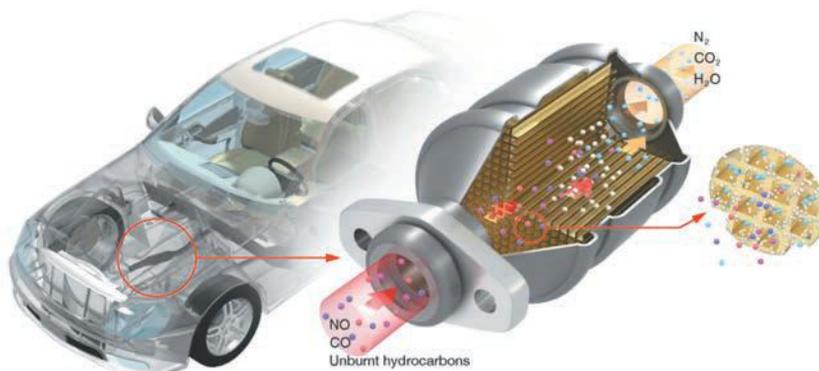


Figure 1.2.10: Three-way catalytic converter.

Exceptional surface area is achieved through the use of channels and the porosity of the alumina, providing greater opportunity for hot exhaust gases passing through to contact the metal catalysts and thus increase the rate of reaction.

The purpose of the three-way catalyst is to simultaneously remove carbon monoxide, oxides of nitrogen, and unburnt hydrocarbon components of the fuel through catalysed redox reactions.

Carbon monoxide

The adsorption of carbon monoxide and oxygen onto the surface of the three metals, in particular palladium, catalyses the oxidation of carbon monoxide to carbon dioxide (Figure 1.2.11).

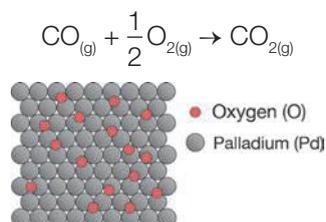
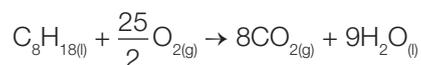


Figure 1.2.11: Oxygen atoms on the surface of a palladium catalyst.

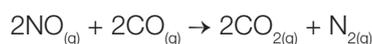
Unburnt hydrocarbons

The adsorption of hydrocarbons (saturated, unsaturated and aromatic) onto the surface of the metals, in particular platinum, catalyses their oxidation.



Nitric oxide

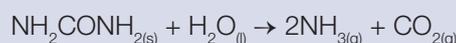
Nitric oxide can be removed by reduction with carbon monoxide. Of the three platinum-group metals, rhodium is the most effective component for catalysing this reaction.



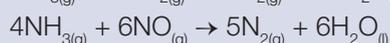
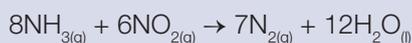
Science as a human endeavour

Catalysts used in diesel engines

Oxides of nitrogen can be removed from diesel emissions through selective catalytic reduction (SCR). SCR involves the addition of urea into the exhaust system where it forms ammonia.



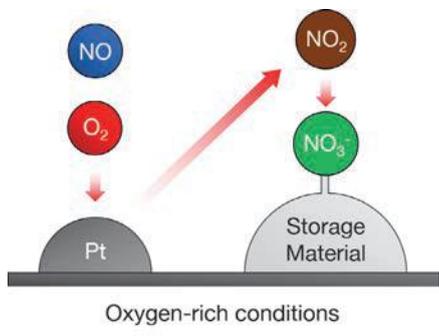
The ammonia adsorbs onto a catalyst such as vanadium oxide, to catalyse the formation of nitrogen and water.





Question

9. Lean Nitrogen Oxide Traps (LNT) have been developed for lean-burning (oxygen-rich combustion) internal combustion engines, such as diesel engines. The aim of LNTs is to reduce emissions of oxides of nitrogen.
- (a) Under lean, oxygen-rich conditions, nitric oxide (NO) undergoes oxidation to nitrogen dioxide (NO₂) in the presence of a platinum catalyst.



- (i) **Describe** one advantage of reducing motor vehicle emissions of oxides of nitrogen.
-
-
-
- (2 marks) **KA1**

- (ii) **Write an equation** for the conversion of nitric oxide to nitrogen dioxide.
-
- (2 marks) **KA4**

(b) Nitrogen dioxide is temporarily adsorbed onto the surface of a zeolite (porous silicate) material as nitrate ions, NO₃⁻.

- (i) **State and explain** whether this conversion represents an oxidation or reduction reaction.
-
-
-
- (3 marks) **KA2**

Eventually the zeolite material becomes completely coated with adsorbed nitrate ions. The surface is flushed with diesel fuel to generate rich, oxygen-deprived conditions. During these conditions, nitric oxide (NO) and carbon monoxide (CO) are generated in higher concentrations and sent through a catalytic converter.

- (ii) **State** the type of combustion in which carbon monoxide is a product.
- (1 mark) **KA1**
- (iii) **State** one advantage of the catalytic converter having a highly porous structure.
-
- (1 mark) **KA1**
- (iv) **Write a balanced equation** for the conversion of nitric oxide and carbon monoxide to nitrogen and carbon dioxide.

(2 marks) **KA4**

1.3 Volumetric analysis

Science understanding

Concentrations can be described by using a number of standard conventions.

Calculate concentration and interconvert units, including: mol L⁻¹, g L⁻¹, %w/v, ppm, and ppb.

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Volumetric analysis

Volumetric analysis is a **quantitative** analytical technique used to determine amounts or concentrations of unknown reagents. Calculations are applied to fixed stoichiometric ratios in chemical reactions. A **titration** is a laboratory procedure undertaken to determine these concentrations through measured quantities.

Titration is widely used in monitoring concentrations in the environment, and in the quality control of consumer products. Examples of where quantitative analysis may be used include water quality checks, wine production, and in administering some medicines.

In these applications, the concentrations measured may vary considerably. Because of this, a range of units are applied as standard convention, to allow concentrations to be expressed appropriately.

Review of quantities

Measuring and calculating quantities related to moles and concentration requires a working knowledge of a range of units.

Quantity	Symbol	Definition	Unit
Mass	m	A measure of the amount of matter.	g
Volume	V	The space that a substance occupies.	L (dm ³)
Density	ρ	The mass per unit volume.	kg L ⁻¹
Avogadro's constant	N _A	The number of fundamental particles contained in exactly 12 g of carbon-12 is 6.022 × 10 ²³ , this number represents Avogadro's constant.	
Mole	n	Measure of the amount of fundamental particles (atoms, ions, molecules, formula units) in a given mass of material.	mol
Molar mass	M	The mass of one mole of a substance.	g mol ⁻¹

Derivation of equations from units

Equations encountered in volumetric analysis can be derived from units using **dimensional analysis** (an analysis of the relationship between quantities).

Mass and moles

Equations for both mass and moles can be derived from the unit of molar mass.

Molar mass

$$M = \frac{\text{g}}{\text{mol}} = \frac{m}{n} \quad \text{rearrangements} \quad n = \frac{m}{M} \quad \text{and} \quad m = n \times M$$

Question

10. Platinum, palladium and rhodium are present in three-way catalytic converters in motor vehicles in varying quantities.

(a) A catalytic converter from a truck was analysed to determine the mass of each element present.

Complete the table, calculating the mass and moles for each element:

Element	Symbol	Atomic mass	m (g)	n (mol)
platinum	Pt	195.1	2.93	
palladium	Pd	106.4		0.0325
rhodium	Rh	102.9	8.61	

(3 marks) **KA2**

(b) Developments in materials science have allowed chemists to bind platinum nanoparticles to nanofibers on the surface of catalytic converters.

Suggest one advantage of the use of nanoparticles of platinum.

.....
 (1 mark) **KA3**

Mass concentration and molar concentration

Equations for mass and concentration can be derived from their respective units.

Mass concentration represents the mass, in grams, of solute per litre of solution.

Mass concentration (ρ) g L⁻¹

$$\rho = \frac{\text{g}}{\text{L}} = \frac{m}{V} \quad \text{rearrangements} \quad V = \frac{m}{\rho} \quad \text{and} \quad m = \rho \times V$$

Molar concentration (also referred to as molarity) represents the moles of solute, in mol, per litre of solution.

The units of molar concentration are moles per litre (mol L⁻¹).

$$c = \frac{\text{mol}}{\text{L}} = \frac{n}{V} \quad \text{rearrangements} \quad V = \frac{n}{c} \quad \text{and} \quad n = c \times V$$

Percentage weight per unit volume represents the mass of solute, in grams, per 100 mL of solution.

Percentage weight per unit volume (c) %w/v.

$$\frac{\text{g}}{100 \text{ mL}} = \frac{m}{V} \times 100\%$$

Concentration conversions

Multiple conventions are used to convey concentration, which are often linked to a specific application. Monitoring trace amounts of substances in bodies of water and the atmosphere may require the application of units in the range of **parts per million (ppm)** or **parts per billion (ppb)**. The concentration of commercial products is more commonly expressed as percentage weight per volume (%w/v).

Commonly encountered concentration units include: mole per litre (mol L^{-1}), gram per litre (g L^{-1}), parts per million (ppm), part per billion (ppb) and percentage weight per unit volume (%w/v). Interconversion can be undertaken between concentration units (Figure 1.3.4).

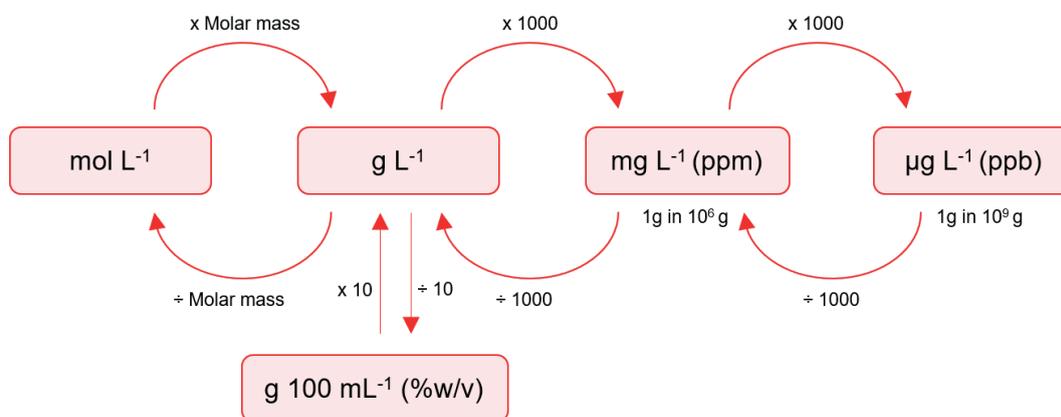


Figure 1.3.1: Processes for concentration conversions.

Simple conversions

Simple conversions require the application of an appropriate factor or the calculation of moles or mass.

Worked example

Monochloramine (NH_2Cl) can be used as a disinfectant in water supplies as an alternative to chlorine due to its greater stability. Monochloramine can be added to the water supply at what is considered a safe concentration of 4.0 ppm.

- (a) **Calculate** this concentration in %w/v.

	Explanation	Calculation
STEP 1	Equate ppm with mg L^{-1} .	$4.0 \text{ ppm} = 4.0 \text{ mg L}^{-1}$
STEP 2	Convert from mg L^{-1} to g L^{-1} by dividing by a factor of 10^3 .	$\frac{\text{mg}}{\text{L}} \div 10^3 = \frac{\text{g}}{\text{L}}$ $= \frac{4.0}{10^3} = 0.0040 \text{ g L}^{-1}$
STEP 3	Convert from g L^{-1} to g 100 mL^{-1} by dividing by 10. Equate g per 100 mL^{-1} with %w/v.	$= \frac{0.0040}{10} = 0.00040$ $= 4.0 \times 10^{-4} \text{ g 100 mL}^{-1}$

Question

11. Bottled water is analysed for trace elements, a number of which are required to be displayed on packaging. Analysis of one brand of bottled water produced the following results.

		Atomic mass	Concentration units			
		g mol ⁻¹	mol L ⁻¹	g L ⁻¹	ppm	ppb
lead	Pb	207.2		0.00020		
cadmium	Cd	112.4	9.65 × 10 ⁻⁷			
arsenic	As	74.92			0.050	
mercury	Hg	200.6				180
zinc	Zn	65.38			4.0	
selenium	Se	78.96		0.0015		
sodium	Na	22.99	6.05 × 10 ⁻⁴	0.0139	13.9	13900
calcium	Ca	40.08	2.07 × 10 ⁻⁴	0.0083	8.3	8300
magnesium	Mg	24.31	5.64 × 10 ⁻⁴	0.0137	13.7	13700

- (a) Complete the table above by calculating the unknown concentrations.

(4 marks) KA2

- (b) Sodium, calcium and magnesium concentrations are commonly displayed on bottled water.
- (i) Arsenic is lethal to humans at a concentration of 763 ppm. Calculate the volume of bottled water, containing arsenic at a concentration of 0.05 ppm, required to reach lethal levels in a 55.0 kg adult.

(3 marks) KA4

- (ii) Suggest one reason why it is important to analyse other elements, even if their values are not displayed.

.....
 (1 mark) KA3

Complex conversions

Complex conversions require the construction and rearrangement of statements through dimensional analysis.

Worked example

Sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$), sodium fluoride (NaF) and tin(II) fluoride (SnF_2) are common sources of fluoride in toothpaste. There are health concerns related to absorption of high levels of fluoride in human beings.

- (a) **Calculate** the percentage composition of F in $\text{Na}_2\text{PO}_3\text{F}$.

	Explanation	Calculation
STEP 1	Percentage composition represents the molar mass of the element expressed as a percentage of the molar mass of the compound. Determine the atomic mass of fluorine and the molar mass of sodium mono fluoride. Substitute the values into the equation and calculate the %.	$\% \text{ composition} = \frac{M(\text{element})}{M(\text{compound})} \times 100$ $= \frac{19.00}{((2 \times 22.99) + 30.97 + (3 \times 16.00) + 19.00)} \times 100$ $= \frac{19.00}{143.95} \times 100 = 13.20\%$

- (b) In one brand of toothpaste the fluoride concentration is 13 g kg^{-1} .

- (i) **Calculate** the percentage, by mass, of fluoride in the toothpaste.

	Explanation	Calculation
STEP 1	Percentage mass (also referred to as %w/w) represents the mass of an element as a percentage of the mass of the compound or mixture.	$\%w/w = \frac{m(\text{element})}{m(\text{compound})} \times 100$
STEP 2	Recognise that percentage represents a number out of 100. Analyse the unit of g per kg and convert to g for both.	$13 \text{ g in } 1 \text{ kg}$ $= 13 \text{ g in } 1000 \text{ g}$
STEP 3	Convert to a mass out of 100 g.	$= 1.3 \text{ g in } 100 \text{ g} = 1.3\%$

- (ii) A 32 kg child uses 0.80 g of a 110 g tube of the toothpaste to brush their teeth and swallows all of the toothpaste while brushing.

Calculate the concentration, in ppm, of fluoride that the child consumes.

	Explanation	Calculation
STEP 1	Concentration of fluoride is 13 g in 1 kg or 1.3% by mass.	$13 \text{ g in } 1 \text{ kg} = 1.3\%$
STEP 2	Multiply the 0.8 g consumed by 1.3%.	$= 0.8 \times 0.013$ $= 0.0104 \text{ g}$
STEP 3	Consider that the mass of fluoride calculated is now contained in a 32 kg child.	$= 0.0104 \text{ g in } 32 \text{ kg}$
STEP 4	Calculate the mass, in g, of fluoride in 1 kg.	$= \frac{0.0104}{32} \text{ g in } 1 \text{ kg}$
STEP 5	Calculate the mass, in mg, of fluoride in 1 kg. Equate that $1 \text{ mg kg}^{-1} = 1 \text{ mg L}^{-1} = \text{ppm}$.	$= \frac{0.0104}{32} \times 10^3 \text{ mg in } 1 \text{ kg}$ $= 0.33 \text{ ppm}$

Question

12. Swordfish contains some of the highest recorded levels of mercury due to biomagnification (increased concentration through the food chain) in this deep-sea species. Mercury is absorbed in the fish as methyl mercury.
- (a) **Calculate** the mass of mercury, in mg, contained in a 150 g portion of swordfish with a mercury concentration of 0.995 ppm.

(3 marks) **KA2**

- (b) **Calculate** the concentration of mercury, in ppm, present in a 75 kg adult who has consumed 150 g of swordfish containing mercury at a concentration of 0.995 ppm.

(3 marks) **KA2**

- (c) Mercury is a cumulative poison, building in concentration through repeated consumption or exposure. It has been recommended that people should not consume seafood with mercury levels above 1 ppm.

General population	Children (up to 6)	Pregnant women
2–3 serves of any fish or seafood not listed below	2–3 serves of any fish or seafood not listed below	2–3 serves of any fish or seafood not listed below
OR	OR	OR
1 serve per week of shark, marlin, or swordfish	1 serve per fortnight of shark, marlin, or swordfish	1 serve per fortnight of shark, marlin, or swordfish

Explain the recommendations made, for the daily intake of fish and seafood for the general population compared to children, and pregnant women.

.....

.....

.....

..... (2 marks) **KA3**

Science understanding

Apply SI prefix conventions to quantities.

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? Science inquiry skills

Skills in context

Scientific notation and SI prefixes

Measurements and calculations in chemistry often require the representation of values as either very large or very small numbers. These numbers can be made more manageable by applying SI prefixes. Each SI prefix has a prefix symbol as well as a unit symbol.

Unit prefix	Unit prefix symbol	Multiplying Factor		Examples	
				Unit name	Unit symbol
tera	T	1 000 000 000 000	10^{12}	terawatt	TW
giga	G	1 000 000 000	10^9	gigalitre	GL
mega	M	1 000 000	10^6	megajoule	MJ
kilo	k	1 000	10^3	kilogram	kg
-	-	1	10^0	-	-
milli	m	0.001	10^{-3}	millimole	mmol
micro	μ	0.000 001	10^{-6}	microlitre	μL
nano	n	0.000 000 001	10^{-9}	nanometre	nm
pico	p	0.000 000 000 001	10^{-12}	picogram	pg

Both large and small numbers are often expressed in chemistry using scientific notation. Scientific notation allows for the number of significant figures to be clearly expressed.

Example

The following table expresses values as integers and in scientific notation for quantities in the biosphere.

Example	Integer	Scientific notation	Unit	Significant figures
Volume of fresh water on Earth	10 530 000	1.053×10^7	kL	4
Concentration of H^+ in acid rain at a pH of 5.6	0.00002512	2.512×10^{-5}	mol L^{-1}	4
Concentration of atmospheric CO_2	404	4.04×10^2	ppm	3

Science understanding

Knowledge of the mole ratios of reactants can be used in quantitative calculations.

Perform stoichiometric calculations when given the reaction equation and the necessary data.

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Stoichiometry

Stoichiometry uses the ratios obtained from balanced chemical equations to determine unknown quantities from known quantities.

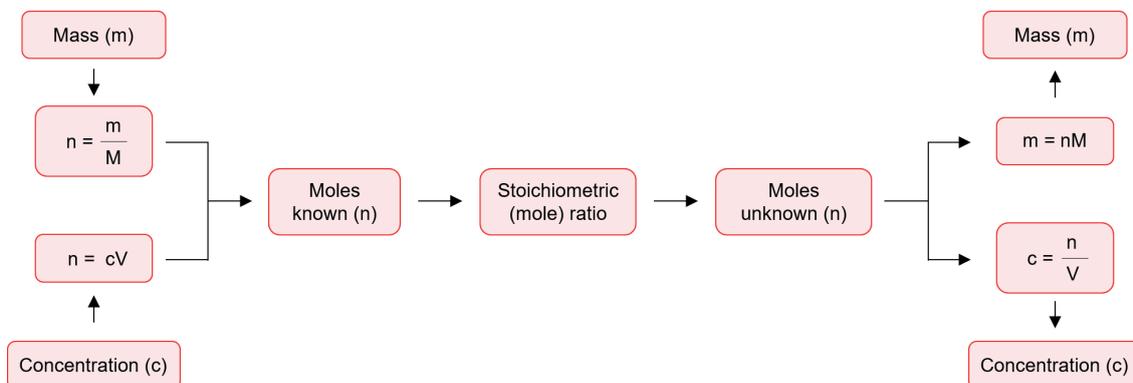


Figure 1.3.2: Processes for stoichiometric calculations.

Mass–mass stoichiometry

The moles are determined from the mass of a known species. A stoichiometric (mole) ratio is applied to the unknown species and then the mass is determined.



Science as a human endeavour

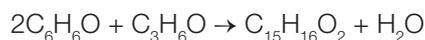
Bisphenol A (BPA) as a synthetic molecule has been used in the production of polycarbonate and as a coating on some food and beverage container packaging.

Health concerns have been expressed over the use of BPA for food packaging, in particular beverages stored in polycarbonate. Current studies have not provided sufficient evidence of the absorption of BPA compounds at levels that are considered to be detrimental to human health. Some countries, such as France, have taken precautionary action to place BPA products on a register of substances of very high concern.

Worked example

Bisphenol A (BPA) is a synthetic molecule used in the formation of the group of polymers called polycarbonates. Polycarbonates are often used to store food and water.

- (a) Bisphenol A can be formed from the condensation reaction between phenol (C_6H_6O) and propanone (C_3H_6O) shown in the equation below.



Approximately 3.6×10^6 tonnes of BPA is used by manufacturers each year.

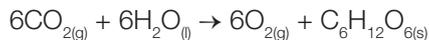
Calculate the mass, in kg, of phenol that would be required to produce this quantity of BPA.

	Explanation	Calculation
STEP 1	Convert the mass of the known (BPA) into grams. Calculate the molar mass of BPA.	$m = 3.6 \times 10^6 \times 10^6 \text{ g}$ $M(C_{15}H_{16}O_2) = ((15 \times 12.01) + (16 \times 1.008) + (2 \times 16.00))$ $= 228.278 \text{ g mol}^{-1}$
STEP 2	Calculate the number of moles of BPA.	$n = \frac{m}{M}$ $= \frac{3.6 \times 10^{12}}{228.278}$ $= 1.577 \times 10^{10} \text{ mol}$
STEP 3	Apply the stoichiometric ratio to determine the unknown moles of phenol.	$= \frac{n(\text{phenol})}{n(\text{BPA})} = \frac{2}{1}$ $n(\text{phenol}) = 2 \times n(\text{BPA})$ $= 2 \times 1.577 \times 10^{10} \text{ mol}$ $= 3.154 \times 10^{10} \text{ mol}$
STEP 4	Calculate the molar mass of phenol. Calculate the mass of phenol from the moles and molar mass.	$M(C_6H_6O) = ((6 \times 12.01) + (6 \times 1.008) + (16.00))$ $= 94.108 \text{ g mol}^{-1}$ $m = n \times M$ $= 3.15 \times 10^{10} \times 94.108$ $= 2.968 \times 10^{12} \text{ g} = 2.968 \times 10^9 \text{ kg}$

Question

13. A mature eucalypt tree can absorb 21.8 kg of carbon dioxide per year.

(a) Carbon dioxide is converted into glucose through photosynthesis, shown in the equation below:



(i) **Calculate** the mass of glucose, in kg, formed by a mature eucalypt tree in one year.

(6 marks) **KA4**

(ii) **Calculate** the mass of oxygen, in g, generated by a mature eucalypt tree in one year.

(3 marks) **KA4**

(b) The average vehicle produces approximately 4.7 tonnes (1 tonne = 1000 kg) of carbon dioxide per year.

(i) **Calculate** the number of mature eucalypt trees required to offset the annual emissions of carbon dioxide from one motor vehicle.

(2 marks) **KA4**

(ii) **State** one conclusion that can be drawn from these findings.

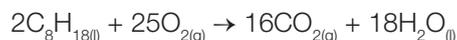
.
 (1 mark) **KA3**

Limiting-excess calculations

In some cases, the number of moles of reactants present is not consistent with the stoichiometric ratio. In these instances, one reagent will limit, through the stoichiometric ratio, the consumption of other reagents and hence the amount of products that may be formed.

Worked example

Octane, a component of petrol, undergoes combustion according to the following equation.

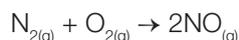


The mass of one litre of octane is 692 g. If this mass of octane underwent combustion with 3.0×10^3 g of oxygen, determine the limiting reagent and hence calculate the mass of carbon dioxide produced per litre of octane undergoing combustion.

	Explanation	Calculation
STEP 1	Calculate the moles available from both reactant species using the mass and molar mass for both octane and oxygen.	$n = \frac{m}{M}$ $n(\text{C}_8\text{H}_{18}) = \frac{692}{114.224} = 6.058 \text{ mol}$ $n(\text{O}_2) = \frac{3000}{32.00} = 93.75 \text{ mol}$
STEP 2	Consider the stoichiometric ratio applied to reactants. Determine which reactant is completely consumed (the limiting reagent) and which has moles remaining (the excess reagent).	$n(\text{C}_8\text{H}_{18}) : n(\text{O}_2) = 2:25$ $6.058:75.72 \text{ (can be achieved)}$ $7.50:93.75 \text{ (cannot be achieved)}$ <p>\therefore octane is the limiting reagent</p>
STEP 3	Using the number of moles from the limiting reagent and the stoichiometric ratio, determine the number of moles of carbon dioxide produced.	$= \frac{n(\text{CO}_2)}{n(\text{C}_8\text{H}_{18})} = \frac{8}{1}$ $n(\text{CO}_2) = c(\text{C}_8\text{H}_{18}) \times 8$ $= 48.446 \text{ mol}$
STEP 4	Using the molar mass of carbon dioxide, and the calculated number of moles, calculate the mass of carbon dioxide.	$M(\text{CO}_2) = (12.01 + (2 \times 16.00))$ $= 44.01 \text{ g mol}^{-1}$ $m = n \times M$ $= 48.446 \times 44.01 = 2133 \text{ g}$

Question

14. The high temperatures generated in an internal combustion engine allow the formation of nitric oxide according to the equation below:



0.300 g of oxygen (O_2) and 1.60 g of nitrogen (N_2) were available as diatomic molecules in 1 L of air that had been heated to a very high temperature.

- (a) **Determine** the limiting reagent.

(5 marks) **KA4**

- (b) Hence, **calculate** the mass of nitric oxide produced.

(4 marks) **KA4**



Science as a human endeavour

Bio-Active methods

Trials are being undertaken wherein exhaust recycling systems are fitted to tractors during seeding. The exhaust emissions from diesel engines are diverted through pipes into freshly cultivated soil. Carbon dioxide and oxides of nitrogen enter the soil and are thought, through this agitation, to increase microbial activity.

Field tests have shown increases in soil nutrient levels, crop productivity, and protein levels in crops. Trials comparing renewable biodiesel with diesel derived from fossil fuels have indicated that both fuels are able to generate higher crop yields when used in the Bio-Active method.

Dilution

Dilution allows solutions of higher concentrations to be accurately made up at lower concentrations. This is important in volumetric analysis where working concentrations and volumes need to remain relatively low.

Serial dilutions may also be used to generate sets of solutions from a single standard, for the construction of calibration graphs in instrumental analysis. Many consumer products also require dilution before use. Examples include garden fertilisers and flavouring used to make up carbonated drinks.

Typically, dilution is achieved through the addition of solvent to a volume of an existing solution (Figure 1.3.3). In this procedure, the measured volume contains a set number of moles of solute which remains unchanged. The fixed moles of solute are distributed through the diluted solution on the addition of solvent to a desired volume. An expression for dilution can be derived by equating the number of moles.

$$c_{\text{original}} = \frac{n_{\text{original}}}{V_{\text{original}}} \text{ and } c_{\text{diluted}} = \frac{n_{\text{diluted}}}{V_{\text{diluted}}}$$

$$n_{\text{original}} = n_{\text{diluted}} \text{ therefore } c_{\text{original}} \times V_{\text{original}} = c_{\text{diluted}} \times V_{\text{diluted}}$$

$$c_1 \times V_1 = c_2 \times V_2$$



Figure 1.3.3: Stages in dilution.

Worked example

Copper sulfate is added, in low concentrations, to waterways and reservoirs to control the growth of blue-green algae.

Mount Bold reservoir in the Adelaide Hills required the upper level of the water to be treated with a volume of 1.848 GL of water. 1000 L of concentrated copper sulfate solution was added to achieve a final concentration of 1.800 ppm. Calculate the concentration of the original solution.

	Explanation	Calculation
STEP 1	Identify the values which represent c_1 , V_1 , c_2 and V_2 from the information provided, hence identify the unknown.	$c_1 \times V_1 = c_2 \times V_2$
STEP 2	Rearrange the equation to determine the unknown variable.	$c_1 = \frac{c_2 \times V_2}{V_1}$
STEP 3	Substitute the known values into the equation and calculate the unknown.	$c_1 = \frac{1.8 \times 1.848 \times 10^9}{1000}$ $c_1 = 3.326 \times 10^7 \text{ ppm}$

Question**1**

15. The herbicide DCMU, commercially known as Diuron[®], is used to control weeds in a range of cereal crops across Australia. Farmers purchase the herbicide in drums at a concentration of 900 g L^{-1} . The concentrated herbicide is then diluted to a recommended concentration suitable for spraying onto crops.
- (a) **Calculate** the concentration of the commercial stock herbicide, in mol L^{-1} , given that the molar mass of Diuron[®] is 233.1 g mol^{-1} .

(2 marks) **KA4**

- (b) In one application of the herbicide, two 20 L drums of Diuron[®] were added to a spray unit of 6000 L capacity and diluted with water.

Calculate the final concentration of the diluted solution, in mol L^{-1} .

(3 marks) **KA4**

Science understanding

A titration can be used to determine the concentration of a solution of a reactant in a chemical reaction.

Describe and explain the procedure involved in carrying out a titration, particularly rinsing glassware and determining the end-point.

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Standard solutions

A **standard solution** is a prepared solution that contains a precisely known concentration. Standard solutions are used to determine the concentration of unknown solutions during **titrations**, and to calibrate analytical instruments.

A standard solution is prepared in a volumetric flask. An accurately measured volume of an appropriate solvent is added to an accurately weighed mass (hence number of moles) of solute. The solute chosen for the preparation is referred to as a **primary standard**. The compound chosen as the primary standard is selected due to its *stability*, *purity*, and *detectability* during a reaction.

Question

16. Anhydrous sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) were supplied analytical reagents (provided at an analytical grade of purity) for the preparation of separate standard solutions.

Each compound was required to prepare individual 0.100 mol L^{-1} standard solutions for analysis during an acid–base titration, with an appropriate indicator.

A detectable colour change was evident during the reaction.

- (a) The sodium carbonate was supplied as an anhydrous analytical-grade reagent.

- (i) **State** whether the solution prepared would be acidic or alkaline.

..... (1 mark) **KA1**

- (ii) **Suggest** one reason why anhydrous sodium carbonate is chosen.

.....
..... (1 mark) **KA1**

- (iii) **Suggest** one reason why it is important to use an analytical-grade reagent.

.....
..... (1 mark) **KA1**

Each compound was weighed out accurately, using their relatively large molar mass, onto separate watch glasses on an electronic balance.

- (b) The samples were left for a period of time, and it was noted that the appearance of the sodium hydroxide had altered. On reweighing it was discovered that the mass of the sodium carbonate had not changed, but the mass of the sodium hydroxide had increased. The masses are summarised in the following table.

	Anhydrous sodium carbonate	Sodium hydroxide
Initial mass	1.103 g	4.002 g
Final mass	1.103 g	7.601 g

- (i) **Calculate** the number of moles of sodium hydroxide present initially.

(2 marks) **KA4**

Sodium hydroxide absorbs water (it is hygroscopic), but it also absorbs carbon dioxide. Assume that the increase in mass of the sodium hydroxide is due to water.

(ii) **Calculate** the moles of water absorbed.

(3 marks) **KA4**

(iii) Hence, **determine** the formula of the hydrated compound.

(2 marks) **KA4**

(iv) A sample of sodium hydroxide had been left exposed to air for an extended period of time before being weighed and used in the final preparation of a standard solution.

Explain the effect of this exposure on the final concentration of the sodium hydroxide solution.

.....

 (2 marks) **IAE4**

(v) Hence, **suggest** one reason why sodium carbonate, rather than sodium hydroxide, is often chosen as an effective primary standard.

.....
 (1 mark) **KA1**

Common glassware used during volumetric analysis

A range of glassware is used during the production of standard solutions, dilutions, and in performing titrations. This includes both standard and volumetric glassware.

Glassware	Resolution	Typical tolerance and uncertainty (Class A glassware)	Cleaning procedure
250 mL volumetric flask	Holds an accurate measure 250 mL	+/- 0.12 mL	Rinsed with distilled water
25 mL volumetric pipette	Delivers an accurate measure 25 mL	+/- 0.03 mL	Rinsed with distilled water and then the solution to be transferred
50 mL burette	0.1 mL (predictions may be made to 0.05 mL)	+/- 0.03 mL	Rinsed with distilled water and then the solution to be transferred
250 mL conical flask	25 mL	+/- 10 mL	Rinsed with distilled water
100 mL measuring cylinder	1 mL	+/- 0.6 mL	Rinsed with distilled water

? Science inquiry skills

Skills in context

Resolution

Resolution of an instrument is related to the smallest measurable increment. Different apparatus provide different levels of resolution. Glassware is selected for an intended purpose, dependent on the level of resolution required.

Example

An approximate volume of 50 mL of solution can be transferred to a reaction vessel using a beaker, conical flask, or measuring cylinder. Recording the volume of a titration to the closest millilitre requires the use of a burette reading to a resolution of the closest 0.1 mL.

Preparation of a standard solution

A standard solution is prepared to have a desired concentration and volume. This involves working back from the concentration (c), to calculate the required number of moles (n) for the set volume (V) of the chosen volumetric flask. The mass (m) is then calculated after determining the molar mass (M) of the compound.

A number of successful methods are used in laboratories in the preparation of a standard solution.

Method 1

- Place a clean dry beaker onto the pan of the electronic balance and tare (zero) the balance.
- Using a clean dry spatula, carefully add the mass of solute to the beaker until a value is achieved that is close to that calculated. Record this value to the full resolution of the balance.
- Add a small volume of water to the beaker, and completely dissolve the solute by stirring with a clean glass stirring rod.
- Transfer the solution in the beaker to a volumetric flask, using a clean dry funnel.
- Ensure to rinse all residues present in the beaker and funnel into the volumetric flask, including the surface of the stirring rod.
- Rinse down the internal neck of the flask, ensuring to add less than half of the total volume of the volumetric flask.



Figure 1.3.4: Weighing out the solute.

Method 2

- Tare (zero) the electronic balance.
- Place a clean dry watch glass onto the pan of the balance and record its mass to the full resolution of the balance.
- Using a clean dry spatula, carefully add the mass of solute to the watch glass until a mass is achieved close to that calculated. Record this value to the full resolution of the balance.
- Carefully transfer the solute to the volumetric flask through a clean dry funnel.
- Return the watch glass to the balance and reweigh to account for remaining solute on the surface.
- Rinse all residues on the surface of the funnel and internal neck of the flask into the volumetric flask, ensuring to add less rinsings than half of the total volume of the volumetric flask.

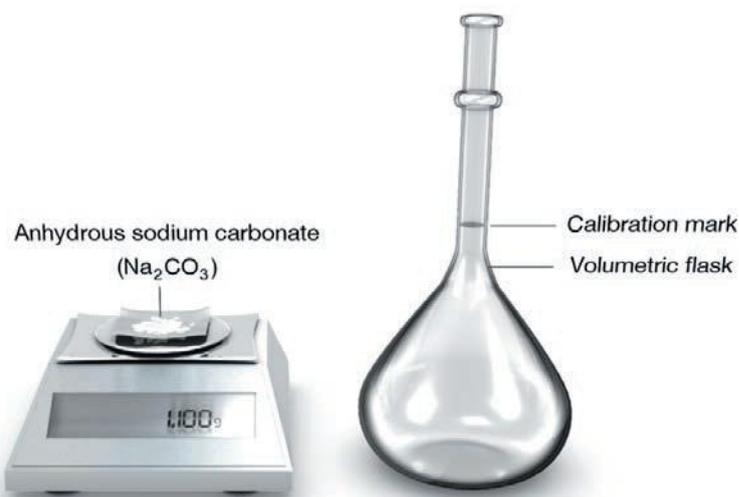


Figure 1.3.5: Alternative weighing of the solute.

Volumetric pipette: preparation and use

Volumetric pipettes are available in a range of volumes and are used to deliver an accurate volume (aliquot) of aqueous solution or liquid material.

Prior to use, several important steps are undertaken to ensure their accuracy in delivering desired quantities of reactants.

Preparation

- Initially the pipette should be checked to ensure it is free from defects.
- The pipette is initially cleaned thoroughly with distilled water to remove remaining contaminants from previous use.
- The pipette is cleaned by drawing up a small volume of water with a bulb or syringe type filler, removing the filler, and running the water over the internal surfaces, while holding the pipette horizontally. A small volume of water is run through the pipette when it is returned to a vertical position.
- This process may be repeated several times to ensure the removal of contaminants.
- If the pipette is being used to simply deliver a volume of distilled water, then the preparation is complete.

Delivery

- To prepare the volumetric pipette for the delivery of a solution, further steps are necessary.
- A small volume of the solution being delivered is drawn into the pipette with a pipette filler, the filler removed and the solution run horizontally over internal surfaces and through the tip of the pipette on returning it to the vertical position.
- The filler is then returned to the pipette in readiness to draw up the desired volume of solution.
- The pipette is lowered into the solution to avoid the generation of air bubbles while drawing up solution.
- The solution is drawn past the calibration mark, the pipette removed from the solution and the meniscus of the solution slowly lowered to the calibration mark by carefully releasing solution. This step is undertaken with the pipette held vertically at eye level until the bottom of the meniscus sits directly on the calibration line.
- The **aliquot** (volume) is then carefully transferred to a conical flask.
- The aliquot is released with the tip of the pipette touching the inside of the flask (or alternative glassware) to avoid any splashing and consequent loss of volume (Figure 1.3.8).
- The pipette is removed from the surface. Any solution remaining in the tip of the pipette is removed by touching the tip onto the inner glass surface of the flask until the final volume of material has been transferred. Volume remaining after this procedure is accounted for in the calibration of the pipette.
- A wash bottle is used to rinse the neck of the flask and ensure that all the solution, and therefore all moles, are present.
- Two to three drops of indicator may be added at this point if the aliquot has been delivered for use in an acid–base titration.

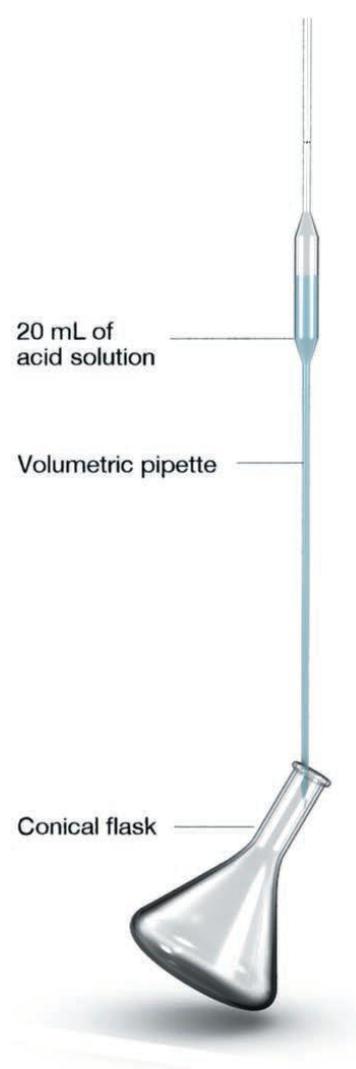


Figure 1.3.8:
Delivery from the
volumetric pipette.

The burette: preparation and use

Burettes are available in a range of volumes (typically 50 mL is chosen) and are used to accurately deliver **titres** (repeated volumes).

Prior to use, several important steps are undertaken to ensure their accuracy in delivering desired volumes (and therefore moles) of reactants.

Preparation

- Initially the burette should be checked to ensure it is free from defects.
- The burette is initially cleaned with distilled water to ensure that any remaining impurities from previous use have been removed.
- A small volume of distilled water is introduced to the burette through a clean funnel. The burette is held horizontally and the water run over the internal surfaces.
- On returning the burette to the vertical position, a small amount of distilled water is run through the tap assembly.
- This process may be repeated if there are signs of remaining contaminants.
- This entire cleaning process is then repeated with the solution to be delivered.

Delivery

- The burette is filled with the assistance of a clean funnel. A small volume of solution is run through the tap assembly until the tip is filled with solution (it is important to remove the air bubble).
- The burette is clamped vertically.
- The burette is filled to below the zero mark, with the meniscus read at eye level (Figure 1.3.9).
- The initial volume is read from the bottom of the meniscus at eye level and recorded.
- For a rough titration, with the tap wide open, swirling continuously, and then closed when an observable change in colour is first noted. (The purpose of a rough titration is to establish an approximate volume required for proceeding titrations.)
- Periodically during the titration, the sides of the conical flask are washed to ensure all reactants are present in the reacting solution.
- The equivalence point is established when the mole ratio of reacting quantities is met. The endpoint is recognised as a permanent observable change past the equivalence point (point where the stoichiometric ratio has been achieved) (Figure 1.3.10).
- Titration is typically repeated until three **concordant titres** are obtained. Concordant titres are generally recognised as being within 0.1 mL of one another, depending on the **titrant** (known reagent) and **analyte** (unknown reagent).

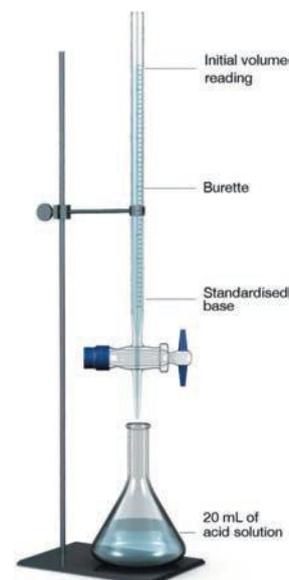


Figure 1.3.9:
Preparation of the burette.

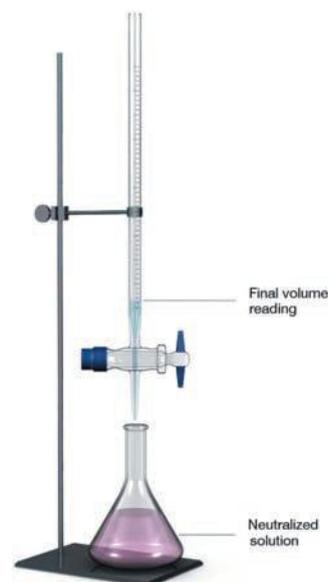


Figure 1.3.10:
Reaching the endpoint of the titration.



Science as a human endeavour

Biodiesel production

Titration is used in the production of biodiesel. The oils used as raw materials vary in acidity. Achieving a successful yield of biodiesel requires a knowledge of how much sodium hydroxide must be added during the formation of biodiesel from oils. Sodium hydroxide is required to neutralise the acidity of the oils, and then additional sodium hydroxide is required in the reaction to convert the oils to biodiesel.

An acid–base titration is undertaken initially to determine the level of acidity present. The correct quantities of base can then be added to optimise production.

? Science inquiry skills

Skills in context

Precision

Precision, with reference to a set of data, is determined by the degree of uniformity of the values. Precision is linked to the reproducibility and reliability of producing consistent data and is evaluated through the **range** evident in sets of data or the amount of **scatter** evident around a line of best fit if graphing the data.

Accuracy

Accuracy, with reference to a set of data, is evaluated through conformity with a true or accepted value. Accuracy is linked to the **validity** (how effectively the procedure generates valid conclusions) of the investigation. Accuracy is evaluated by obtaining an average for the data set and making comparisons with the accepted value.

Precision and accuracy may be visualised using a target (Figure 1.3.11).

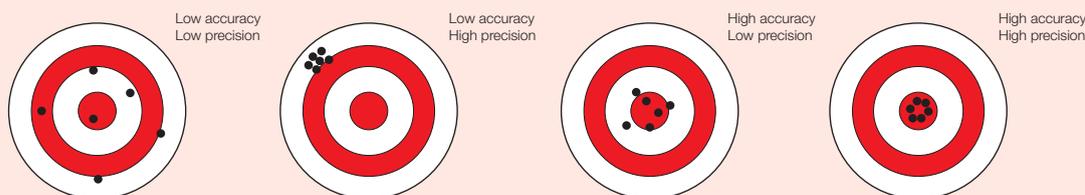


Figure 1.3.11: Visual representation of precision and accuracy.

Random errors

Random errors are variations in the measurements taken for experimental data due to limitations of the experimenter and the precision of the apparatus. Random errors are linked to the precision of the data obtained. When evaluating random errors, their significance and impact needs to be considered with respect to evidence of the variation in the data obtained.

Example

Variation in the colour and intensity of the indicator obtained at the endpoint when using acid–base indicators or self-indicating redox reactions is an example of random error in titration. Human perception of colour change and the ability of the experimenter to control flow from the tap during a titration results in colour differences. Depending on the skill and technique of the experimenter, this error will typically generate quite small variation in recorded volumes.

Systematic errors

Systematic errors are recurrent errors inherent in the apparatus or experimental method. As the name suggests, the errors are present in the system or procedure. When evaluating systematic errors, the significance and impact of this consistent difference needs to be considered with respect to the magnitude of the data obtained. Systematic errors are linked to the accuracy of the measurements.

Repeating the titration procedure using different glassware and fresh stock solutions will identify one or more systematic errors but will not eliminate the source(s) of error from the analysis and may even introduce error of greater magnitude.

Example 1

Glassware such as volumetric pipettes, volumetric flasks, and burettes have all been manufactured within the limits of manufacturing tolerances (Refer to Page 48) and therefore have inaccuracies associated with their use. The selection and use of different glassware will result in accumulated systematic error from the inherent differences in calibration of each piece of glassware. A volumetric pipette used with great skill may still have a calibration difference of up to 0.03 mL, delivering 20.03 mL instead of the stated 20.00 mL.

Example 2

Some chemical reagents degrade over time in storage. Hydrogen peroxide is stored at low temperatures in an opaque black plastic container, as it decomposes when exposed to sunlight. Solutions stored for extensive periods may have lower concentrations of peroxide available for reaction. Over the duration of a titration, fluctuations in recorded titres may also be evident as hydrogen peroxide decomposes over time.

Question

18. Dentists are interested in the impact of food acids and organic acids present in commonly consumed beverages on the degradation of tooth enamel. A series of titrations were undertaken to determine the presence of acids in white wine, orange juice and lemonade. The following data was obtained.

	Rough titre (mL)	Titre 1 (mL)	Titre 2 (mL)	Titre 3 (mL)	Titre 4 (mL)	Titre 5 (mL)	Titre 6 (mL)
White wine	12.05	11.90	11.85	11.90	11.95	11.75	11.90
	Rough titre (mL)	Titre 1 (mL)	Titre 2 (mL)	Titre 3 (mL)	Titre 4 (mL)	Titre 5 (mL)	Titre 6 (mL)
Orange juice	17.60	18.20	17.20	17.40	17.35	18.35	17.50
	Rough titre (mL)	Titre 1 (mL)	Titre 2 (mL)	Titre 3 (mL)	Titre 4 (mL)	Titre 5 (mL)	Titre 6 (mL)
Lemonade	12.05	9.70	9.65	9.50	9.25	9.20	8.90

(a) **State** whether the average titre for the concordant values of white wine or lemonade offers a higher degree of precision.

..... (1 mark) **IAE3**

(b) The same white wine was titrated by 10 other groups, with an average of 11.80 mL obtained.

(i) **State** the reason for averaging the values obtained by 10 other investigations.

..... (1 mark) **IAE4**

(ii) One group obtained an average titre of 11.75 mL. **State** and **explain** whether this value offers a higher or lower degree of accuracy compared to the concordant values stated for white wine above.

..... (2 marks) **IAE3**

(c) The range in titre values for orange juice is 0.15 mL for the concordant titres, and 1.0 mL for all titre values, excluding the rough titre.

(i) **State** whether this low precision is likely to be due to the presence of random or systematic error.

..... (1 mark) **KA1**

(ii) **Suggest** one reason why there is such variance in the precision of values for the titration with orange juice.

..... (1 mark) **IAE4**

(d) A supersaturated solution is present in lemonade, where a maximum concentration of carbon dioxide gas is dissolved at a given temperature. **Suggest** one reason why the titre values over the duration of the investigation are decreasing.

..... (1 mark) **KA2**

Science understanding

Determine the concentration of a solution of a reactant in a chemical reaction by using the results of a titration.

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Direct titration (solution stoichiometry)

A **direct titration** is an analytical technique where a solution of unknown concentration is directly determined by applying the stoichiometric (mole) ratio from a known reaction equation.

Worked example

Salinity can be determined as a measure of the chloride ion concentration in solution. A direct titration with silver nitrate can be used to determine the chloride ion concentration.

A sample of water from the mouth of a river near the ocean was analysed. A 20 mL water sample was diluted in a 100 mL volumetric flask. A 20 mL aliquot of diluted sample was transferred to a conical flask using a volumetric pipette, with the addition of potassium chromate as an indicator.

A precipitate of silver(I) chloride was formed when silver(I) nitrate solution was transferred (dropwise) to the sample of river water. When all the chloride ions precipitated, the excess silver ions underwent reaction with chromate ions as an indicator to achieve a red-brown colour.

The diluted sample was titrated with 0.100 mol L^{-1} silver nitrate (AgNO_3) until the first permanent colour was achieved. The process was repeated until concordant values were obtained.

	Rough Titre	Titre 1	Titre 2	Titre 3	Titre 4
Volume (mL)	16.55	15.60	15.65	15.80	15.55

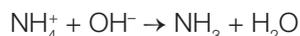


	Explanation	Calculation
STEP 1	Calculate the known number of moles of silver ions (Ag^+) from the average of the volume of the concordant titres and the stated concentration of silver nitrate solution.	$\text{Average titre} = \frac{15.60 + 15.65 + 15.55}{3}$ $n(\text{Ag}^+) = 0.01560 \times 0.100$ $= 0.001560 \text{ mol}$
STEP 2	Using the stoichiometric ratio from the equation provided, calculate the moles of the unknown, chloride ions (Cl^-).	$n(\text{Ag}^+) : n(\text{Cl}^-) = 1:1$ $\therefore n(\text{Cl}^-) = 0.00156 \text{ mol}$
STEP 3	Using the moles of chloride ions and the volume of the aliquot, calculate the concentration of chloride ions in mol L^{-1} .	$c = \frac{n}{V}$ $c(\text{Cl}^-) = \frac{0.00156}{0.0200}$ $= 0.0780 \text{ mol L}^{-1}$
STEP 4	Calculate the original concentration prior to dilution.	$c(\text{Cl}^-)_{\text{original}} = \frac{100}{20} \times 0.078$ $= 0.390 \text{ mol L}^{-1}$
STEP 5	Convert the original concentration to ppm by multiplying by the molar mass of chloride ions and then a factor of 10^3 .	$\frac{\text{mol}}{\text{L}} \times M \rightarrow \frac{\text{g}}{\text{L}} \times 10^3 \rightarrow \frac{\text{mg}}{\text{L}} = \text{ppm}$ $c(\text{Cl}^-)_{\text{original}} = 0.390 \times 35.45 \times 10^3$ $= 13825.5 \text{ mg L}^{-1}$ $= 13800 \text{ ppm}$

Question

19. Most nitrogen fertilisers contain water-soluble ammonium ions, (NH_4^+). High concentrations of ammonium ions in bodies of water can indicate the presence of fertiliser runoff. The increased concentration of ammonium ions may lead to **eutrophication** (increased nutrient concentration) in the waterway.

A sample of water was analysed for the presence of ammonium ions through titration with a previously standardised $0.00200 \text{ mol L}^{-1}$ sodium hydroxide (OH^-) solution, according to the equation below:



A 20.0 mL sample of water required an average titre of 10.2 mL to achieve the endpoint.

- (a) **Calculate** the moles of sodium hydroxide required to reach the endpoint.

(2 marks) **KA4**

- (b) Hence, **determine** the moles of ammonium ions present.

(1 mark) **KA4**

- (c) **Calculate** the concentration of ammonium ions, in mol L^{-1} , in the sample of water.

(3 marks) **KA4**

Back titration

A **back titration** is a two-stage analytical technique, where a known amount of an excess of one reagent is added to a reagent of unknown concentration. The remaining excess reagent undergoes a secondary reaction with a differing reagent (Figure 1.3.12).

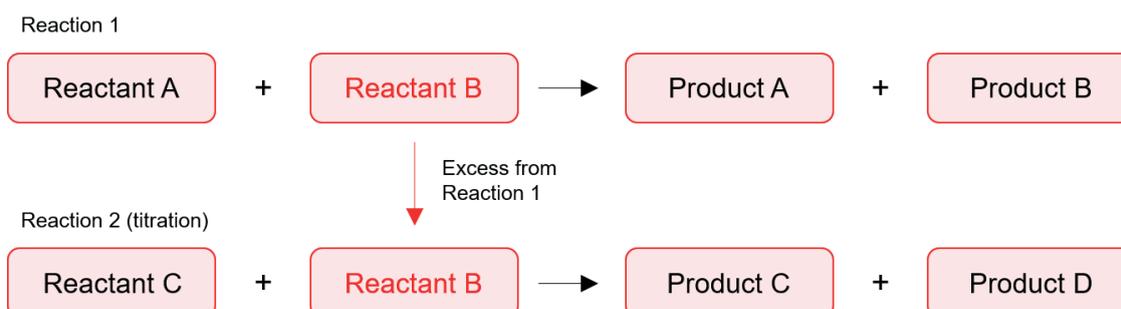


Figure 1.3.12: Mapping of quantities in a back titration.

Worked example

1

The concentration of carbon dioxide (CO₂) in air can be determined through an acid–base back titration. A 3.50 L sample of air was bubbled through 50.00 mL of 0.0200 mol L⁻¹ barium hydroxide (Ba(OH)₂) precipitating barium carbonate (BaCO₃).



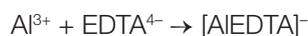
The excess Ba(OH)₂ was titrated with 0.0316 mol L⁻¹ hydrochloric acid (HCl). An average titre of 38.58 mL was achieved in reaching the endpoint.

	Explanation	Calculation
STEP 1	Calculate the original number of moles of barium hydroxide, Ba(OH) ₂ , from the volume and concentration supplied prior to the reaction. Label the quantity as the <i>original</i> .	$n = c \times V$ $n(\text{Ba(OH)}_2)_{\text{original}} = 0.0200 \times 0.05000$ $= 0.00100 \text{ mol}$
STEP 2	Determine all quantities working ‘back’ from Equation 2 to Equation 1. Calculate the known number of moles of hydrochloric acid (HCl) by using the average volume of the concordant titres for Equation 2 and the concentration of aqueous HCl.	$n(\text{HCl}) = 0.0316 \times 0.03858$ $= 0.001219 \text{ mol}$
STEP 3	Using the mole ratio from Equation 2, calculate the moles of the unknown, excess Ba(OH) ₂ , from the calculated moles of HCl. Label the quantity as the <i>excess</i> .	$\frac{n(\text{Ba(OH)}_2)}{n(\text{HCl})} = \frac{1}{2}$ $n(\text{Ba(OH)}_2)_{\text{excess}} = \frac{n(\text{HCl})}{2}$ $n(\text{H}_2\text{SO}_4) = \frac{0.001219}{2}$ $= 0.0006096 \text{ mol}$
STEP 4	Ba(OH) ₂ links Equation 2 to Equation 1. Calculate the reacted moles by subtracting the excess from the original number of moles of Ba(OH) ₂ calculated prior. Label the quantity as the <i>reacted</i> .	$n(\text{Ba(OH)}_2)_{\text{reacted}} = n(\text{Ba(OH)}_2)_{\text{original}} - n(\text{Ba(OH)}_2)_{\text{excess}}$ $n(\text{Ba(OH)}_2)_{\text{reacted}} = 0.00100 - 0.0006096$ $= 0.0003904 \text{ mol}$
STEP 5	Using the mole ratio from Equation 1, calculate the moles of the unknown carbon dioxide (CO ₂) from the calculated moles of reacted Ba(OH) ₂ .	$\frac{n(\text{CO}_2)}{n(\text{Ba(OH)}_2)} = \frac{1}{1}$ $\therefore n(\text{CO}_2) = 0.0003904 \text{ mol}$
STEP 6	Calculate the concentration of CO ₂ in mol L ⁻¹ .	$c = \frac{n}{V}$ $c(\text{CO}_2) = \frac{0.0003904}{3.50} = 0.0001115 \text{ mol L}^{-1}$
STEP 7	Convert the concentration into ppm.	$\frac{\text{mol}}{\text{L}} \times M \rightarrow \frac{\text{g}}{\text{L}} \times 10^3 \rightarrow \frac{\text{mg}}{\text{L}} = \text{ppm}$ $c(\text{CO}_2) = 0.0001115 \times 44.01 \times 10^3$ $= 4.91 \text{ mg L}^{-1}$ $= 4.91 \text{ ppm}$

Question

20. Aluminium sulfate (Alum) can be added to domestic water supplies as a coagulant/flocculant to remove fine clay particles. By using a back titration with EDTA and a suitable indicator, the concentration of aluminium ions can be determined.

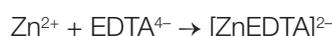
A 25 mL sample of water was transferred to a volumetric flask along with 30.0 mL of 0.010 mol L⁻¹ EDTA.



- (a) **Calculate** the original number of moles of EDTA.

(2 marks) **KA4**

The excess EDTA was titrated with 0.0010 mol L⁻¹ zinc sulfate.



Concordant titres below were obtained.

	Rough titre	Titre 1	Titre 2	Titre 3
Volume (mL)	53.15	52.90	52.80	52.70

- (b) (i) **Calculate** the number of moles of zinc ions (Zn²⁺) that reacted with the excess EDTA.

(3 marks) **KA4**

- (ii) Hence, **calculate** the moles of excess EDTA.

(1 mark) **KA4**

- (iii) **Calculate** the moles of EDTA that reacted with the aluminium ions, Al³⁺.

(2 marks) **KA4**

- (iv) Hence, **calculate** the concentration, in mol L⁻¹, of Al³⁺ present in the water sample.

(3 marks) **KA4**

- (v) **Express** the concentration of Al³⁺, in ppm, present in the water sample.

(2 marks) **KA4**

Indirect titration

An **indirect titration** is a two-stage analytical technique whereby the product from an initial reaction undergoes a secondary reaction with a different reagent (Figure 1.3.13).

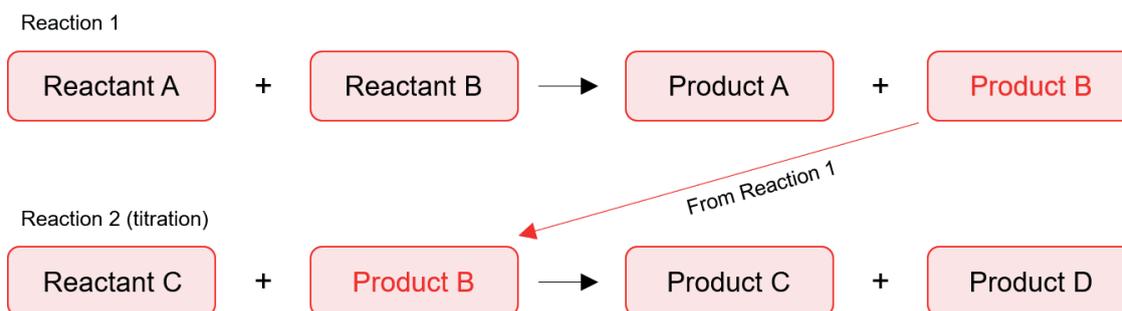
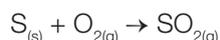


Figure 1.3.13: Flowchart of calculations in an indirect titration.

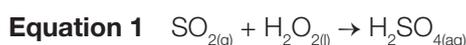
Worked example

The sulfur content of coal can be indirectly determined. The combustion of coal releases sulfur dioxide formed from the sulfur impurities present. The sulfur dioxide can be analysed on formation of sulfuric acid.

On the combustion of a sample of coal, of mass 8.06 g, the sulfur impurities were converted to sulfur dioxide gas (SO_2).



The sulfur dioxide gas produced was then bubbled through an aqueous solution of hydrogen peroxide (H_2O_2), forming sulfuric acid (H_2SO_4).



The sulfuric acid was then titrated against 0.100 mol L^{-1} sodium hydroxide (NaOH).



An average titre of 44.2 mL was obtained.

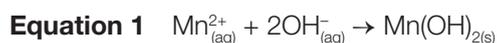
	Explanation	Calculation
STEP 1	The moles of sulfur dioxide (SO_2) in Equation 1 are indirectly determined from Equation 2. Calculate the known number of moles of NaOH, using the average volume of the concordant titres for Equation 2 and the concentration of aqueous NaOH.	$n = c \times V$ $n(\text{NaOH}) = 0.100 \times 0.0442$ $= 0.00442 \text{ mol}$
STEP 2	Using the stoichiometric ratio from Equation 2, calculate the moles of the unknown H_2SO_4 from the calculated moles of NaOH.	$\frac{n(\text{H}_2\text{SO}_4)}{n(\text{NaOH})} = \frac{1}{2}$ $n(\text{H}_2\text{SO}_4) = \frac{n(\text{NaOH})}{2}$ $n(\text{H}_2\text{SO}_4) = \frac{0.00442}{2}$ $= 0.00221 \text{ mol}$
STEP 3	The moles of H_2SO_4 reacting in Equation 2 are the product of Equation 1. Hence, the two quantities can be equated.	$\therefore n(\text{H}_2\text{SO}_4) = 0.00221 \text{ mol}$
STEP 4	Using the mole ratio from Equation 1, calculate the moles of the unknown SO_2 from the moles of H_2SO_4 .	$\frac{n(\text{SO}_2)}{n(\text{H}_2\text{SO}_4)} = \frac{1}{1}$ $\therefore n(\text{SO}_2) = 0.00221 \text{ mol}$
STEP 5	Equate the moles of elemental sulfur (S) with SO_2 .	$\therefore n(\text{S}) = n(\text{SO}_2) = 0.00221 \text{ mol}$

	Explanation	Calculation
STEP 6	Calculate the mass of elemental sulfur.	$m = n \times M$ $m(\text{S}) = 0.00221 \times 32.06$ $= 0.0709 \text{ g}$
STEP 7	Calculate the percentage of S by mass in the original sample of coal. (Note: rounding occurs at the final stage.)	$\%m(\text{S}) = \frac{m(\text{S})}{m(\text{coal})} \times 100$ $= \frac{0.0709}{8.06} \times 100$ $= 0.879\%$

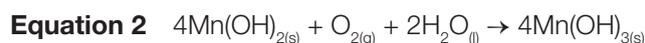
Question

21. The biochemical oxygen demand (BOD) can be used to determine the quality of a body of water. It is determined over a five-day period, at a controlled temperature, by measuring the amount of oxygen required to oxidise the organic components in the sample. A value of approximately 2–8 ppm would be expected for moderately polluted waters.

STAGE 1 A 100 mL water sample was collected in a sealed container with an equal volume of manganese(II) chloride and sodium iodide introduced. The manganese(II) ions were precipitated as manganese(III) hydroxide.



The precipitated manganese(II) hydroxide was oxidised by the dissolved oxygen, yielding manganese(III) hydroxide.



- (a) **Assign** oxidation numbers to manganese in Equation 2 and hence state whether manganese(II) hydroxide is the oxidising agent or reducing agent in this reaction.

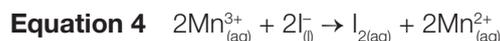
.....
..... (2 marks) **KA4**

STAGE 2 Sulfuric acid was added to the manganese(III) hydroxide precipitate, releasing manganese ions (Mn^{3+}) in aqueous solution.

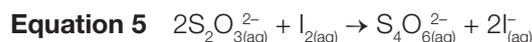
- (b) **Write an ionic equation (Equation 3)** to represent this stage.

(2 marks) **KA4**

STAGE 3 The Mn^{3+} ions oxidise the iodide ions (I^-) in solution.



- (c) The resulting volume of solution the solution was titrated with $0.0200 \text{ mol L}^{-1}$ sodium thiosulfate solution, using starch as an indicator. An average titre of 20.2 mL was achieved.



- (i) **Calculate** the number of moles of thiosulfate that reacted with iodine in Equation 5.

(2 marks) **KA4**

(ii) Hence, **calculate** the number of moles of iodine that reacted in Equation 5.

(2 marks) **KA4**

(iii) Hence, **determine** the number of moles of iodine that reacted in Equation 4.

(1 mark) **KA1**

(iv) The mole ratio of the species linked from reactions represented in Equations 2–5 are summarised below:

	Equation 2	Equation 3	Equation 4	Equation 5
Ratio	1:4	1:1	2:1	2:1
Species	$O_2:Mn(OH)_3$	$Mn^{3+}:Mn(OH)_3$	$Mn^{3+}:I_2$	$S_2O_3^{2-}:I_2$

(1) Using the information provided in the table, **calculate** the moles of oxygen present in the original water sample.

(3 marks) **KA4**

(2) **Calculate** the concentration, in mol L⁻¹, of oxygen in the original water sample.

(2 marks) **KA4**

(3) **Convert** this concentration to ppm of oxygen in the original water sample.

(3 marks) **KA4**

(4) Hence, **state** whether the sample of water is likely to be polluted.

.....
 (1 mark) **IAE3**

1.4 Chromatography

Science understanding

Chromatography techniques, including thin layer chromatography (TLC), gas chromatography (GC), high-performance liquid chromatography (HPLC), and ion chromatography (IC), involve the use of a stationary phase and a mobile phase to separate the components of a mixture.

The rate of movement of the components is caused by the differences between the strengths of the interactions between atoms, molecules, or ions in the mobile and stationary phases.

Predict the relative rates of movement of components along a stationary phase on the basis of their polarities and charge, given the structural formulae or relative polarities of the two phases.

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Principles of chromatography

Chromatography is an analytical technique applied in the separation of mixtures. The technique allows for the isolation and, in some applications, identification of individual components of a heterogeneous (non-uniform composition) or homogeneous (uniform composition) mixture. The components present in a mixture may include elements, molecules, or charged ions.



Science as a human endeavour

Origins of chromatography

Mikhail Tsvet is widely recognised as one of the first people to effectively develop the technique of chromatography “colour writing” in applications of early methods of both paper and column chromatography. Tsvet, a botanist, invented the principles of chromatography and used chromatographic methods to separate yellow, orange and green pigments from plants (xanthophylls, carotenes and chlorophylls).

While still using similar principles of adsorption applied to earlier methods, many of today’s modern applications of chromatography have shown significant advancements in sensitivity of analysis, and include environmental, food, forensic and pharmaceutical analysis.



Separation in chromatography is achieved by the extent of interaction between the individual components in the mixture and the **stationary phase**. In some applications of chromatography (TLC and column), interaction with the **mobile phase** also influences the separation. The stationary phase consists of a solid material on which components interact with the surface of the material through **adsorption**. The **mobile phase** is a fluid (something that flows; gas or liquid) comprised of molecules of a chosen polarity that drive the separation. The polarity of the fluid selected may range from highly polar to non-polar.

The strength of interactions between phases determines the extent of the separation. Components separate due to their relative levels of adsorption to the stationary phase, and, in some techniques, **solubility** in the mobile phase. Components that are more strongly adsorbed to the stationary phase travel at a slower rate. Conversely, components that are less strongly adsorbed to the stationary phase travel at a faster rate.

The polarity, size, and charge of the mixture to be separated are all important factors in determining the level of interaction with each phase, and, therefore, the effectiveness of the separation.

Adsorption chromatography

Adsorption chromatography involves interactions on the surface of the adsorbent material used as the stationary phase (Figure 1.4.1). Some methods of chromatography also involve interactions within the structure of the stationary phase between liquid phases (referred to as **adsorption** or **partition** chromatography).

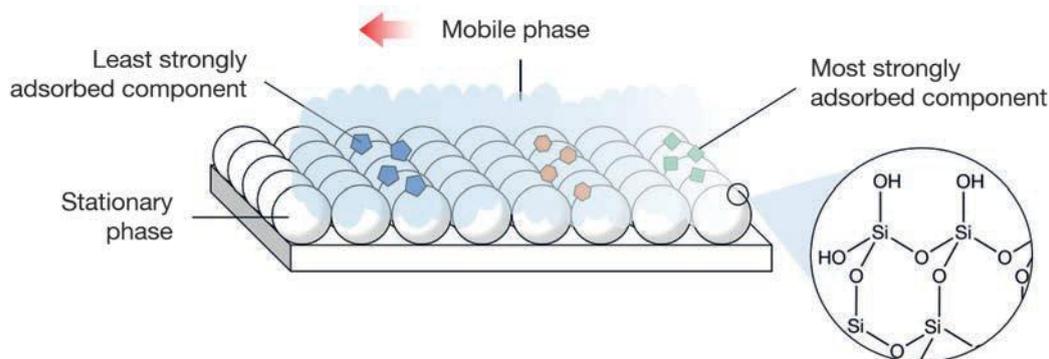


Figure 1.4.1: Adsorption of particles onto the surface of a stationary phase.

Chromatographic methods – including thin-layer chromatography (TLC), gas chromatography (GC), high-performance liquid chromatography (HPLC) and ion-exchange chromatography (IC) may all utilise the principle of adsorption, depending upon the materials chosen as the stationary phase.

Thin-layer chromatography (TLC)

Thin-layer chromatography (TLC) is a technique used to separate components of a mixture on the thin surface of a stationary phase (Figure 1.4.2). A thin layer of adsorbent material (examples include silica or alumina) is bonded to the surface of an inert sheet of material (glass, aluminium or polymer) as the stationary phase.

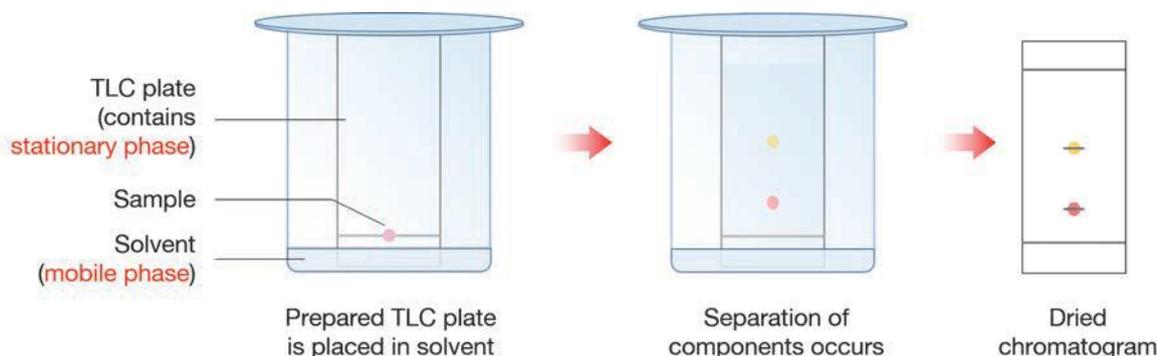


Figure 1.4.2: Chromatographic separation using thin layer chromatography

A pencil line is drawn near the bottom of the plate to indicate the **origin** (the point where the mixture is introduced) of the separation. A sample mixture (or series of mixtures) is spotted onto the line using a micropipette drawn from a fine capillary. The spotted mixture is allowed to dry and the plate is carefully lowered into a beaker or cell that contains a small volume of solvent as the mobile phase. Care is taken to ensure that the solvent sits below the origin. A watch glass or lid is placed on top to generate a saturated environment and reduce evaporation. The solvent moves up the plate, past the mixture, due to **capillary action** (upward force due to adhesion) formed by the tiny gaps between grains of adsorbent material.

As the solvent moves up the plate, components travel with the mobile phase and experience different levels of adsorption to the stationary phase. The level of interaction of each component with the stationary and mobile phases determines the rate of movement.

Once the components on the **chromatogram** (separated components on the stationary phase) have been resolved, the plate is removed from the solvent before the **solvent front** (the furthest point the solvent has travelled) reaches the top of the plate. The distance that the solvent and components have travelled is recorded. The varying rates of movement of the components allow for, in most cases, separation based on the distance travelled.

A different solvent may be chosen as the mobile phase when separation is minimal or one or more components of the mixture cannot be resolved. The polarity of the phases may also be reversed by changing the type of stationary phase (non-polar or polar) and solvent chosen.

Colourless components may be identified through reactions with additional reagents (such as ninhydrin, in the case of amino acids) in conjunction with the use of alternative light sources (such as ultraviolet for plates that have been treated with a fluorescing agent).

Science understanding

Data from chromatography techniques can be used to determine the composition and purity of substances.

Calculate and apply R_f values and retention times in the identification of components in a mixture.

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R_f retardation factor

The distance each component has travelled can be measured and compared to the distance the solvent has travelled to establish a ratio referred to as the R_f , **retardation factor** (Figure 1.4.3). This can be applied in the identification of components in a mixture.

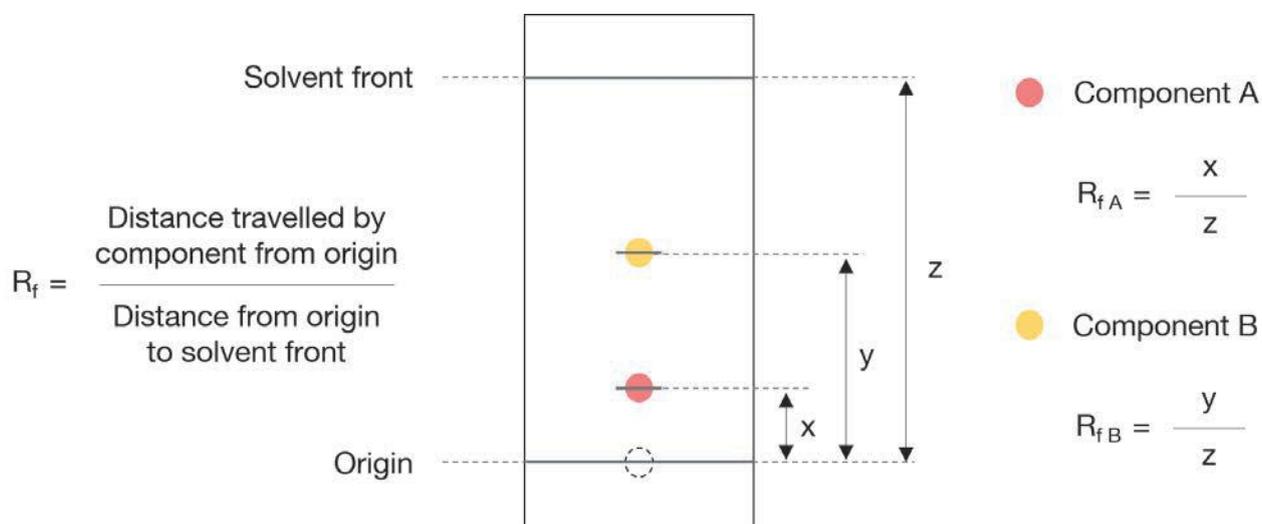


Figure 1.4.3: Determination of R_f .

$$R_f = \frac{\text{distance from the origin to the centre of the component}}{\text{distance from the origin to the solvent front}}$$

As evident in Figure 1.4.3, an R_f value closer to one indicates that the component has travelled to a position close to the solvent front at the top of the chromatogram. An R_f value closer to 0.1 would indicate that the component remained close to the origin at the bottom of the chromatogram.

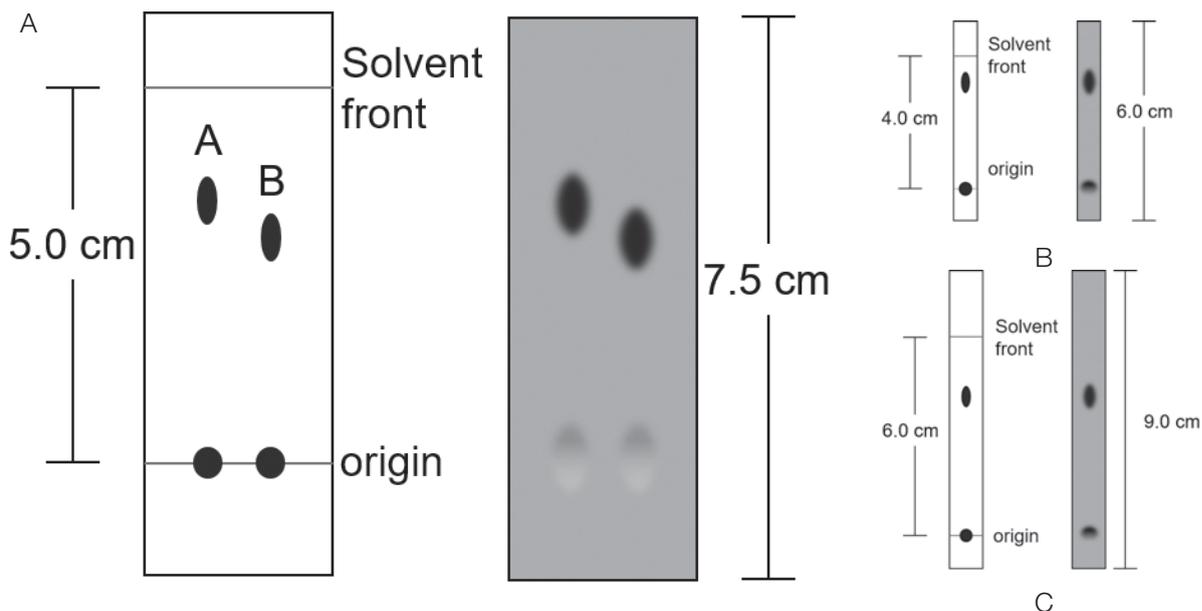
Question

22. Technetium-99m (Tc) is the most common radiopharmaceutical used in medical diagnostic procedures. It is used as a radioactive tracer that can be detected within the human body.

Different oxidation states of technetium target different areas of the human body. Technetium is generated as TcO_4^- (pertechnetate ion) with an oxidation state of +7. A reducing agent can be added to generate a +3, or +4, TcO_2 (technetium dioxide), oxidation state.

Thin-layer chromatography is employed to detect which species have been successfully generated. A radio chromatogram is produced.

(a) TLC, using silica as a stationary phase, was used to analyse the effectiveness of the production of TcO_2 from TcO_4^- . A chromatogram was prepared as a reference from samples of TcO_2 and TcO_4^- .



(i) **Calculate** the R_f of each component in chromatogram A.

(4 marks) **KA4**

(ii) Using the data provided in the table, **identify** the components as TcO_2 and TcO_4^- .

.....
 (2 marks) **KA4**



Science as a human endeavour

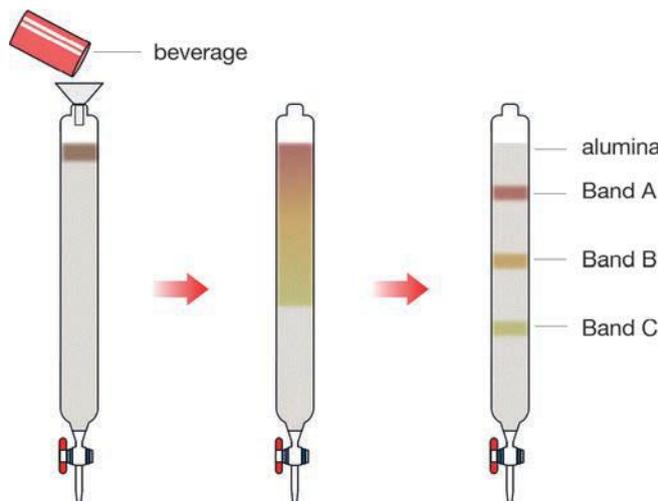
Food colouring

Natural and synthetic food colours undergo safety assessment before they can be made available to the public. Additives may be banned in some regions due to their potential health risks, such as being known carcinogens. The regulation of colours and additives in Australia is managed by Food Standards Australia and New Zealand (FSANZ). Colours and additives are often isolated through applications of chromatography.

Question

23. Artificial colours are added to many foods and beverages. Column chromatography was used to analyse artificial food colours in a beverage. The column was packed with alumina as a polar stationary phase; separation occurred using a non-polar solvent.

(a) **Consider** the diagram of the separation below.



(i) **State** and **explain** which component was least polar.

.....

 (3 marks) IAE3

(ii) At a later stage during the separation, Band A appeared to be separating into two components. **Suggest** one change that could be made to the procedure to separate these components more effectively.

.....
 (1 mark) IAE4

(b) Consider the same separation performed as thin-layer chromatography.

State and **explain** which component would produce the largest R_f value.

.....

 (3 marks) IAE3

Gas chromatography

Gas chromatography (GC) is effective at separating gaseous or volatile (low boiling-point) mixtures. Mixtures that are susceptible to degradation at high temperature are not suitable for gas chromatography. The mixture is introduced in very small quantities via a microlitre pipette. The sample is injected through a diaphragm into one end of a coiled chromatography column. The column is housed in a thermostatically controlled oven to ensure the mixture, if not already a gas, is converted to a gaseous state. On entering the column, the components are transported through the column by an inert **carrier gas** (usually hydrogen, nitrogen or helium) as the mobile phase (Figure 1.4.5). The flow rate of the gas and temperature of the oven can both be controlled to assist in the separation.

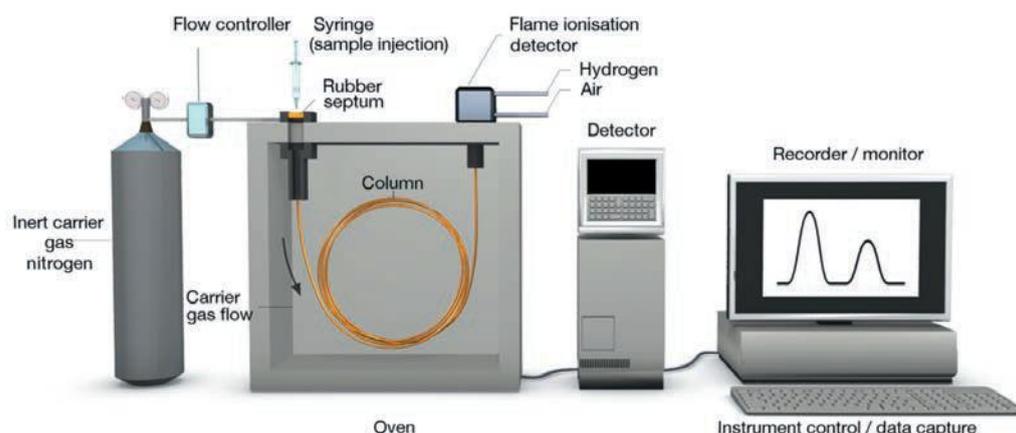


Figure 1.4.5: Schematic of gas chromatography.

The column contains the stationary phase. There are two commonly used types of columns; **capillary columns** (Figure 1.4.6) where the stationary phase coats the internal surface of the column, and **packed columns** where the column is completely packed with adsorbent material.

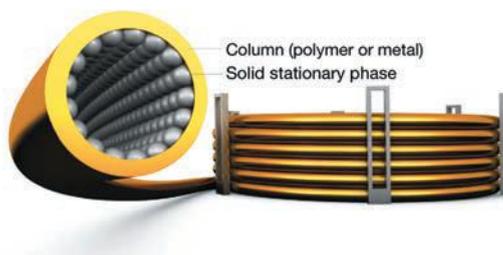


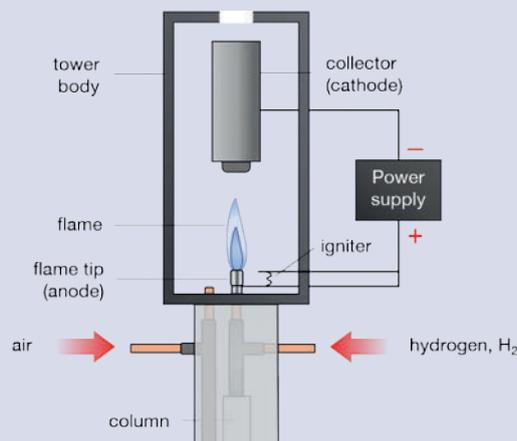
Figure 1.4.6: Capillary column.

While the gaseous components travel with the carrier gas, they interact to varying extents with the stationary phase inside the column. Components that are more strongly adsorbed to the stationary phase travel at a slower rate and are retained in the column for longer periods of time before **eluting** (leaving the column). Conversely, components that are less strongly adsorbed to the stationary phase are retained for a shorter period of time. The components may then be sent to a **flame-ionisation detector** to assist in identification.

Science as a human endeavour

Flame-ionisation detector

In 1957, McWilliam and Dewar of Imperial Chemical Industries of Australia and New Zealand (ICI/ANZ) in Melbourne, Australia, contributed to the development of the first flame ionisation detectors (FID). FIDs have been applied widely to gas chromatography at the detector stage. The mixture eluting the column undergoes combustion with hydrogen and air. The number of ions generated is proportional to the concentration of the organic component. Ions that are formed allow a current to be recorded. The current produced is proportional to the number of ions produced and, therefore the concentration.



Retention time

The chromatogram produced by quantitative methods of analysis conveys a record of the time taken for each component to elute the column, as well as a measure of relative concentration of that component in the mixture.

A chromatogram can be used for qualitative analysis through the identification of the peaks generated in a graph of **retention time**. The time taken from the injection of the sample to detection after eluting the column is recorded as retention time. Retention times can be compared with known standards, under the same set of conditions, to allow positive identification of components (Figure 1.4.7).

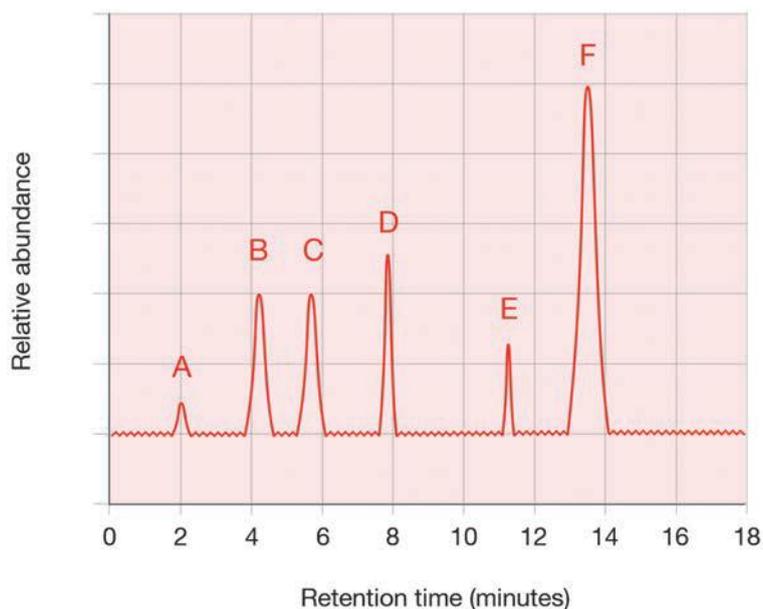


Figure 1.4.7: Quantitative chromatogram with retention times.

Figure 1.4.7 shows the retention times of six components of a mixture. Component F has the longest retention time. Component F experienced the strongest adsorption to the stationary phase and took the longest time to elute.

Quantitatively, component A is present at the lowest concentration and component F at the highest concentration. Component B and C are present in equal concentrations.



Science as a human endeavour

Identifying the origin of oil spills

One challenging application of gas chromatography (GC) is in the identification of components in oil from oil spills. This may be due to accidental or deliberate discharges of oil from ships.

Environmental analysis of oils can be used to determine their point of origin for both the offending ship and even the company or region responsible for supply. GC can identify the components remaining in the oil spill (highly volatile components will be lost in the environment) as well as identifying biomarkers. The organisms and even geology present in specific locations where the oil has formed over millions of years, leaves traces of organic molecules as unique indicators. These indicators can be traced to oil supplies and specific geographical locations where the oil originated from.

High-performance liquid chromatography

High-performance liquid chromatography (HPLC, also known as high-pressure liquid chromatography) is an alternative quantitative technique to gas chromatography. The separation of a mixture can be made more efficient if smaller adsorbent particles are used as the stationary phase and packed into a shorter column. Due to the stronger capillary forces experienced, the solvent must be forced through the column under pressure.

The column is packed with an adsorbent material of small particle size, hence very large surface area. The mobile phase, referred to as an eluent in this technique, is pumped through the column under high pressure and at a constant flow rate. The sample is once again injected into the system, with components transported by the liquid solvent (Figure 1.4.8).

Components that are more strongly adsorbed to the stationary phase travel at a slower rate. Components that are less strongly adsorbed to the stationary phase travel at a faster rate. Components elute the column at different times. The detector registers the retention time and intensity of each component, which can then be compared to known standards. HPLC is effective for mixtures that may breakdown at the higher temperatures experienced in the oven during GC.

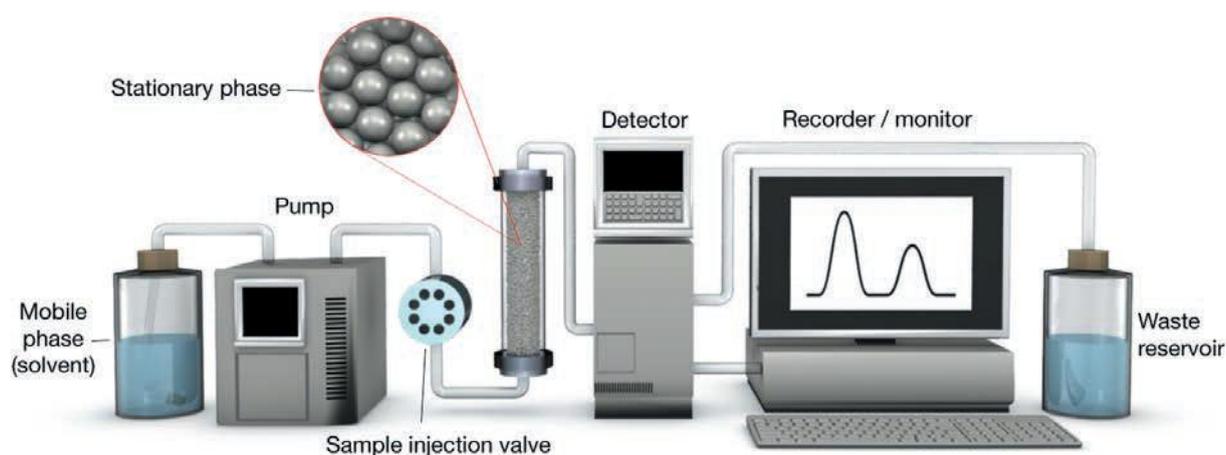


Figure 1.4.8: Schematic of high-performance liquid chromatography.



Science as a human endeavour

Wastewater analysis and drugs: a European multi-city study

The 2015 SCORE Wastewater Monitoring Campaign analysed wastewater in over 60 European cities and towns. In some instances, similar analysis had occurred over a four- to five-year period. Samples from water treatment plants were analysed for urinary biomarkers of the target drug or metabolic products (products formed when the body breaks down a drug) these included analysis of the residues for amphetamine, methamphetamine, MDMA, cocaine, and cannabis. The studies revealed patterns of illicit drug use linked to geographical location and population demographic.

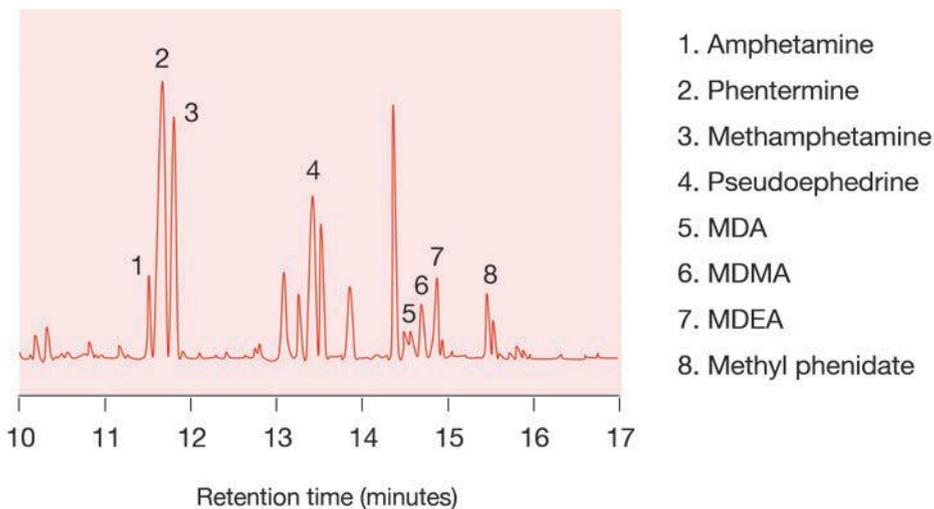
High-performance liquid chromatography and mass spectrometry (ions identified on mass-charge ratio) were used in the separation and measurement of the residual drugs. Based on the level of residual drug entering wastewater, researchers were able to back-calculate the consumption of illicit drugs in populations.

Subsequently similar studies have been undertaken in Australia.

Question

25. Wastewater in Adelaide, South Australia, was analysed using high-performance liquid chromatography (HPLC) over a two-week period. Researchers tested for residues of cocaine, amphetamine, methamphetamine and MDMA.

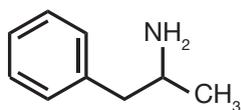
(a) The chromatogram below was used in the identification of the targeted drugs.



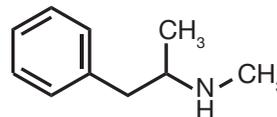
Determine the retention time of MDMA, to three significant figures.

..... (2 marks) **KA1**

(b) Amphetamine and methamphetamine have very similar chemical structures shown below:



Amphetamine



Methamphetamine

(i) **Identify** the structural difference between the two molecules.

..... (1 mark) **KA1**

(ii) Using the chromatogram and structure of the molecules above, **explain** whether the stationary phase used for the separation is more likely to be polar or non-polar.

.....

 (3 marks) **IAE3**

Science understanding

Ion chromatography (also known as ion exchange chromatography) is used to remove either cations or anions from a mixture by replacing them with ions of another type.

Explain, using equilibrium principles, how ions attached to the surface of a resin can be exchanged with ions in aqueous solution.

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Ion chromatography

Ion chromatography (IC) relies upon the principle of ion-exchange in an **equilibrium system** (reactions that proceed in both the forward and backward directions).

Ion-exchange chromatography utilises a solid **ion-exchange resin** as the stationary phase. The column is packed with porous beads. The resin can be prepared with either a positively or negatively charged surface. Ions of opposite charge bond to the surface of the resin from solution. These ions are exchangeable with ions from the sample mixture, depending upon their type, magnitude of charge, charge distribution and charge density.

Exchange resin	Exchange group	Example	Structure
Anion exchange column (positive resin surface)	Anions	Diethylaminoethyl (DEAE)	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_3 \\ \\ \text{---O---C---C---N}^+\text{---H} \\ \\ \text{H}_2\text{C}-\text{CH}_3 \end{array}$
Cation exchange column (negative resin surface)	Cations	Carboxymethyl (CM)	$\begin{array}{c} \text{O} \\ \\ \text{---O---C---C---O}^- \end{array}$

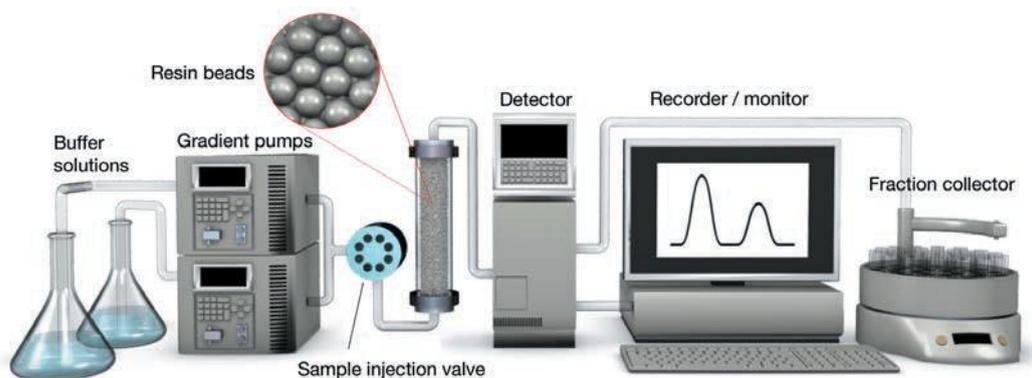


Figure 1.4.9: Schematic of ion-exchange chromatography.

As the liquid mobile phase passes through the resin, exchangeable ions take up binding sites (Figure 1.4.9). Ions with greater charge-density generate stronger electrostatic attraction or repulsion with the stationary phase. For example, if using a negatively charged resin surface, highly positive ions would be strongly attracted, slight positive ions less. Slightly negatively charged ions would undergo weak repulsion, and highly negative, strong repulsion.

An equilibrium is established between ions bound to the resin surface and ions in solution (Figure 1.4.10).

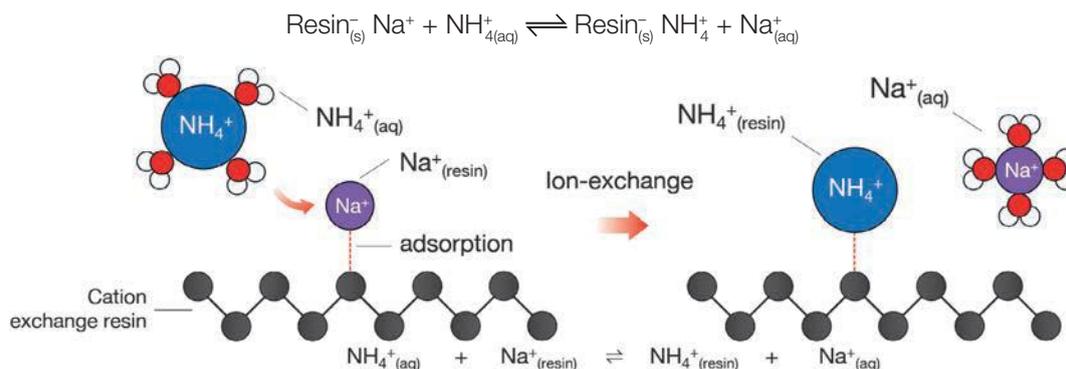


Figure 1.4.10: Ion exchange on the resin surface.

Only strongly interacting species remain attached to the resin after the solvent has been eluted from the column. Species strongly bound to the surface may then need to be removed. To achieve this removal from the resin surface, ion concentration or pH may be altered to weaken the **electrostatic interactions** (attraction of positive and negative charges).

Flooding the resin column with a high concentration of aqueous sodium ions will place a stress on the equilibrium system. According to **Le Châtelier's Principle** (refer to Page 119), the equilibrium system will counteract the introduced change by shifting the position of equilibrium to the left, favouring the backward reaction. Sodium ions will bind to the surface of the resin and exchangeable ions on the surface will be released into aqueous solution and elute.

Ion-exchange chromatography is effective at separating amino acids and proteins that are susceptible to changes in functional groups due to altered pH. Amino groups may become protonated at low pH or returned to molecular species as higher pH (refer to pages 217 and 218).

Question

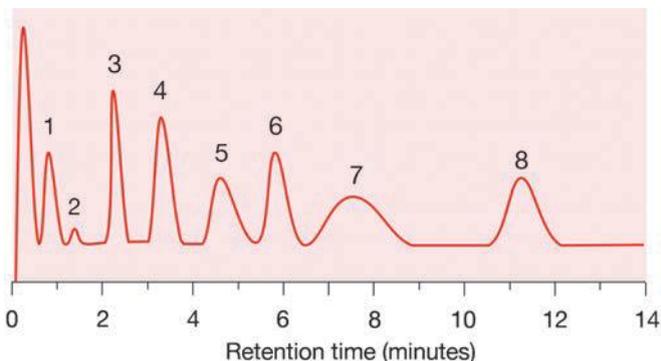
26. Ammonium nitrate is a fertiliser added by farmers to increase crop yield in nitrogen-deficient soils. Fertiliser run-off from soils may enter local waterways and lead to **eutrophication** (increased nutrient concentrations).

(a) Ammonium nitrate fertilisers were applied on farming land near a creek. The creek was analysed to determine nitrate levels.

(i) **State** the property of nitrate and ammonium ions that allows them to be absorbed by plants.
 (1 mark) **KA1**

(ii) **State** whether an anion or cation exchange column would be used for the analysis of nitrate ions.
 (1 mark) **KA1**

(b) The chromatogram below was obtained for a range of anions present in the creek water.



- 1. Fluoride, F⁻
- 2. Hydrogencarbonate, HCO₃⁻
- 3. Chloride, Cl⁻
- 4. Nitrite, NO₂⁻
- 5. Bromide, Br⁻
- 6. Nitrate, NO₃⁻
- 7. Monohydrogenphosphate, HPO₄²⁻
- 8. Sulfate, SO₄²⁻

Explain why the retention time of nitrate ions present in the water is shorter compared to that of sulfate ions.

.....

 (3 marks) **IAE3**

(c) To regenerate the resin in the column for future use, the column is flooded with a solution containing a high concentration of sodium borate (Na₃BO₃).



Explain, using equilibrium principles, how the resin is regenerated.

.....

 (3 marks) **IAE3**

1.5 Atomic spectroscopy

Science understanding

Flame tests and atomic absorption spectroscopy (AAS) are analytical techniques that can be used to identify elements; these methods rely on electron transfer between atomic energy levels

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Principles of spectroscopy

Spectroscopy is an important branch of analytical chemistry. It uses the interactions between matter and electromagnetic radiation to reveal details of the atomic and chemical structure of elements and compounds.

The experimental findings from different types of spectroscopy support our theoretical understanding of atomic structure. Evidence of these interactions is observed in everyday phenomena. Characteristic colours are seen when compounds of metallic elements are introduced to a flame, or a potential difference is applied. For example: streets lit with sodium (orange) and mercury (white) vapour lamps; pyrotechnics (fireworks) exploding with a range of vivid colours.

The emission of coloured light is the result of the transitions of electrons in the energy levels of atoms, ions and molecules. The presence of elements can be determined by their characteristic emissions.

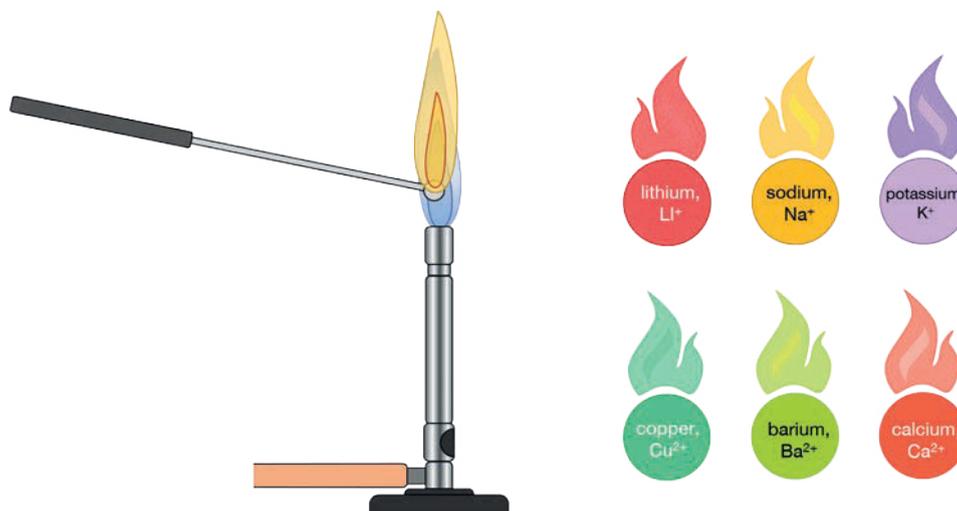


Figure 1.5.1: Flame colours from atomic emission.

Flame tests are used to detect the presence of a chemical element or compound in a mixture. Most metals emit a characteristic colour when energised (Figure 1.5.1). Electron transitions during atomic emission is determined by the arrangement of electrons in atoms.

Science understanding

Write the electron configuration using subshell notation of an atom of any of the first 38 elements in the periodic table.

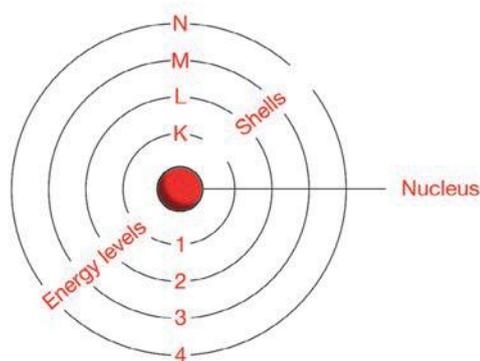
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Electron configuration

The **electron configuration** represents the distribution of electrons in atomic shells and subshells. The arrangement determines the position of an element on the periodic table. The **main group number** represents the number of electrons in the valence shell. The **period number** represents the number of occupied shells in one atom of that element. Elements are positioned in one of four blocks (s, p, d, f) depending on the identity of the highest energy subshell in one atom of that element.

The Bohr model

The **Bohr model** of the atom provides a simple model for the consideration of energy levels and distribution of electrons in the atom (Figure 1.5.2). Electrons within shells have different energies. The possible energies of electrons are referred to as energy levels. Electrons transition between energy levels in atoms. Electrons transition to higher energy levels through absorption of energy and lower energy levels through the emission of energy.



In order from highest to lowest energy level (n):

$$n = 4 > n = 3 > n = 2 > n = 1$$

Figure 1.5.2: Bohr model of the atom.

The quantum (Schrödinger) model

The **quantum model** is based on mathematical descriptions, which give the probability of finding electrons in the region of space surrounding the nucleus. These regions are visualised three-dimensionally as orbitals (Figure 1.5.3). Orbitals have different shapes, represented in different axes.

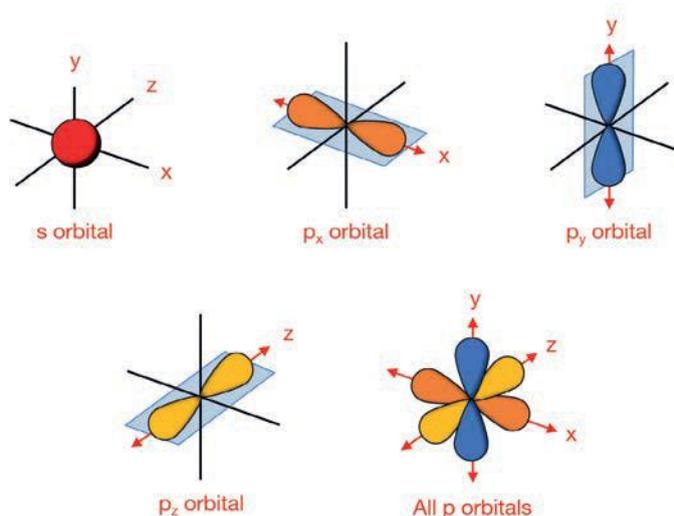


Figure 1.5.3: Atomic orbitals.

Energy sequence

Electrons are arranged in energy levels around the atomic nucleus. Each level (shell) consists of one or more subshells. Subshells hold a maximum number of electrons based on the number of orbitals present. Each orbital can hold a maximum of two electrons as shown in the table below.

Shell/Principal quantum number (n)	Subshell	Orbitals	Electrons	Maximum
K (n=1)	s	1	2	2
L (n=2)	s	1	2	8
	p	3	6	
M (n=3)	s	1	2	18
	p	3	6	
	d	5	10	
N (n=4)	s	1	2	32
	p	3	6	
	d	5	10	
	f	7	14	
				$2n^2$

Electrons fill shells and subshells in order of increasing energy.

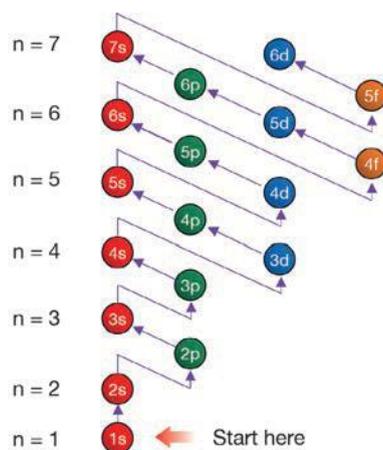


Figure 1.5.4: Energy sequence.

Lower energy subshells are filled first. Electrons fill higher subshells in order of increasing energy. This is referred to as the **Aufbau principle** (Figure 1.5.5).

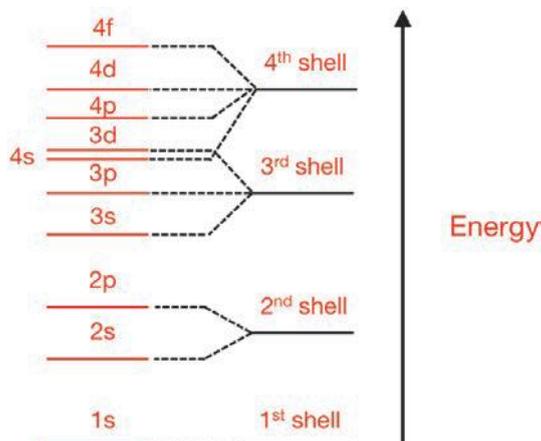


Figure 1.5.5: The Aufbau principle.

Subshell electron configuration

The **electron configuration** of an element is written using subshell notation. The shell number is written first, followed by the subshell (s, p, d, f). Finally, the number of electrons is written as a superscript to the right of the subshell (Figure 1.5.6).

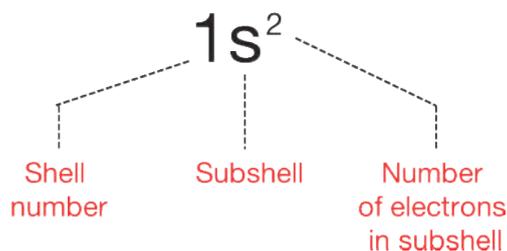


Figure 1.5.6: Electron configuration using subshell notation.

Question

27. The electron configurations for the first 20 elements are considered below.

Element	Symbol	Atomic number	Subshell electron configuration	Block
hydrogen	H	1	$1s^1$	s
helium	He	2	$1s^2$	s
lithium	Li	3	$1s^2 2s^1$	s
beryllium	Be	4		s
boron	B	5	$1s^2 2s^2 2p^1$	p
carbon	C	6		p
nitrogen	N	7	$1s^2 2s^2 2p^3$	p
oxygen	O	8		p
fluorine	F	9		p
neon	Ne	10	$1s^2 2s^2 2p^6$	p
sodium	Na	11		s
magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$	s
aluminium	Al	13		p
silicon	Si	14		p
phosphorous	P	15		p
sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$	p
chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$	p
argon	Ar	18		p
potassium	K	19		s
calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	s

(a) **Complete** the table of electronic configuration, using subshell notation, for the remaining elements.

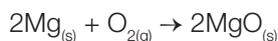
(10 marks) **KA4**

(b) **Identify** one trend in the table above, evident in the electronic configuration.

.....
 (1 mark) **KA1**

Electron configuration of ions

Ions are formed when electrons are added and removed from atoms. Electrons are added and removed from the highest energy subshell in an atom. **Cations** are formed when one or more electrons are removed from an atom. **Anions** are formed when one or more electrons are added to the highest energy subshell. The electron configuration of an anion or cation reflects the number of electrons added or removed from an atom. Consider a strip of magnesium burning in oxygen.



Two electrons are removed from the highest energy subshell in magnesium.

Magnesium atom (Mg)	Magnesium cation (Mg ²⁺)
1s ² 2s ² 2p ⁶ 3s ²	1s ² 2s ² 2p ⁶

Two electrons are added to the highest energy subshell in oxygen.

Oxygen atom (O)	Oxygen anion (O ²⁻)
1s ² 2s ² 2p ⁴	1s ² 2s ² 2p ⁶

Ions take on the stable electron configuration of the Group 8 noble gases.

Question

28. Iodine deficiency leads to intellectual and developmental disabilities.

- (a) Historically, dairy foods have contained high levels of iodine from the sterilisation of udders and dairy equipment. These techniques have been phased out, limiting iodine intake in the population. The World Health Organization recommends an average daily intake of 150 µg of iodine for an adult.

- (i) Analysis of Australian cows milk showed an average content of 13 µg per 100 mL.

Calculate the daily consumption of cows milk, in L, required to achieve the recommended daily intake of iodine.

(2 marks) **KA4**

- (ii) **Suggest** why this level may still be achieved without a high daily consumption of cows milk.

.....
 (1 mark) **KA3**

- (b) Since 2009, bakers in Australia have been required to replace regular salt (NaCl) with iodised salt (NaI) to increase iodine intake in the general population.

- (i) **Write**, using subshell notation, the electronic configuration of sodium.

..... (2 marks) **KA4**

- (ii) **Write**, using subshell notation, the electronic configuration of the sodium ion.

..... (2 marks) **KA4**

- (iii) **Write**, using subshell notation, the electronic configuration of the chloride ion.

..... (2 marks) **KA4**

- (iv) **State** one similarity that would be expected between the configuration of the chloride and iodide ion.

.....
 (1 mark) **KA1**

Electron configuration of the transition elements and beyond

The electrons of the first 20 elements fill shells and subshells in accordance with the Aufbau principle. Atoms that have 21–30 electrons have one or more electrons in the 3d subshell. The 3d subshell is lower in energy than the 4s subshell in all elements that have more than 20 electrons. The 19th electron of scandium ($Z = 21$) is located in the 3d subshell. The 20th and 21st electrons of scandium are located in the higher energy 4s subshell. The electron configuration of scandium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$.

Exceptions – chromium and copper

Atoms of chromium (24) and copper (29) are exceptions to the sequence. They both contain a half-filled 4s subshell. This allows each orbital in the 3d subshell to be half or completely filled, which is a more stable configuration for these elements.

Element	Symbol	Atomic number	Subshell electron configuration	Block	4s	3d				
scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	d	↑↓	1				
titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	d	↑↓	1	1			
vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	d	↑↓	1	1	1		
chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	d	↑	1	1	1	1	1
manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	d	↑↓	1	1	1	1	1
iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	d	↑↓	↑↓	1	1	1	1
cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	d	↑↓	↑↓	↑↓	1	1	1
nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	d	↑↓	↑↓	↑↓	↑↓	1	1
copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	d	↑	↑↓	↑↓	↑↓	↑↓	↑↓
zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	d	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

The electrons of elements 31–38 fill subshells in order of increasing energy. Elements 31–36 have electrons in the 4p subshell. Elements 37 and 38 have electrons in the 5s subshell.

Element	Symbol	Atomic number	Subshell electron configuration	Block
gallium	Ga	31	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$	p
germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$	p
arsenic	As	33	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$	p
selenium	Se	34	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$	p
bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$	p
krypton	Kr	36	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$	p
rubidium	Rb	37	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$	s
strontium	Sr	38	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$	s

Question

29. Gold, silver, copper, platinum and palladium are all precious metals that are found in e-waste from discarded computers, televisions and mobile phones.

(a) Gold, silver, copper, platinum and palladium are all found in the d-block

(i) **State** what is common to the subshell electronic configuration of these elements.

.....
 (1 mark) **KA1**

(ii) Copper can be extracted from copper ores containing the mineral covellite (CuS).

Identify the charge on the copper ion present in the mineral covellite.

..... (1 mark) **KA1**

(iii) **Write** the electronic configuration of copper, using subshell notation.

..... (2 marks) **KA4**

(iv) Copper can exist as Cu⁺ and Cu²⁺ ions.

Write the electronic configuration of copper in these species, using subshell notation.

Cu⁺.....

Cu²⁺..... (4 marks) **KA4**

(b) The expected and actual electronic configurations of copper and palladium are shown below.

Cu	Expected	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁹	Pd	Expected	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶ 4d ⁸ 5s ²
	Actual	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹ 3d ¹⁰		Actual	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶ 4d ¹⁰

Suggest why these elements exhibit the actual subshell electronic configuration rather than the expected.

..... (1 mark) **IAE3**

(c) Silver is used in electronic circuitry due to its low electrical resistance. When exposed to hydrogen sulfide in air, silver is oxidised and loses conductivity, forming silver sulfide (Ag₂S) and hydrogen gas.

(i) **Write** a balanced equation for the reaction.

(2 marks) **KA4**

(ii) **Identify** the oxidising agent.

..... (1 mark) **KA1**



Science as a human endeavour

e-waste

As consumer electronics become cheaper and more abundant, they are increasingly viewed as disposable. Mobile phones, computers, and televisions are either shredded and added to landfill waste in Australia or shipped to countries like China for processing.

In landfill, electronics have the potential to leach toxic products from the range of polymers used in their production. There is also the possibility that potentially hazardous metals may be released into the environment. While electronics may only represent a small component of household waste, they represent a large proportion of toxic waste.

Economically, it means that by dumping or exporting this waste, Australia is potentially losing precious metals that could be recycled and reused. It is estimated that from one tonne of mobile phones, 100 kilograms of copper, three kilograms of silver, and 200 grams of gold can be extracted.

These metals are usually extracted from ores in very energy-intensive processes. Ironically the percentage of these metals present in consumer devices is often much higher than that found naturally in the ore they are extracted from.

Many countries, including Australia, are researching methods for the extraction and recycling of the precious metals in electronic devices. Some methods have been highly effective, yielding greater than 95% of the metal present in the product. In South Australia, one project aims to grind the e-waste to a powder and use froth flotation, a technique common to the mining industry, to float the precious metals off on the surface of bubbles.

(d) Consider the information above, which outlines the impact of e-waste.

(i) **Discuss** how the production and disposal of local e-waste is a global issue.

.....

 (2 marks) **KA3**

(ii) **State** how metal production techniques have been beneficial to the recycling of precious metals.

.....
 (1 mark) **IAE3**

Science understanding

Explain the effect of the absorption or emission of radiation on the electronic configuration of electrons in atoms or ions.

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Absorption and emission

Electrons occur naturally in the **ground state** (lowest energy level) of an atom or ion. Electrons may be promoted to higher energy levels (**excited state**) through the absorption of photons. **Photons** (discrete quantised amounts of energy) may be supplied as heat, light or electrical energy. Electrons in the excited state are energetically unstable and return to lower energy levels (Figure 1.5.7). The energy equivalent to the transition ($E = h\nu$) is emitted from the atom as electromagnetic radiation.

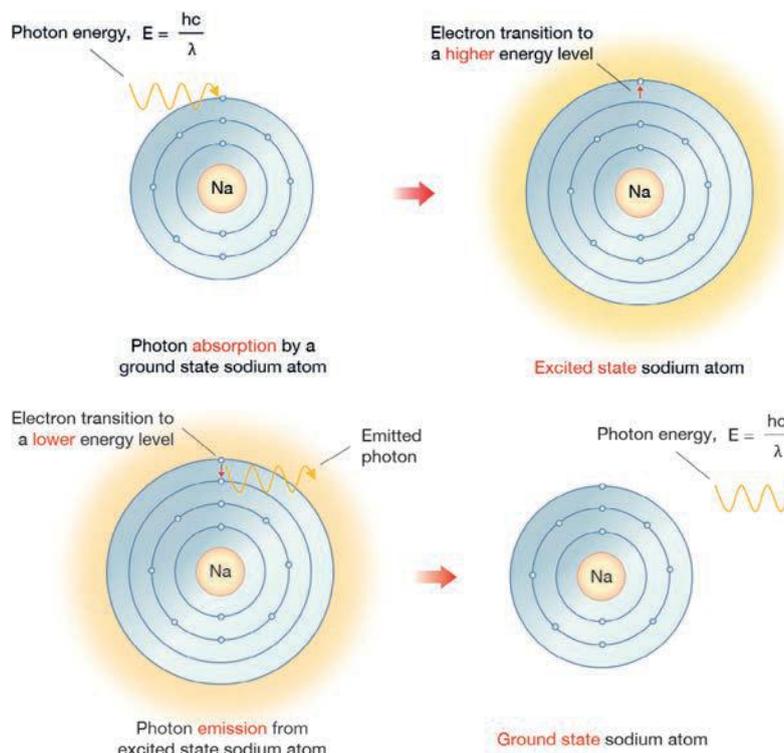


Figure 1.5.7: Atomic absorption and emission.

Transitions may occur between multiple energy levels for both the excitation of electrons during absorption and during emissions while returning to lower energy levels (Figure 1.5.8). Emitted photons have specific frequencies and wavelengths. The frequency and wavelength of a photon is related to its energy. This generates a series of emissions that are characteristic of a particular element.

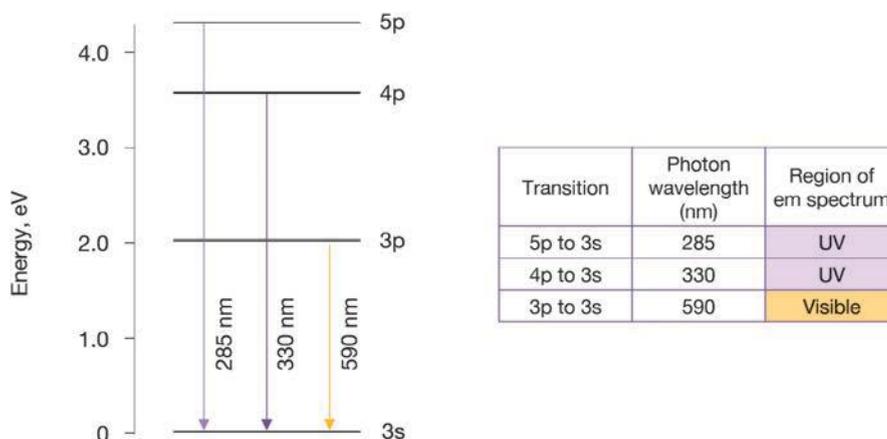


Figure 1.5.8: Energy transitions.

Emissions may occur in the visible or ultraviolet regions of the electromagnetic spectrum or outside of these regions. The visible region is of greatest interest for **flame emission** and **atomic spectroscopy**.

Science understanding

The wavelengths of radiation emitted and absorbed by an element are unique to that element and can be used to identify its presence in a sample.

Explain why some wavelengths of radiation emitted and absorbed by an element are unique to that element.

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Atomic emission spectroscopy

Atomic emission spectroscopy is an analytical technique that utilises the characteristic emission spectra of elements in their identification. The technique can also utilise the intensity of the emission to quantitatively determine the relative concentration of a chemical element in a mixture.

A characteristic set of wavelengths is emitted by each element under investigation, based upon their unique energy levels and electron configuration.

Flame emission spectroscopy

The compound to be analysed is sprayed from solution into a high-energy flame (or excited with a potential difference in a gaseous sample). The heat from the flame evaporates the solvent and breaks bonds in the compounds to release atoms in a free atomic state. Outer shell electrons in atoms absorb energy and are promoted to higher energy levels. Emission of electromagnetic radiation occurs on the return of electrons to lower energy levels.

This emission can be directed through diffraction grating or prism, which separates the characteristic wavelengths present and generates a **line emission spectrum** (Figure 1.5.9).

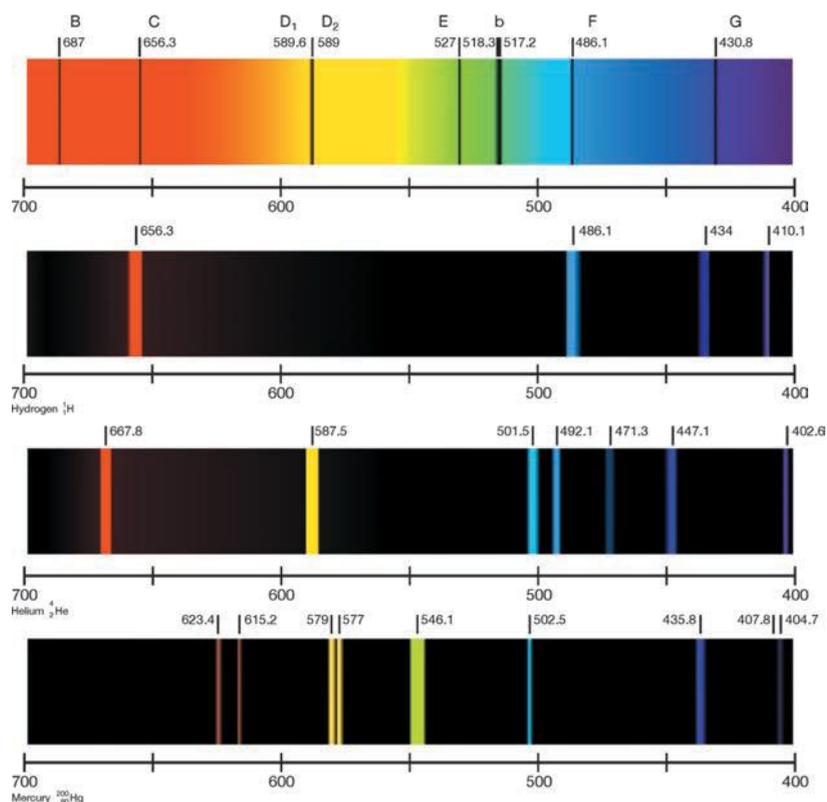


Figure 1.5.9: Line absorption spectrum of the Sun and emission spectra of selected elements (hydrogen, helium and mercury).

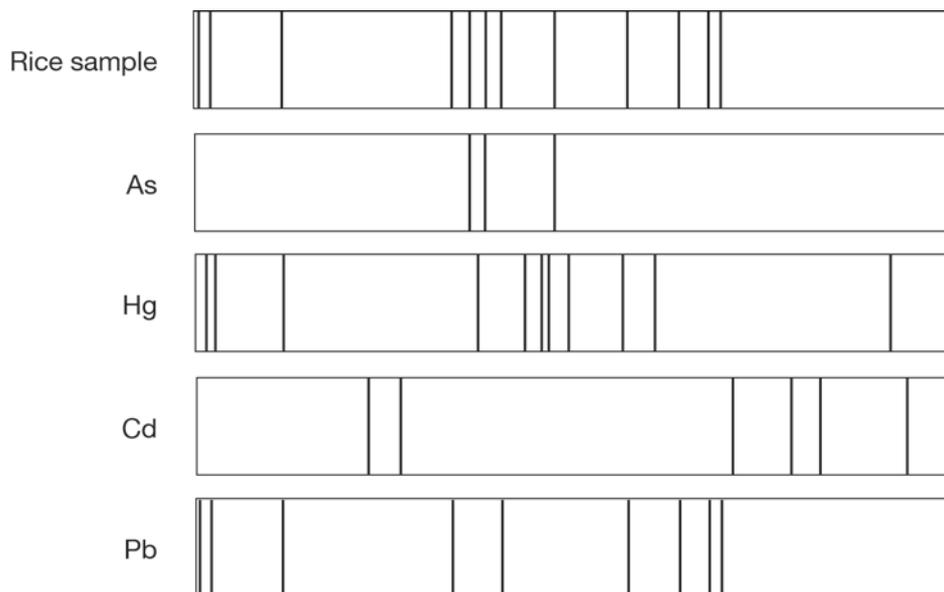
Line emission spectra can be used to indicate the presence of elements. Wavelengths emitted are characteristic of elemental composition, as certain wavelengths are unique to particular elements.

Question

30. Arsenic levels in the environment have been increasing due to pollution from industry. Inorganic arsenic has been detected in rice at concerning concentrations. Rice typically contains approximately ten times more arsenic than any other grain. Rice is highly efficient at taking arsenic out of soils, as it is grown in an anaerobic environment.

- (a) (i) **State** which block of the periodic table where arsenic is found.
 (1 mark) **KA1**
- (ii) **Write** the electronic configuration of arsenic, using subshell notation.
 (2 marks) **KA4**

(b) Flame emission spectroscopy was used to determine the presence of arsenic and other potential harmful elements in a rice sample. The line emission spectra produced for the rice sample and identifiable elements are shown below:



- (i) **State** and **explain** whether arsenic was present in the rice sample.

 (2 marks) **IAE3**

- (ii) **Identify** one other element of concern that is present in the rice sample.
 (1 mark) **IAE3**

(c) A particular brand of rice cakes was analysed and the arsenic concentration was determined to be 606 ppb. **Calculate** the mass of arsenic, in mg, consumed from a single rice cake of 1.02 g.

(3 marks) **KA4**

Science understanding

Atomic absorption spectroscopy is used for quantitative analysis.

Explain the principles of atomic absorption spectroscopy in identifying elements in a sample.

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Atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) is a highly sensitive and selective quantitative analytical technique. It is used primarily in the detection of individual metallic elements in a sample. Concentrations can be detected in the ppm (parts per million) range, and in applications of the technique (using a graphite furnace), the ppb (parts per billion) range.

A **hollow cathode lamp** is selected for the analysis of the element under investigation. The sealed lamp contains an inert gas (such as argon), the anode and a hollow cathode coated in the element of interest (Figure 1.5.10).

A voltage is applied across the electrodes. This removes atoms from the surface of the cathode, allowing their outer-shell electrons to undergo excitation. A pulsed beam of emitted radiation is directed through a window at the top of the lamp to pass directly through the long thin flame.

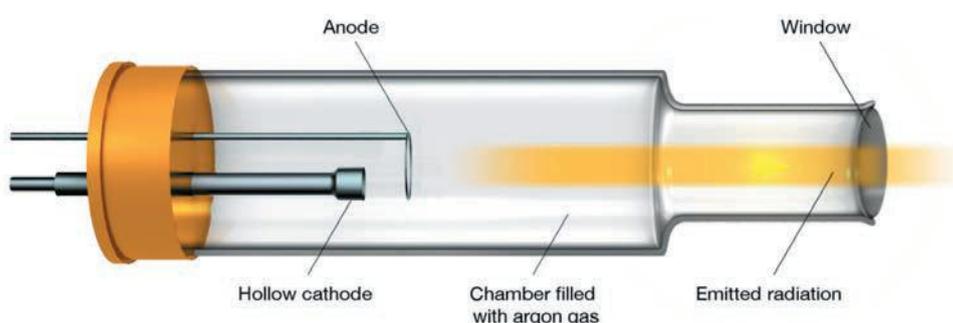


Figure 1.5.10: Hollow cathode lamp.

The original incident beam is also split into a secondary beam prior to passing through the flame. The alternative beam is directed to the detector to establish an **incident** (initial, prior to the flame) reading of the light intensity.

A **nebuliser** system draws up the sample through a capillary, aspirating (spraying) it into the oxy-acetylene fuel mixture entering the flame of the burner head (Figure 1.5.11).

The heat energy from the flame quickly evaporates the solvent and breaks down the compounds in the sample into atoms in a free atomic state.

Outer shell electrons are promoted to higher energy levels in the atom. The electrons return to lower energy levels in the atom. This results in the emission of electromagnetic radiation. The specific wavelengths of radiation present in the emission correspond to the energy transitions undertaken by electrons.

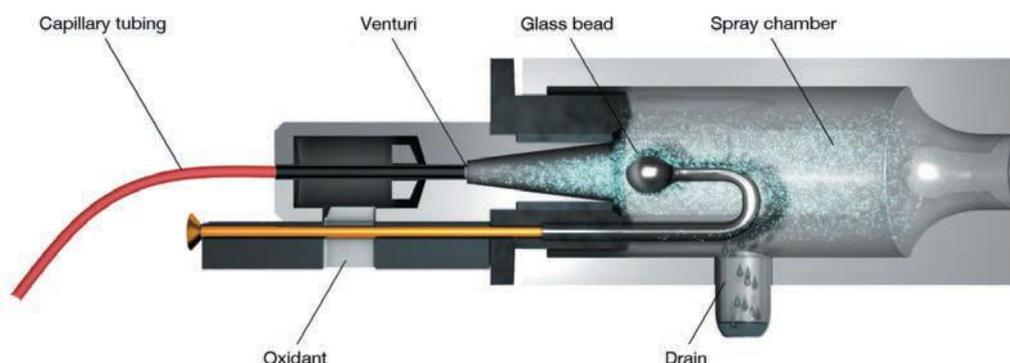


Figure 1.5.11: Nebuliser.

Atoms in the flame absorb radiation from the incident beam at matching wavelengths (atomic absorption).

If the element of interest is present in the aspirated sample, all wavelengths will be absorbed. The resulting atomic emission is released in all directions, reducing the intensity of the incident radiation.



The **transmitted** beam (passing through the flame) of lower intensity is directed to a **monochromator**. A monochromator consists of a diffraction grating or prism, used to separate the radiation into individual wavelengths. One wavelength is selected for detection, which is unique to the element under investigation.

The detector is set to measure the intensity of the selected wavelength. The intensity for this wavelength is compared between the incident and transmitted beams. A mathematical relationship is then applied to determine the absorbance.

$$A = \epsilon \times l \times c$$

A = absorbance

$$\therefore A \propto c$$

ϵ = molar attenuation coefficient

l = path length

c = concentration

With ϵ and l constant in the equation, the relationship demonstrates that the absorbance is proportional to the concentration of the element under investigation.

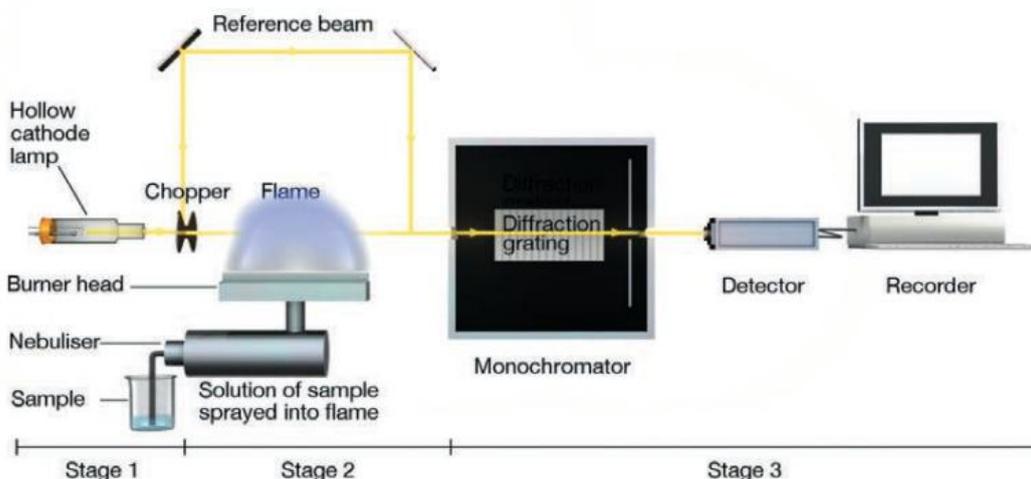


Figure 1.5.12: Atomic absorption spectroscopy.

Science as a human endeavour

Atomic absorption spectroscopy

In the 1950s, atomic emission spectroscopy was used to identify the presence of a small number of elements.

In 1952, a team of Australian chemists led by Sir Alan Walsh at the CSIRO trialled methods that utilised the absorption characteristics of the elements instead of their emission. This technique proved effective for 65 elements at the time. Alan Walsh approached manufacturing industries to develop the new apparatus required for the technique. With the support of his team of researchers, Walsh endeavoured to demonstrate the effectiveness of this new technique, but was met initially with scepticism. Today, with worldwide acceptance in the scientific community, AAS has been recognised as one of the most significant developments in modern spectroscopic analysis, used extensively in mining, agriculture, manufacturing and medicine.



Question

31. Studies were undertaken to analyse samples of hair from the general population to determine the presence of lead. Exposure to high levels of lead can lead to intellectual disability. Comparisons were made with an equal number of males and females in a specific age group to determine patterns of exposure.

250 mg samples of hair were digested in 50 mL of nitric acid (HNO₃) to prepare solutions that were analysed using atomic absorption spectroscopy (AAS).

(a) **State** the characteristic of the lamp chosen for the analysis.

..... (1 mark) **KA1**

(b) The unknown solutions were aspirated into the burner flame.

(i) **Explain** what happens to the outer-shell electrons in lead atoms that enter the beam of radiation directed through the flame.

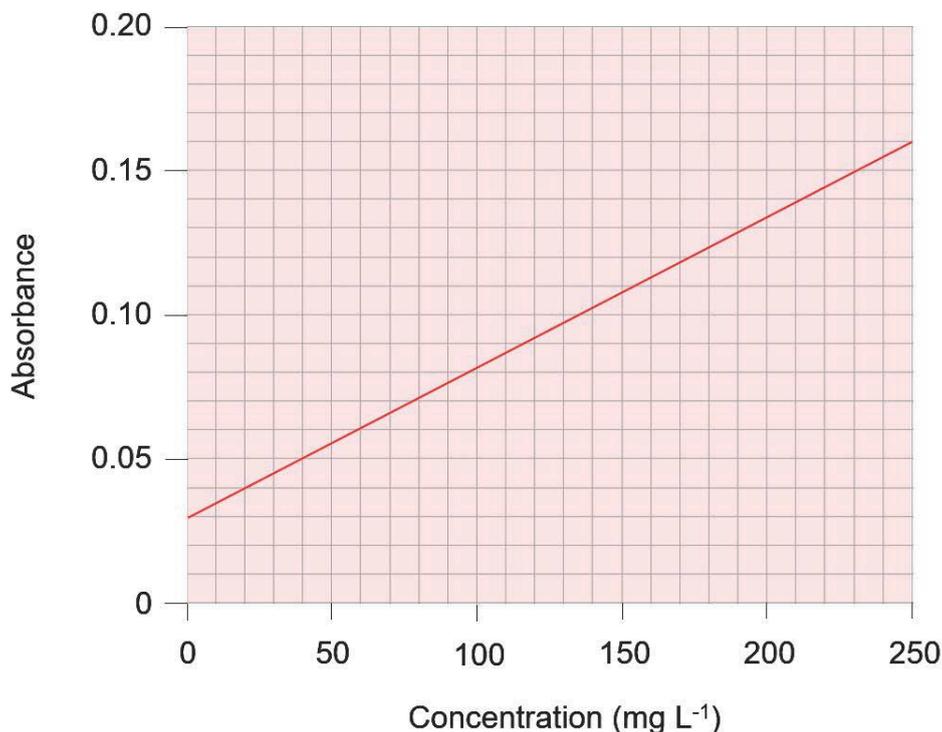
.....

 (2 marks) **KA1**

(ii) **Suggest** why the products from this sample, passing through the burner head, were extracted by an exhaust fan.

.....
 (1 mark) **IAE1**

(c) The following calibration graph was constructed from known solutions of lead.



(i) A line of best fit was applied to the data obtained.

(1) **Suggest** why the calibration line does not pass through the origin.

.....
 (1 mark) **IAE4**

(2) To the axes above, **apply** a second calibration line that demonstrates greater accuracy.

(1 mark) **IAE4**



The mean concentration of lead in females in the 20 to 30 age group samples was considerably higher than males. This was thought to be due to the absorption of lead compounds present in cosmetics.

(ii) Using the original calibration graph, **determine** the concentration of lead, in mg L⁻¹, from an absorbance reading of 0.052, for males in the 20 to 30 age band.

. (2 marks) **KA4**

(iii) Using the original calibration graph, **determine** the absorbance for a mean concentration of lead of 194 ppm recorded for females in the 20 to 30 band.

. (2 marks) **KA4**

(d) Cadmium, arsenic and chromium were also present in comparable concentrations.

(i) **Explain** why the presence of these elements did not interfere with the analysis for lead.

.
.
.
.
.
.
. (3 marks) **KA2**

(ii) **State** two changes that would need to be made to the calibration of the AAS for the detection of cadmium.

.
.
.
. (2 marks) **KA1**

Science understanding

Describe the construction and use of calibration graphs in determining the concentration of an element in a sample.

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Calibration graphs

A calibration graph is constructed for an element of interest from a set of prepared solutions. The range of concentrations selected will depend on the expected concentration of the element in the unknown sample and the limitations of the apparatus. Typically, very dilute solutions are used with quantities in the ppm or ppb range.

A set of standard solutions are prepared for the element under investigation. The standard solutions prepared have increasing concentrations. A blank of distilled/deionised water is also included to serve as a reference for calibration.

Each solution may be prepared individually at a desired concentration or generated through a serial dilution of a stock solution.

A blank is initially introduced to the AAS to calibrate the apparatus. The prepared solutions are then added sequentially from lowest to highest concentration.

Each solution, including the blank, will register an absorbance reading that is plotted on a calibration graph.

The graph is plotted with absorbance (the dependent variable) against concentration (the independent variable). A line of best fit is applied to the data. This typically generates a straight line (linear fit).

The unknown solutions are then introduced to the AAS and an absorbance reading recorded for each individual solution.

Unknown concentrations can then be interpolated from the constructed calibration graph (see Figure 1.5.13). The software used for AAS generates the graph and undertakes the associated concentration determination from the readings.

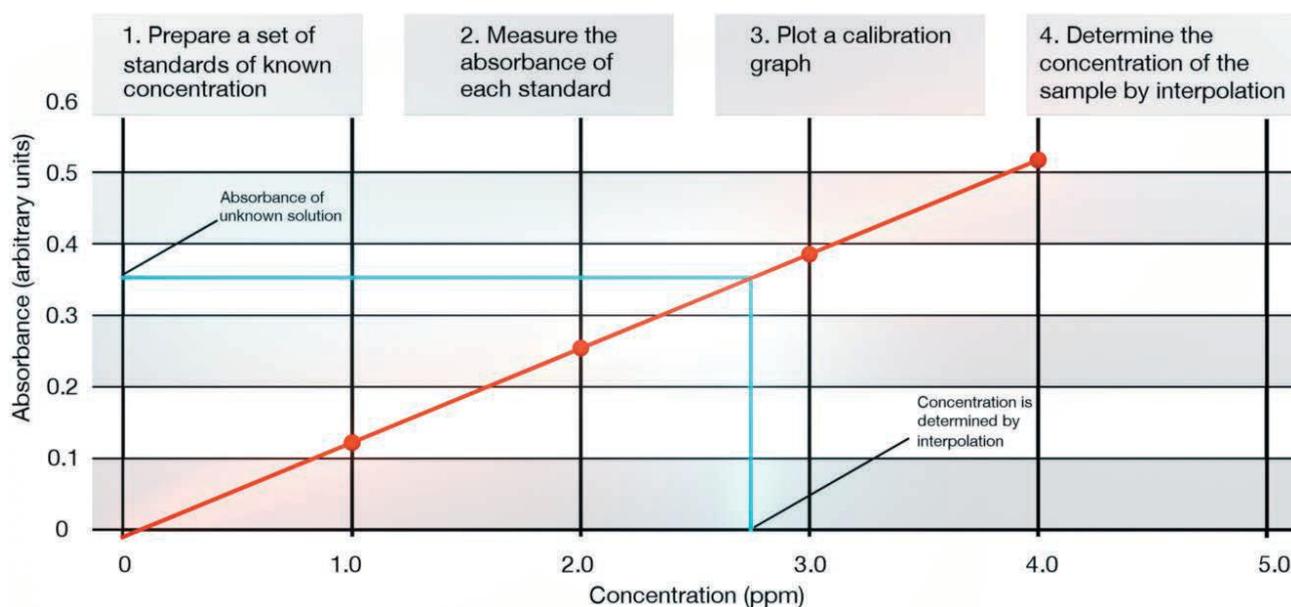


Figure 1.5.13: Construction of an AAS calibration graph.

(v) Deposits of silicon dioxide can be removed from components by immersion in hot concentrated sodium hydroxide (NaOH), which forms sodium silicate (Na₂SiO₃) in aqueous solution.

(1) **Write a balanced equation** for the reaction described above.

(2 marks) **KA4**

(2) **State** whether the silicon dioxide is demonstrating properties of an acidic or basic oxide in this reaction.

..... (1 mark) **KA1**

(b) Lubricating oil in a jet engine was analysed for the presence of tin from solder in cooling systems. AAS was performed with the use of a graphite furnace. A concentration of 0.326 µg mL⁻¹ was recorded.

Determine the concentration of tin in ppb.

(2 marks) **KA4**

(c) Many alloy components used in planes are made from titanium due to its strength and low density. Excessive wear in the lifetime of the component may be indicated by higher concentrations of titanium in lubricating oil.

(i) **State** whether titanium is a metal, non-metal or metalloid.

..... (1 mark) **KA1**

(ii) Titanium oxidises in air to form titanium dioxide, TiO₂.

Write the electronic configuration of titanium in TiO₂.

..... (2 marks) **KA4**

(iii) (1) Using the provided grid and axes, construct a calibration graph for the analysis of titanium in lubricating oils.

Concentration (ppb)	Absorbance
0	0.0100
200	0.0360
400	0.0710
600	0.108
800	0.144
1000	0.180



(6 marks) **IAE2**

(2) **State** the feature of the graph that indicates high precision.

.....
 (1 mark) **KA1**



? Science inquiry skills

Skills in context

Graphing in atomic absorption spectroscopy

Constructing a calibration graph requires the inclusion of a number of the following features (Figure 1.5.14).

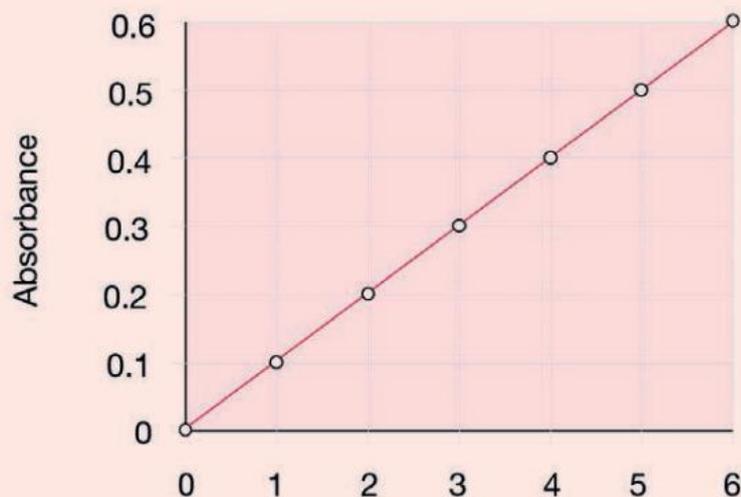


Figure 1.5.14: Features of a typical AAS graph.

Feature		Explanation
(1)	Identified variables	The concentration is altered in AAS, and therefore it represents the independent variable . The absorbance is measured, and therefore it is the dependent variable .
(2)	Labelled axes	Quantities need to be identified and attributed to each axis. Variables are generally plotted with the dependent variable on the y-axis and the independent variable on the x-axis. Absorbance is plotted on the y-axis and concentration on the x-axis.
(3)	Identified units	If applicable, units and prefixes show range and scale. Absorbance is measured in arbitrary units, so units are not required (some graphs may express the value as a percentage). Concentration is typically expressed in ppm, ppb, g L ⁻¹ or mol L ⁻¹ (with appropriate prefixes applied).
(4)	Application of an appropriate scale	Appropriate scale and size assists in plotting and conveying the data. The data should use the majority of the space provided. The scale used for AAS data would include the range for the prepared standard solutions.
(5)	Plotted data points	Data points need to be recorded clearly and accurately to allow interpretation of the line of best fit and an evaluation of the degree of scatter and hence precision. At least three data points are used to reduce the effect of random errors and establish trends. A line graph is applied to the AAS data.
(6)	Construction of a line of best fit	The line of best fit is applied to allow interpretation of the correlation with expected or established trends. AAS will typically produce a linear relationship, where absorbance is proportional to concentration.

Analysis of spectroscopy graphs

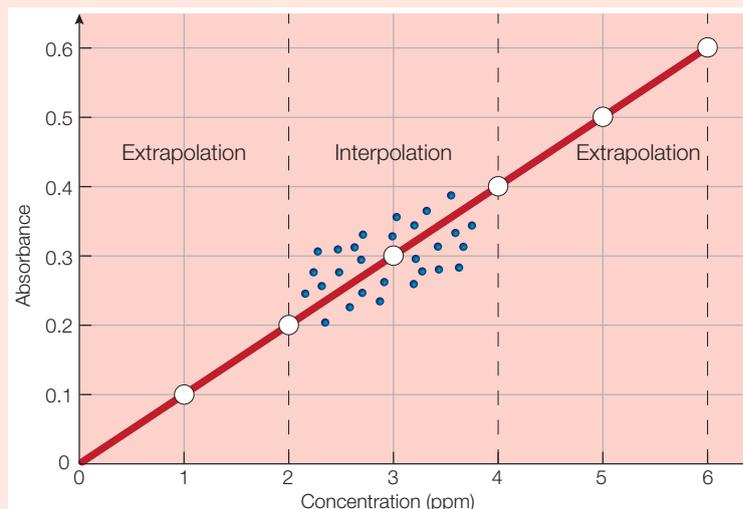


Figure 1.5.15: Interpretation of a graph.

Interpolation and extrapolation

Interpolation requires the determination of data points derived from the range of data provided. In AAS, concentrations for unknown samples are interpolated from the calibration line within the data. **Extrapolation** requires extension beyond the provided data based on an established trend (Figure 1.5.15). If the unknown values sit outside of the data, a new calibration graph would be produced or the samples diluted further to fit within the range of standards.

Applying a line of best fit

A **line of best fit** is applied in AAS. Typically, a linear relationship is established, producing a straight line. The line is drawn to leave an equal residual distribution of data points above and below the line of best fit (Figure 1.5.15).

Scatter and precision

Scatter is evident in the distribution of data points around an applied line of best fit. Scatter can also be evident in the calculated range of data collated in a table. In AAS, scatter can be seen in absorbance values if more than one reading is taken at each concentration. However, scatter is more commonly identified in the agreement of the data points around the line of best fit (Figure 1.5.15).

As considered in Page 53, scatter results from **random error**. The greater the degree of scatter, the greater the impact of random errors. Random errors affect the **precision** of data. The greater the degree of scatter, and therefore the effect of random error, the lower the precision of the results.

Random error

Random errors in AAS can cause fluctuations between the predicted absorbance and the measured absorbance for a given concentration. Random errors can occur to both increase or decrease the value obtained. In AAS, random errors occur in the preparation of standard solutions. This includes washing, filling and delivery procedures, and variance in ambient light when readings are taken.

Systematic error

It is expected that the line of best fit for AAS should pass through the **origin** (0,0) (Figure 1.5.15). This would indicate that a concentration of zero produces an absorbance of the same reading. This may not occur in the following situations:

The single data point generated for the blank may be contaminated with the element under analysis (although with good technique unlikely). As only one data point is altered, this would represent a random error.

The readings including the blank solution have not been calibrated. Calibration needs to account for the light reaching the detector from the burner head and any ambient light that enters the apparatus. In this case, all readings would be altered by a consistent amount, in the same way, generating a source of **systematic error**. The line of best fit would sit consistently higher or consistently lower than expected and not pass through the origin.

As considered in Page 53, systematic errors arise from a consistent shift in measured values due to an inherent error in the procedure or apparatus. Systematic errors impact on the **accuracy** of data.

Summary test 1: Monitoring the environment

1. Large quantities of carbon dioxide are emitted during the production of cement. Carbon dioxide is released during the generation of heat and electricity for the plant, and as a product of the calcination phase.
- (a) During calcination, calcium carbonate is heated, decomposing to produce calcium oxide and carbon dioxide.
- (i) **Write** an equation for the decomposition of calcium carbonate.

(2 marks) **KA4**

- (ii) **State** one other human activity that is responsible for increased carbon dioxide levels in the troposphere.

.....
 (1 mark) **KA1**

- (iii) **Explain** how increased levels of atmospheric carbon dioxide have led to an increased average temperature in the Earth's troposphere.

.....

 (3 marks) **KA1**

- (b) 0.927 kg of carbon dioxide is released for every 1 kg of cement produced. 4.18 giga tonnes (Gt) of cement are produced annually around the world.

Calculate the total annual emissions of carbon dioxide from cement production.

(2 marks) **KA4**



- (d) Cement requires limestone, silica, and minerals containing aluminium and iron, obtained from mining. Part of the human contribution to atmospheric carbon dioxide comes from emissions generated from mining practices.

Mining practices have contributed to rising concentrations of atmospheric carbon dioxide. Seeking raw materials and fossil fuels as feedstock, directly releases carbon dioxide into the atmosphere. The combustion of fuels by mining machinery, as well as consumption of fuels associated with electricity production during processing, and further transportation of refined products all contribute emissions.

In an attempt to reduce demands on finite resources and offset emissions of carbon dioxide in the atmosphere, we have sought renewable alternatives. However, mining for the raw materials for future renewable energy infrastructure contributes to overall emissions, as well as severely impacting native species and ecosystems.

Solar panels, wind farms, and battery technologies all require materials processed from mining. Australia is recognised for the plentiful reserves of many renewable energy materials that are in high demand, such as lithium, graphite, and rare earth elements required for high powered magnets. These important resource exports contribute significantly to Australia's current and future economy.

Researchers have begun to map the geographical locations of renewable resources in Australia in comparison to known areas of native biodiversity. This comparison has indicated implications for extracting raw materials in these resource rich locations, with the threat to species and biodiversity. In some cases, the threat to plant and animal life due to mining has been predicted to have a greater impact than the challenges species face from climate change.

The research has put into perspective the need to balance our need for renewable energy materials, emissions from mining, and impact on native ecology. Recommendations from this research allow government to support growth in renewable infrastructure, while planning for conservation and sustainability and limiting impact upon natural biodiversity valued by indigenous people and communities across Australia.

With reference to the key concept of *influence*, explain how considerations around obtaining raw materials for renewable energies exemplifies science as a human endeavour.

.....

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..... (4 marks) KA3

2. Nitrogen dioxide emissions in heavily populated cities are primarily due to the use of motor vehicles.

- (a) Nitrogen dioxide is present in the exhaust emissions from internal combustion engines.

- (i) **State** one requirement for the formation of nitrogen dioxide that is provided during the combustion of fuel in an engine.

.....

..... (1 mark) KA1

- (ii) **Write an equation** for the formation of nitrogen dioxide from nitric oxide.

(2 marks) KA2

(b) When exposed to sunlight, nitrogen dioxide emissions in cities may result in the formation of ground-level tropospheric ozone.

(i) **State** why ultraviolet light is required for the formation of ozone.

.....
 (1 mark) **KA1**

(ii) **Write equations** for the formation of ozone from nitrogen dioxide.

(4 marks) **KA4**

(iii) **State** one undesirable consequence of pedestrians being exposed to elevated concentrations of ozone in the troposphere.

.....
 (1 mark) **KA1**

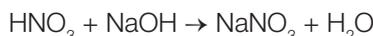
Credit will be given for the correct use of significant figures in answers to part (c). (1 mark)

(c) The concentration of nitrogen dioxide at low levels in air can be determined by bubbling a sample of air through a solution of hydrogen peroxide, oxidising the nitrogen dioxide to nitric acid.



A 5.00 L sample of air was introduced to a solution of hydrogen peroxide.

The nitric acid formed was titrated with 0.100 mol L⁻¹ sodium hydroxide.



A titre value of 9.16 mL was obtained.

(i) Methyl red was used as the indicator. Methyl red is red at a pH below 4.4 and yellow at a pH over 6.2.

State the colour obtained at the endpoint of the titration.

..... (1 mark) **KA2**

(ii) **Calculate** the number of moles of sodium hydroxide that reacted with the nitric acid formed.

(2 marks) **KA4**

(iii) Hence, **calculate** the moles of nitric acid formed.

(1 mark) **KA4**



(iv) **Calculate** the moles of nitrogen dioxide present in the original sample of air.

(1 mark) **KA4**

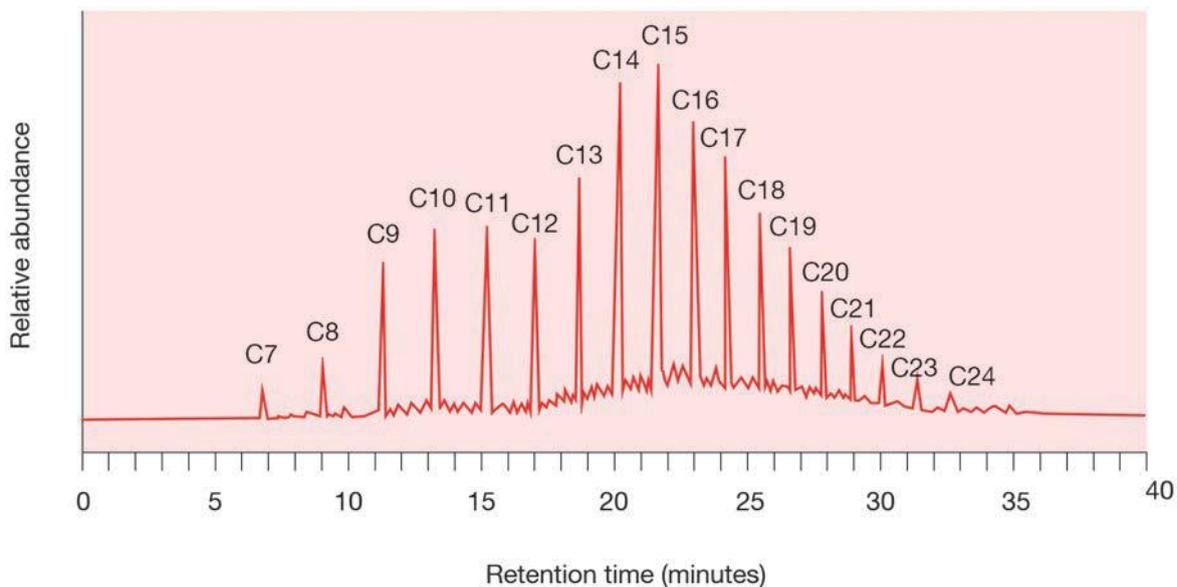
(v) **Calculate** the concentration of nitrogen dioxide, in ppm, in the original sample of air.

(4 marks) **KA4**

3. Remediation of industrial sites for urban redevelopment requires the analysis of soil and groundwater for the presence of potentially harmful wastes.

(a) Oils and fuels present in the soil from small localised spills can be detected using gas chromatography (GC).

The chromatogram below indicates the presence of diesel fuel, due to the range of hydrocarbon peaks present for the alkane series.



(i) **State** the systematic name of the straight chain alkane containing eight carbon atoms.

..... (1 mark) **KA1**

(ii) **Determine** the retention time (in minutes) of the alkane containing 15 carbon atoms. State the answer to three significant figures.

..... (2 marks) **KA4**

(iii) **Describe** the relationship between carbon chain length and retention time.

.....
 (1 mark) **IAE3**

(iv) **State** and **explain** whether the stationary phase chosen for the separation is more likely to be polar or non-polar.

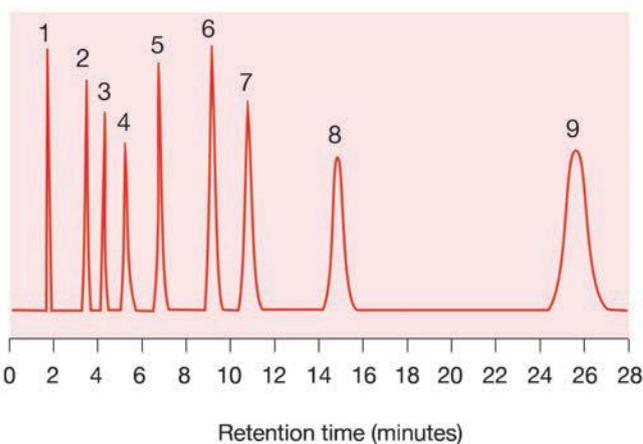
.....

 (2 marks) **IAE3**

(v) **Suggest** one reason why the presence of diesel fuel contamination is more difficult to determine for spills that are not recent.

.....
 (1 mark) **KA2**

(b) Groundwater was analysed from a site that was suspected of being used for market gardening. The groundwater was analysed for the presence of nitrate ions (NO_3^-) and phosphate ions (PO_4^{3-}), which would indicate the possible use of fertilisers.



- 1. Formate, HCOO^-
- 2. Nitrite, NO_2^-
- 3. Glutarate, $\text{C}_3\text{H}_6(\text{COO})_2$
- 4. Phosphate, PO_4^{3-}
- 5. Azide, N_3^-
- 6. Nitrate, NO_3^-
- 7. Molybdate, MoO_4^{2-}
- 8. Arsenate, AsO_4^{3-}
- 9. Phthalate, $\text{C}_6\text{H}_4(\text{COO})_2$

Ion-chromatography (IC) was used to analyse the water sample for the presence of nitrate and phosphate ions. An anion exchange column was used.

(i) **State** the charge on the resin surface in the column.

..... (1 mark) **KA1**

(ii) **State** and **explain** which anion would exhibit the largest retention time.

.....

 (3 marks) **IAE3**

4. Copper chromium arsenate (CCA) has been used for many years to treat pine fencing posts often used in the viticulture industry to support vines. Concern has been raised over the leaching of copper, chromium and arsenic metals from the posts into the surrounding soil.

(a) Chromium trioxide (CrO_3) is one compound used in CCA formulations.

(i) **State** the block of the periodic table to which chromium belongs.

..... (1 mark) **KA1**

(ii) **Write** the electronic configuration of chromium.

..... (2 marks) **KA4**

(iii) **State** the oxidation number of chromium in CrO_3 .

..... (2 marks) **KA1**

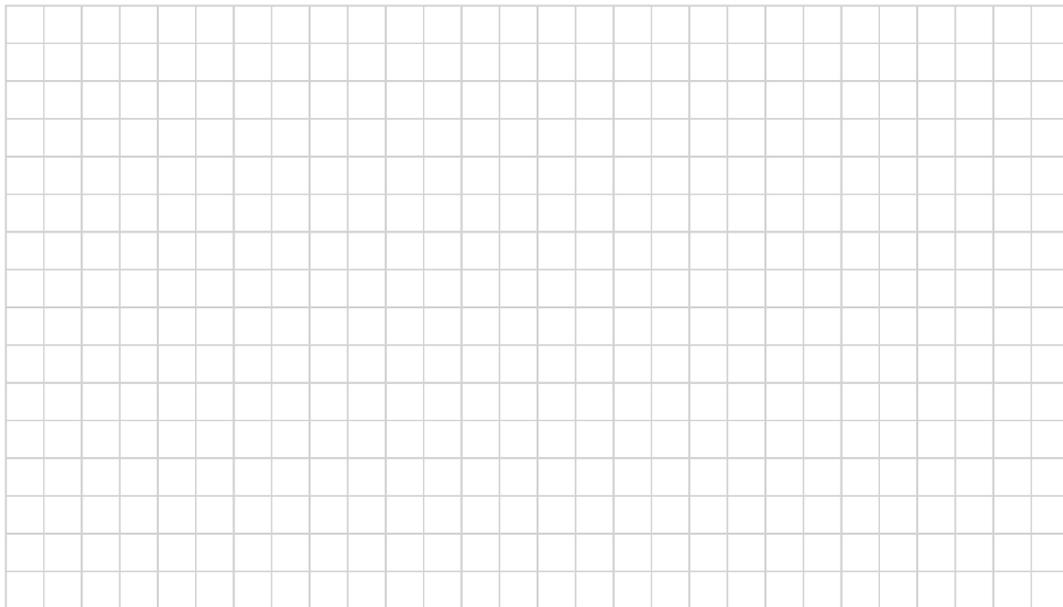
(b) Standard solutions were prepared and analysed for copper producing the following results.

Concentration (ppm)	Absorbance
0	0.00300
5	0.148
10	0.290
15	0.431
20	0.566

(i) **Identify** which column represents the dependent variable.

..... (1 mark) **IAE1**

(ii) Using the grid below, **construct** a calibration graph for the known copper solutions.



(6 marks) **IAE2**

(iii) **State** the characteristic of the graph that indicates a high degree of precision.

..... (1 mark) **KA1**

(iv) **Explain** why the presence of chromium and arsenic do not interfere with the analysis for copper.

.....

 (2 marks) **KA2**

(c) In regions where acid rain has been recorded, there is even greater concern about the use of CCA posts.

Suggest one disadvantage of the use of CCA posts under these conditions.

.....
 (1 mark) **KA2**

Topic 2: Managing chemical processes

2.1 Rates of reaction

Science understanding

The rates of a reaction at different times can be compared by considering the slope of a graph of quantity or concentration of reactant or product against time.

Draw and interpret graphs representing changes in quantities or concentration of reactants or products against time.

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Chemical changes occur when reacting particles form new products. The evidence of chemical change occurring could be observed as follows:

- Gas forming, seen in the reaction vessel and as bubbles if in a liquid
- Colour change in the reaction vessel
- Precipitate formed; insoluble compound formed from two previously soluble compounds
- Light produced
- Heat produced

Law of Conservation of Energy

The Law of Conservation of Energy states that energy cannot be created or destroyed and therefore, the net energy of a system is conserved. The rearrangement of chemical bonds is an energy intensive process hence energy can be converted to heat and light.

Law of Conservation of Mass

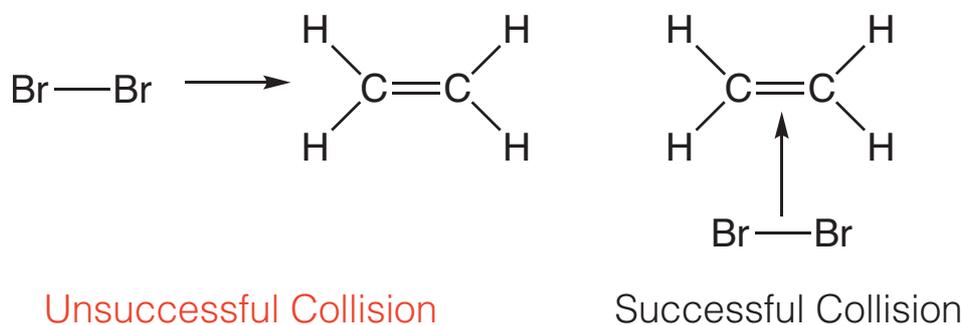
The Law of Conservation of Mass is based on the conservation of energy and states that the total mass of a system is conserved during a reaction and as such, when chemical bonds are rearranged the net mass of the system is constant.

Collision Theory

In any chemical system there are collisions continuously occurring between particles. **Collision Theory** states that for a **successful collision** to occur; collisions occur between reacting particles, these collisions have sufficient energy, these collisions occur with the correct orientation. Reacting particles collide, enabling the chemical bonds to rearrange through the breaking and reforming of bonds. The minimum amount of energy required for a successful collision is termed the **Activation Energy** (E_a) and successful collisions require the collision between reacting particles to meet or exceed E_a . Successful collisions also require the collision between reacting particles to occur with the correct orientation. It is important to note that many **unsuccessful collisions** are occurring at the same time.

Worked example

In the addition reaction between bromine (Br_2) and an alkene such as ethene (C_2H_4), the correct orientation and E_a is required for the collision between these two molecules. The required orientation for the successful collision is shown in the diagram below:



Rate of Reaction

A rate is used to determine how fast or slow a quantity changes with respect to time e.g., the rate at which a beaker is filled with water could be measured in millilitres per second (mL s^{-1}). Likewise, a chemical reaction rate measures how fast or slow reactants are forming products per unit time. The rate of a chemical reaction could be measured either by the rate at that the products are formed or the rate that the reactants are consumed.

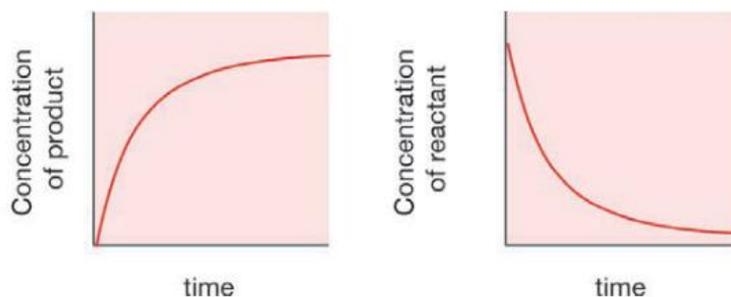


Figure 2.1.1: Changes in the quantity of a product (left) and a reactant (right) with respect to time.

The rate of products forming could be:

- Gas forming in a syringe and measured as the volume change with respect to time e.g., mL sec^{-1}
- Number of moles of products forming e.g., mol sec^{-1}

The rate of reactants being consumed could be:

- Mass of reactants reducing with respect to time e.g., g sec^{-1}
- Concentration of reactant reducing with respect to time e.g., $\text{mol L}^{-1} \text{sec}^{-1}$

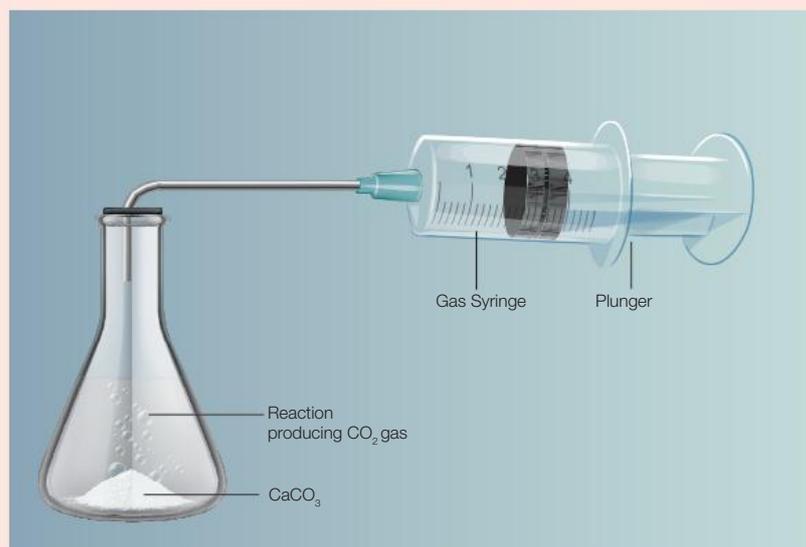
? Science inquiry skills

Skills in context

The slope of a graph can be used to determine the rate of a chemical reaction. Consider the reaction between calcium carbonate (CaCO_3) and hydrochloric acid (HCl) producing carbon dioxide gas (CO_2). The reaction equation is given below:

Possible variables that could be measured for this particular reaction (dependant variables) are the change in mass of CaCO_3 (g sec^{-1}) or the volume of CO_2 produced (mL sec^{-1}).

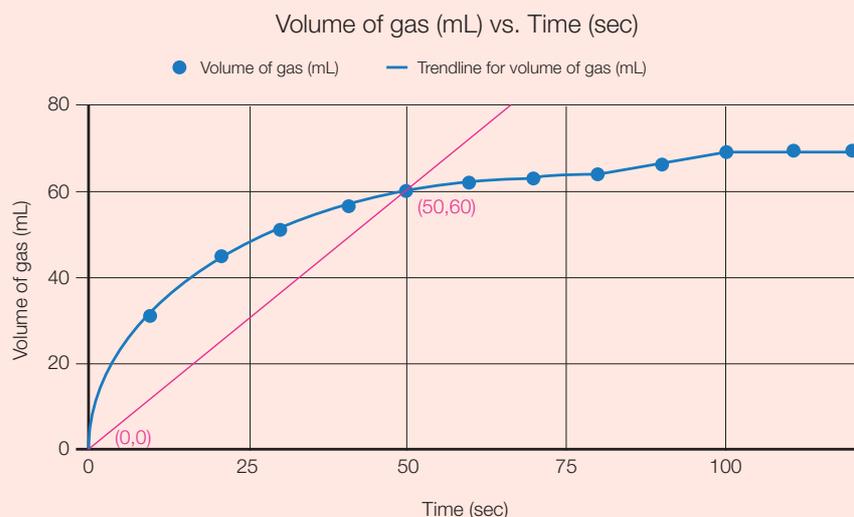
The quantity of carbon dioxide produced can be measured using a gas syringe, a possible setup is shown below:



? Science inquiry skills

The following results were produced:

Time (sec)	Volume of CO ₂ gas (mL)
0	0
10	34
20	46
30	52
40	56
50	60
60	62
70	64
80	66
90	68
100	70
110	70
120	70



For the graph above the average rate of reaction for the first 50 seconds can be determined by finding the slope of a line over that period.

$$\text{slope} = \frac{\Delta y}{\Delta x}$$

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$\text{Average rate of reaction} = \frac{\text{change in volume}}{\text{time elapsed}}$$

$$\therefore \text{Average rate of reaction} = \frac{60 - 0}{50 - 0}$$

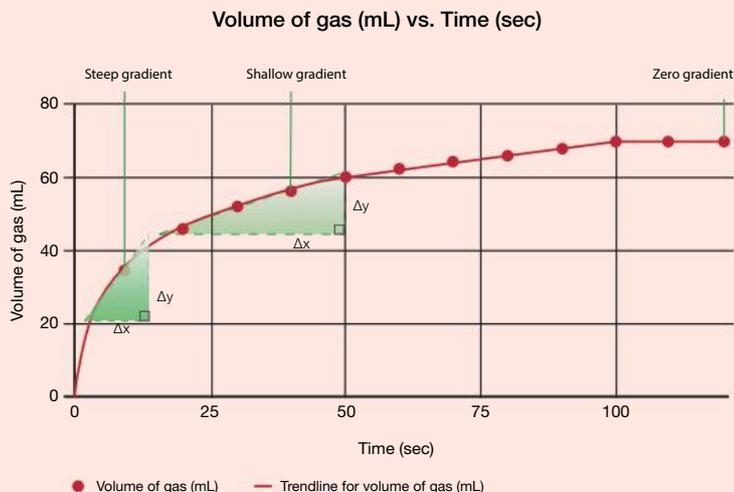
$$\therefore \text{Average rate of reaction} = \frac{60}{50}$$

$$\therefore \text{Average rate of reaction} = 1.2 \text{ mL s}^{-1}$$

Therefore, the average rate of formation of carbon dioxide gas over the first 50 seconds is 1.2 mL s^{-1} .

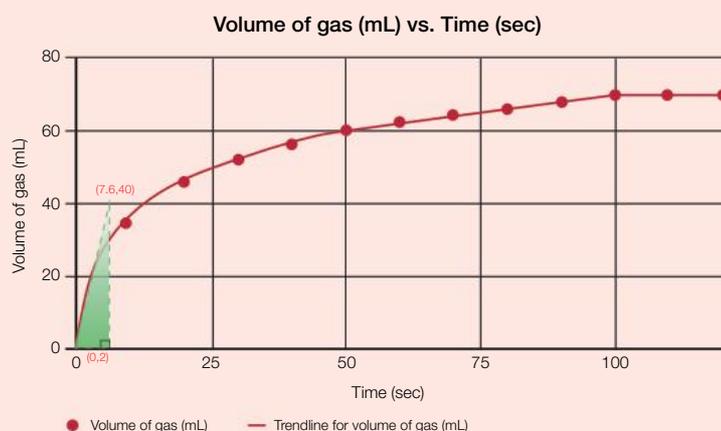
The instantaneous rate of a chemical reaction can be used to determine the rate of reaction at a given point in time. This can be useful for identifying when the rate of production is at its highest.

? Science inquiry skills



The graph above shows the changing rate of the reaction through the tangent lines drawn. It is important to note the following:

- Steep tangent line = fast rate of reaction where the conversion of reactants to products is occurring rapidly
- Shallow tangent line = slow rate of reaction where the conversion of reactants to products is occurring slowly
- Zero gradient
 - For a **non-reversible reaction** = the reaction has stopped converting reactant into products
 - For a **reversible reaction** = the reaction has reached a state of chemical equilibrium (refer to 2.2)



Referring to the tangent line drawn at approximately $t = 2$ seconds the instantaneous rate of reaction can be calculated for this point of the reaction.

Therefore, at approximately $t = 2$ seconds the rate of formation of carbon dioxide gas is 5 mL per second.

$$\text{Instantaneous rate of reaction} = \frac{\Delta y}{\Delta x}$$

$$\text{Instantaneous rate of reaction} = \frac{\text{change in volume}}{\text{time elapsed}}$$

$$\therefore \text{Instantaneous rate of reaction} = \frac{40 - 2}{7.6 - 0}$$

$$\therefore \text{Instantaneous rate of reaction} = \frac{38}{7.6}$$

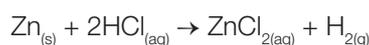
$$\therefore \text{Instantaneous rate of reaction} = 5 \text{ mL s}^{-1}$$

Changes in concentration

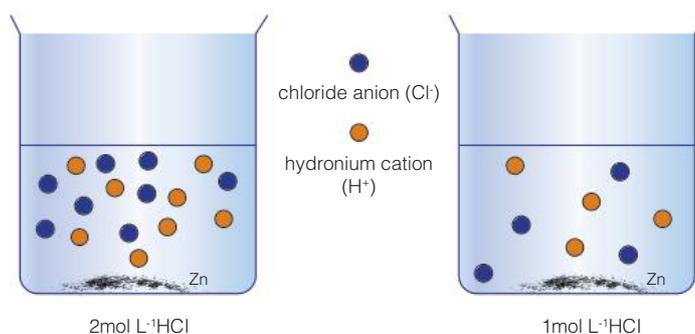
If the concentration of reacting particles is altered the rate of the chemical reaction will change. If the concentration of a species of reacting particles is increased there are more reacting particles in the system. The frequency of collisions is increased. More collisions occur between reacting particles and as a result, a larger number of successful collisions occur. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.

Worked example

Considering the reaction between zinc metal (Zn) and hydrochloric acid (HCl) represented by the reaction equation below.



If the concentration of the hydrochloric acid is increased from 1 mol L⁻¹ to 2 mol L⁻¹, there are more HCl formula units and thus more H⁺ ions available to react with the zinc metal, represented in the diagram below.



The frequency of collisions between H⁺ ions and zinc metal is increased. More collisions occur and as a result a larger number of successful collisions occur between H⁺ ions and zinc metal. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of formation of ZnCl₂ and H₂ gas.

? Science inquiry skills

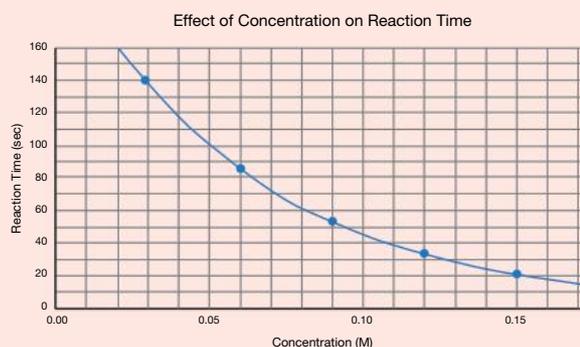
Skills in context

The rate of formation of a precipitate could be used to measure the rate of a chemical reaction. Consider the example of hydrochloric acid reacting with different concentrations of sodium thiosulfate, resulting in an opaque solution from the insoluble sulfur (S) precipitate.

The variable that could be measured in this example is the time taken for the reaction to produce an opaque solution, this is the **dependant variable**. The concentration of sodium thiosulfate is being altered by the scientist and is the **independent variable**.

This experiment is carried out producing the following results:

Conc. Na ₂ S ₂ O ₃ (M)	Reaction Time (sec)
0.15	24.31
0.12	29.96
0.09	51.23
0.06	81.4
0.03	141.63



From the graph above, it can be deduced that as the concentration of sodium thiosulfate increases, the time taken for the solution to become opaque decreases. This indicates that the rate of formation of sulfur is increasing. As the concentration of sodium thiosulfate increases there are more reacting particles in the solution. The frequency of collisions between reacting particles is increased. More collisions occur and as a result a larger number of successful collisions occur between sodium thiosulfate and hydrochloric acid. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of formation of the precipitate sulfur.

Changes in pressure

The pressure of a system is determined by the movement of particles within a given volume. To increase the pressure of a system, the volume of that system is decreased or more particles are introduced into a given volume. The overall effect of these changes is an increase in concentration, represented in the diagram below.

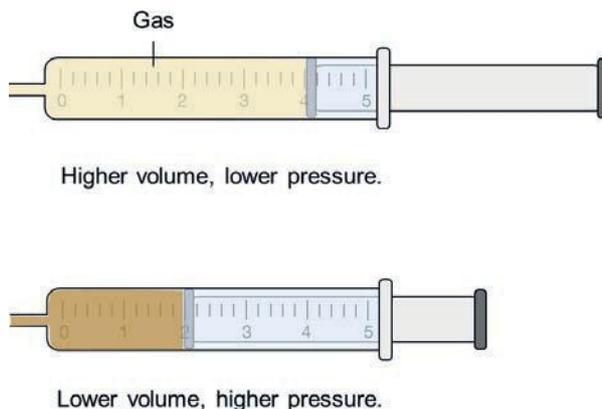


Figure 2.1.2: Relationship between the volume and pressure of a gas.

Change in pressure is effectively a change in concentration applied to a gaseous system.

If the pressure of a system involving particles in the gaseous state is altered the rate of the chemical reaction will change. If the pressure of a system is increased by introducing more particles, the concentration of a species of reacting particles is increased. The frequency of collisions between gaseous particles is increased. More collisions occur between reacting gaseous particles and as a result a larger number of successful collisions occur. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.

If the pressure of a system is increased by reducing the volume of the gaseous system, more collisions occur between gaseous particles. The frequency of collisions between gaseous particles is increased and as a result a larger number of successful collisions occur. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.

Worked example

Consider the reaction between nitric oxide (NO) and oxygen gas (O₂) producing nitrogen dioxide (NO₂).



If the pressure of the reaction vessel is increased by altering the volume of the vessel from 2L to 1L. More collisions occur between nitric oxide and oxygen molecules within the smaller volume. The frequency of collisions between gaseous particles is increased and as a result a larger number of successful collisions between nitric oxide and oxygen molecules occur. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of formation of nitrogen dioxide.

Changes in surface area

The surface area of particles can be increased by division into smaller particles as can be seen by the diagram below.

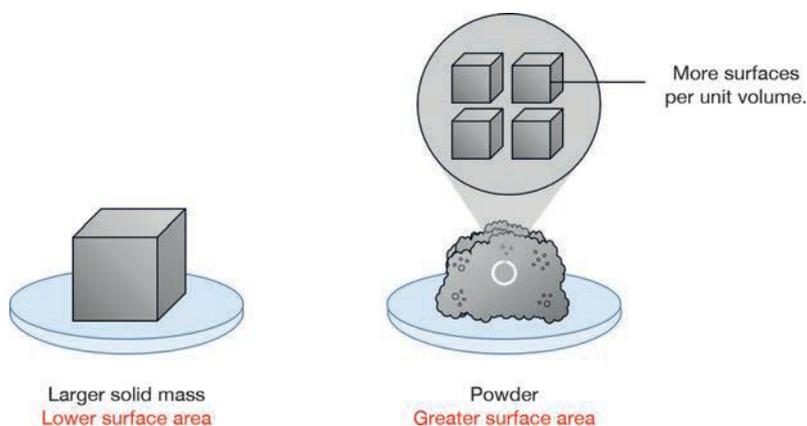


Figure 2.1.3: Samples of solid zinc (metal) with different surface area.

Changes in temperature

If the temperature of a system is altered, the rate of the chemical reaction will change. If the temperature of a system is increased this results in the average kinetic energy of the reacting particles increasing and exhibiting more thermal energy. Therefore, a larger proportion of collisions reach or exceed the Activation Energy.

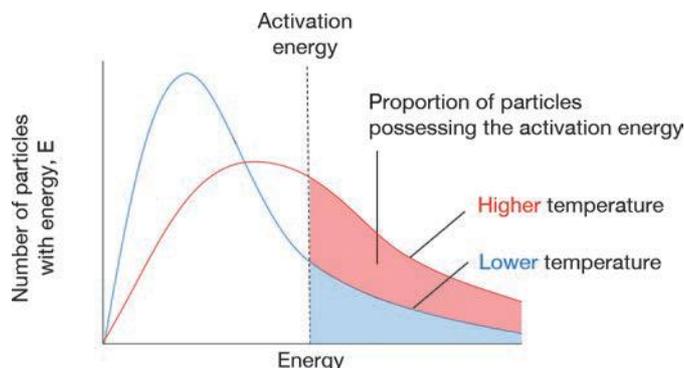
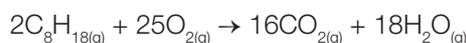


Figure 2.1.4: Effect of temperature on the number of particles possessing the activation energy.

There is an increased frequency of successful collisions occurring. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.

Worked example

Fuels such as octane (C_8H_{18}) react with oxygen gas (O_2) through a combustion reaction represented below.



If the temperature of the reaction mixture is increased from $20^\circ C$ to $1000^\circ C$, this results in the average kinetic energy of the reacting particles increasing and exhibiting more thermal energy. Therefore, there is a larger proportion of collisions between octane and oxygen molecules reaching or exceeding the Activation Energy. There is an increased frequency of successful collisions occurring between the molecules. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of formation of carbon dioxide and water.

Presence of a catalyst

Catalysts are substances that are used to increase or decrease (inhibitor) a rate of reaction; these include enzymes which are biological catalysts.

Positive catalysts provide an alternate reaction pathway with a lower E_a , increasing the rate of chemical reactions.

Negative catalysts, or inhibitors, decrease the rate of chemical reactions, by increasing E_a , or stopping chemical reactions occurring.

If a catalyst is introduced to a system, the rate of the chemical reaction will alter. If a positive catalyst is introduced this would provide an alternative reaction pathway for the reacting particles with a lower Activation Energy. This results in a larger proportion of collisions between reacting particles reaching or exceeding the Activation Energy. There is an increased frequency of successful collisions occurring. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.



Science as a human endeavour

Development

Hydrogen fuel is regarded as the key renewable fuel that would enable Australia to switch away from its heavy reliance on fossil fuels. Hydrogen gas is produced through electrolysis which is an energy intensive process. Green hydrogen is hydrogen gas that is produced through an electrolysis process where the energy is sourced purely from renewable sources. Scientists around the world are always seeking ways to reduce the energy requirements in the production process.

A group of scientists from the Virginia Tech College of Science have developed a new way to use mixed nickel iron hydroxide (MNF) catalysts. This process includes using thin sheets of MNF as a catalyst for the production of hydrogen gas. This reduces the Activation Energy required for splitting the water molecules into hydrogen gas and oxygen gas, leading to more molecules having energy exceeding E_a and therefore more successful collisions. Therefore, the rate of successful collisions per unit time increases, resulting in the formation of hydrogen gas and oxygen gas with lower energy requirements.

Helpful online resources

<https://www.sciencedaily.com/releases/2020/09/200904125114.htm>

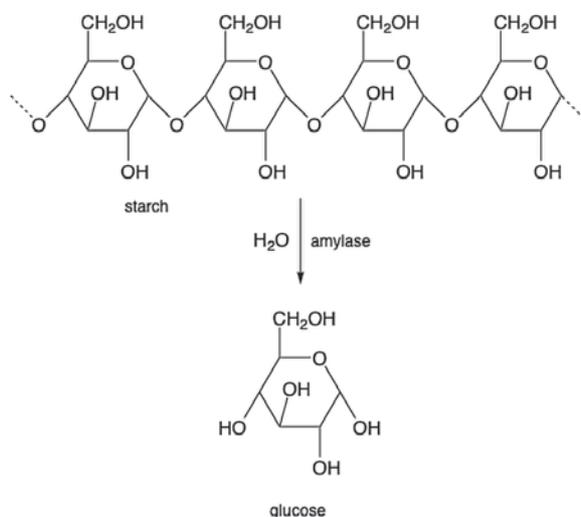


<https://www.nature.com/articles/s41929-020-0496-z>



Worked example

Amylase is an enzyme in human saliva that catalyses the hydrolysis of starch in the mouth, breaking it down to simple sugars, according to the below reaction.



Hydrolysis of starch

Amylase provides an alternative pathway with a lower E_a for the starch to hydrolyse into simpler sugars. This results in a larger proportion of collisions between reacting particles reaching or exceeding the Activation Energy. There is an increased frequency of successful collisions occurring. Therefore, a larger number of successful collisions occur per unit time increasing the rate of hydrolysis of starch molecules.

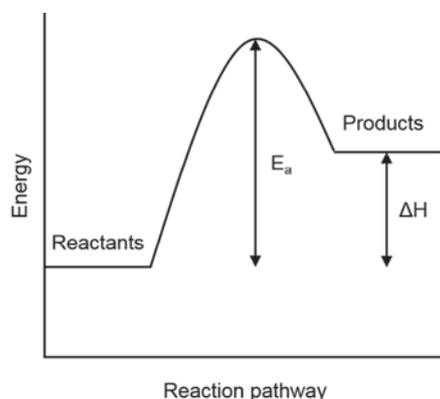


Figure 2.1.5: Energy profile diagrams for an endothermic chemical reaction.

If the overall enthalpy of the products is less than the enthalpy of the reactants, the system has lost energy (ΔH is negative) and the reaction is **Exothermic**. The energy profile diagram below shows the decrease of energy in the system.

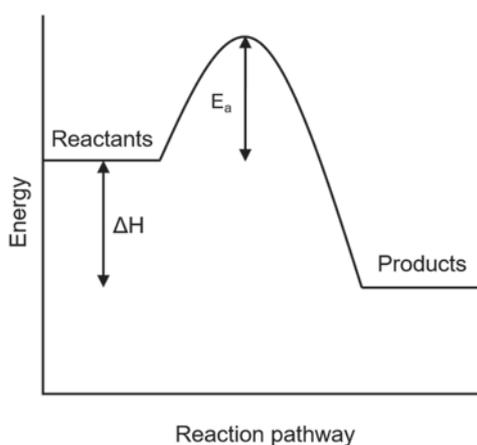


Figure 2.1.6: Energy profile diagrams for an exothermic chemical reaction.

The energy profile diagram for an exothermic reaction with and without a catalyst can be seen below.

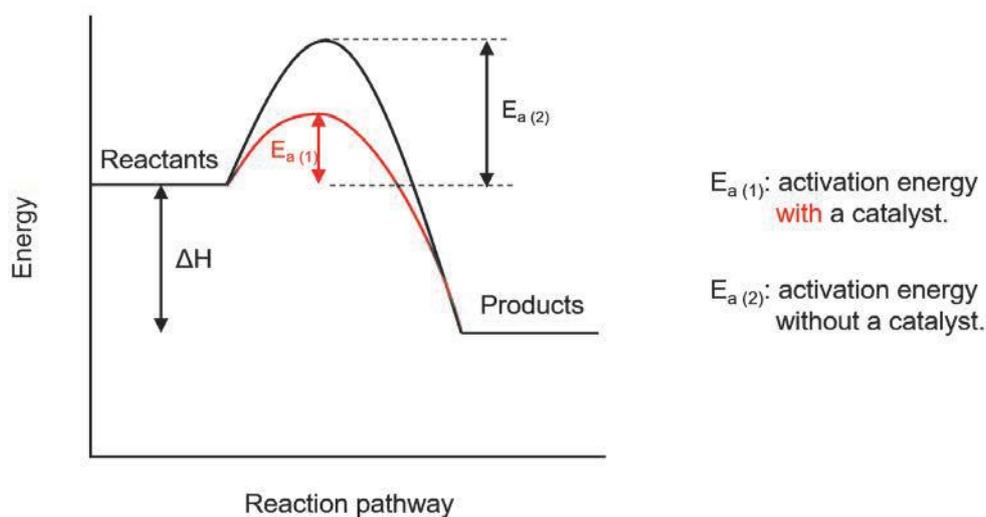


Figure 2.1.7: Energy profile diagram for an exothermic reaction showing the activation energy barriers for the catalysed and uncatalysed reaction pathways.

Note that the reaction with the catalyst provides an alternate pathway with a lower activation energy.

2.2 Equilibrium and yield

Science understanding

Chemical systems may be open or closed.

Over time, reversible chemical reactions carried out in a closed system at fixed temperature eventually reach a state of chemical equilibrium.

The changes in concentrations of reactants and products, as a system reaches equilibrium, can be represented graphically.

Draw and interpret graphs representing changes in quantities or concentration of reactants or products against time.

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2

A chemical system can either be an open system or a closed system. An **open chemical system** is one where both chemical matter and energy can be transferred into and out of the system. A **closed chemical system** has no net loss or gain of matter and only energy can be transferred into and out of the system e.g., thermal energy, light energy.

Chemical reactions can be either **non-reversible reactions** or **reversible reactions**. A non-reversible reaction is one where the chemical reaction proceeds to completion.

Worked example

An example of a non-reversible reaction occurs when baking a cake. One of those reactions is between baking powder and water. The baking powder dissolves in water, releasing the acid and sodium bicarbonate present from their ionic structures and allowing them to react together. This reaction produces carbon dioxide gas which can be seen as the bubbles in your cake and what makes it rise. As the carbon dioxide leaves the chemical system this reaction has lost a product and so cannot proceed in the backward direction.

A reversible reaction is identified by the ability for the reactants to combine producing products and the products combine, producing reactants. If a reversible reaction occurs in a closed chemical system at a fixed temperature, the chemical reaction will eventually reach a state of **chemical equilibrium**. A state of chemical equilibrium is reached when the rate of the forward reaction is equivalent to the rate of the backwards or backward reaction. At chemical equilibrium the net concentrations of reactants and products do not change with time.

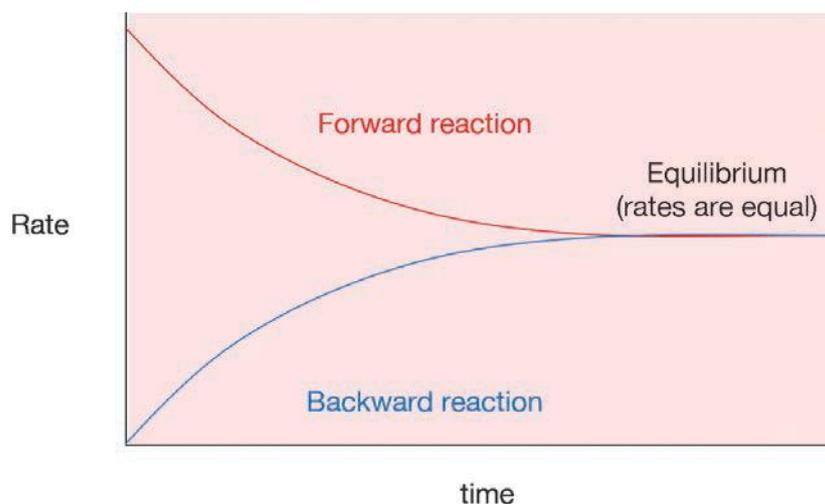
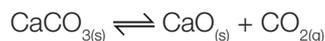


Figure 2.2.1: Rate of formation (forward reaction) and decomposition (backward reaction).

On the macroscopic level there is no observable change to the chemical system when it is in a state of equilibrium. However, on the atomic level there are reactants colliding producing products and products colliding producing reactants at the same rate.

Worked example

Lime or calcium oxide (CaO) is an important compound, and the industrial production of lime occurs according to the following chemical equation. Note the reversible arrow (\rightleftharpoons) used for an equilibrium reaction.



This reaction will eventually reach a state of equilibrium. At equilibrium, calcium carbonate is forming calcium oxide and carbon dioxide. At the same time calcium oxide and carbon dioxide are reacting, producing calcium carbonate.

As a chemical reaction reaches equilibrium the concentrations of reactants and products can be represented graphically, showing the point at which equilibrium is reached. It is important to note that at this point the rate of the forward and backward reactions are equivalent. Hence there is no net change in concentration of reactants or products, indicated by parallel lines and a slope of 0. It is important to note that the reaction has not stopped.

The following graphical representation shows the previous equilibrium reaction for the formation of calcium oxide.

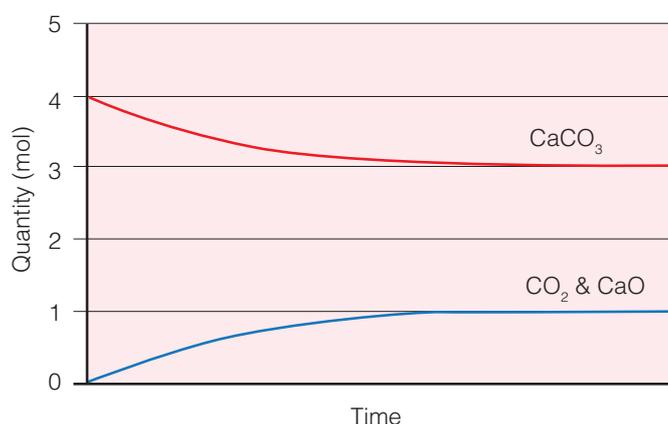


Figure 2.2.2: Changes in the molar quantities of calcium carbonate, carbon dioxide and calcium oxide in a reversible reaction at constant pressure and temperature.

Science understanding

The position of equilibrium in a chemical system at a given temperature can be indicated by a constant, K_c , related to the concentrations of reactants and products.

Write K_c expressions that correspond to given reaction equations for homogeneous equilibrium systems.

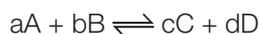
Undertake calculations involving K_c and initial and/or equilibrium quantities of reactants and products for homogeneous equilibrium systems.

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The equilibrium constant, K_c , is used to indicate the position of equilibrium at a given temperature. The expression for K_c is given below.

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

Given a reaction between A and B, forming C and D.



An equilibrium equation can be written to represent the equilibrium constant for the above reaction.

$$K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

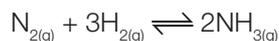
The position of chemical equilibrium can be determined by the K_c value. Understanding the position of equilibrium is useful for identifying whether the products or reactants have the greater concentration.

A K_c much greater than 1 indicates that the concentration of the products is greater than reactants, so the forward reaction is being favoured and the position of equilibrium lies to the right.

A K_c much less than 1 indicates that the concentration of the reactants is greater than products, so the backward reaction is being favoured and the position of equilibrium lies to the left.

Worked example

Consider a reaction between nitrogen and hydrogen forming ammonia.



The expression for this reaction is shown below:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1 \cdot [\text{H}_2]^3}$$

The concentrations of the species in this reaction are recorded below, showing the change in concentration once equilibrium is reached.

	N_2	3H_2	2NH_3
Initial concentration (mol L ⁻¹)	0.600	0.400	1.00
Change in concentration (mol L ⁻¹)	-0.016	-0.048	+0.032
Concentration at equilibrium (mol L ⁻¹)	0.584	0.352	1.032

K_c for these quantities can be calculated by substituting the concentration values into the expression shown above.

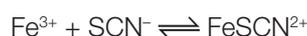
$$\begin{aligned} \therefore K_c &= \frac{[1.032]^2}{[0.584]^1 \cdot [0.352]^3} \\ \therefore K_c &= \frac{1.065024}{0.584 \times 0.04361421} \\ \therefore K_c &= 41.8 \text{ (3sf)} \end{aligned}$$

Note that the value for K_c has no units as it is a constant.

This K_c value indicates that the position of equilibrium lies to the right of the arrow, favouring the products.

Worked example

Consider the reaction between iron (III) ions (Fe^{3+}) and thiocyanate ions (SCN^-) producing iron thiocyanate ions (FeSCN^{2+}).



A 100 mL sealed reaction vessel is used and to it is added 5.04×10^{-4} mol of Fe^{3+} and 2.14×10^{-3} mol of SCN^- . At equilibrium it is determined that the reaction vessel contained 4.00×10^{-4} mol of FeSCN^{2+} .

These values are placed into the table below to calculate the equilibrium moles of Fe^{3+} and SCN^- .

	Fe^{3+}	SCN^-	FeSCN^{2+}
Initial moles	5.04×10^{-4}	2.14×10^{-3}	0.00
Change in moles			
Equilibrium moles			4.00×10^{-4}

The number of moles of FeSCN^{2+} has increased by 4.0×10^{-4} mol.

	Fe^{3+}	SCN^-	FeSCN^{2+}
Initial moles	5.04×10^{-4}	2.14×10^{-3}	0.00
Change in moles			+ 4.00×10^{-4}
Equilibrium moles			4.00×10^{-4}

To calculate the number of moles at equilibrium for the reactants, the stoichiometric ratio is used.

The ratio of FeSCN^{2+} to both reactants is 1:1, therefore if there is an increase of 4.0×10^{-4} mol to the products, there will be a decrease of 4.0×10^{-4} mol for both reactants.

	Fe^{3+}	SCN^-	FeSCN^{2+}
Initial moles	5.04×10^{-4}	2.14×10^{-3}	0.00
Change in moles	$- 4.00 \times 10^{-4}$	$- 4.00 \times 10^{-4}$	$+ 4.00 \times 10^{-4}$ mol
Equilibrium moles			4.00×10^{-4} mol

The number of moles at equilibrium for both reactants can now be determined by subtracting 4.00×10^{-4} moles from both initial mole values.

	Fe^{3+}	SCN^-	FeSCN^{2+}
Initial moles	5.04×10^{-4}	2.14×10^{-3}	0.00
Change in moles	$- 4.00 \times 10^{-4}$	$- 4.00 \times 10^{-4}$	$+ 4.00 \times 10^{-4}$
Equilibrium moles	1.04×10^{-4}	1.74×10^{-3}	4.00×10^{-4}

The reaction vessel is 100 mL in capacity and this is used to calculate the concentrations of all species. The number of moles at equilibrium for all species are divided by 0.100 L to calculate the concentrations in mol L^{-1} .

	Fe^{3+}	SCN^-	FeSCN^{2+}
Equilibrium moles	1.04×10^{-4}	1.74×10^{-3}	4.00×10^{-4}
Concentration at equilibrium (mol L^{-1})	$\frac{1.04 \times 10^{-4}}{0.100}$ $= 1.04 \times 10^{-3}$	$\frac{1.74 \times 10^{-3}}{0.100}$ $= 1.74 \times 10^{-2}$	$\frac{4.00 \times 10^{-4}}{0.100}$ $= 4.00 \times 10^{-3}$

Now that the concentrations at equilibrium are known, the value can be determined.

$$\therefore K_c = \frac{[\text{FeSCN}^{2+}]^1}{[\text{Fe}^{3+}]^1 \cdot [\text{SCN}^-]^1}$$

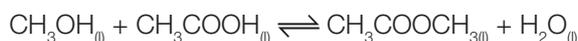
$$\therefore K_c = \frac{4.0 \times 10^{-3}}{1.04 \times 10^{-3} \times 1.74 \times 10^{-2}}$$

$$\therefore K_c = 221 \text{ (3sf)}$$

The K_c value of 221 is much greater than 1 which indicates that the concentration of FeSCN^{2+} ions is greater than the net concentration of Fe^{3+} ions and SCN^- ions. Therefore, the formation of is being favoured and the position of equilibrium lies to the right.

Question

5. 1.2 mol of ethanol (CH_3OH) and 1.2 mol of ethanoic acid (CH_3COOH) are placed into an empty 200 mL vessel and react to form the ester ethyl ethanoate ($\text{CH}_3\text{COOCH}_3$) and water (H_2O) according to the following equation.



- (a) **Write** the equilibrium expression for the reaction.

(1 mark) **KA4**

At equilibrium, the mixture is found to contain 0.5 mol of $\text{CH}_3\text{COOCH}_3$.

(b) **Calculate** the concentration of ethanol at equilibrium.

(3 marks) **KA4**

(c) **Calculate** the value of the equilibrium constant, K_c .

(2 marks) **KA4**

2

Science understanding

The final equilibrium concentrations, and hence position of equilibrium, for a given reaction depend on various factors. Predict and explain, using Le Châtelier's principle, the effect on the equilibrium position of a system of a change in the:

- concentration of a reactant or product
- overall pressure of a gaseous mixture
- temperature of an equilibrium mixture for which the ΔH value for the forward or back reaction is specified.

Predict the change that occurred in a system, or whether a reaction is exothermic or endothermic, given the effect of the change on the equilibrium position of the system.

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In a closed system, equilibrium reactions are in a state of dynamic equilibrium and there is no change in the concentrations of species. If an external change is introduced to the equilibrium system, the system will attempt to counteract the change. According to Le Châtelier's principle the system will shift the position of equilibrium in order to counteract the change that is placed upon it, allowing the system to re-establish equilibrium.

The position of equilibrium can be affected by the following factors:

- Concentration
- Pressure
- Temperature

It is important to note that the addition of a catalyst will not alter the position of a system in equilibrium. A catalyst alters the rate of the chemical reaction and thus the rate of both the forward and backward reaction would change equally, it would therefore have no net effect on equilibrium and reach a state of equilibrium faster.

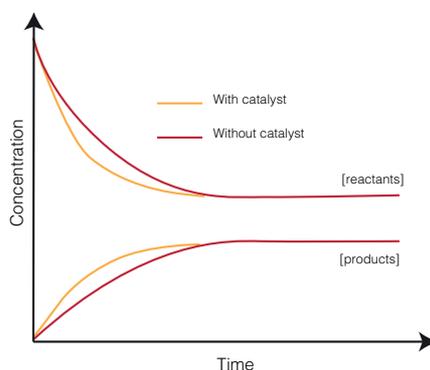


Figure 2.2.3: Effect of the presence of a catalyst on the system reaching a state of equilibrium.

Changes in concentration

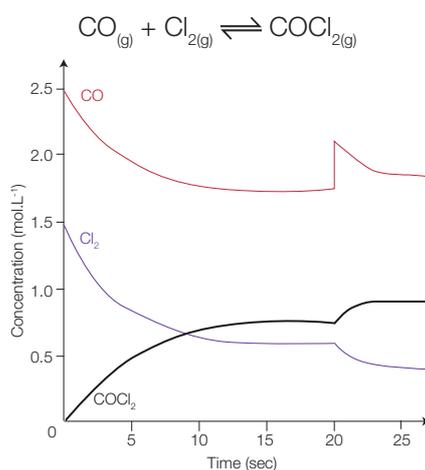
The position of equilibrium is affected if the concentration of one of the reactants is altered when a system is in a state of equilibrium.

If the concentration of a reactant is increased by adding more of the substance to the equilibrium mixture, the system will counteract the introduced change placed on the equilibrium mixture by attempting to reduce the concentration of that reactant. This will result in the forward reaction being favoured in order to convert reactants into products, shifting the position of equilibrium to the right until equilibrium is re-established.

If the concentration of a reactant is decreased by removing some of the substance from the equilibrium mixture, the system will counteract the introduced change placed on the equilibrium mixture by attempting to increase the concentration of that reactant. This will result in the backward reaction being favoured to create more of the lost reactant by converting products into reactants, shifting the position of equilibrium to the left until equilibrium is re-established.

Worked example

The effect of an increase in concentration can be seen in the reaction pathway diagram below representing the reaction between carbon monoxide (CO) and chlorine gas (Cl₂), forming COCl₂.



At $t = 20$ seconds the concentration of CO is increased which introduces a change to the system at equilibrium. According to Le Châtelier's principle the system will attempt to counteract the change in concentration by reducing the concentration of CO. This will result in the forward reaction being favoured in order to convert reactants into products, shifting the position of equilibrium to the right until equilibrium is re-established. Therefore, resulting in the concentration of Cl₂ decreasing and COCl₂ increasing as can be seen in the diagram.

Summary of concentration changes to equilibrium mixtures

Introduced change at equilibrium	Effect on	Effect on the position of equilibrium
Increase in concentration of reactant	No change	Shifts the position of equilibrium in the direction that reduces the reactant concentration (right)
Decrease in concentration of reactant	No change	Shifts the position of equilibrium in the direction that increases the reactant concentration (left)
Increase in concentration of product	No change	Shifts the position of equilibrium in the direction that reduces the product concentration (left)
Decrease in concentration of product	No change	Shifts the position of equilibrium in the direction that increases the product concentration (right)

Summary of concentration changes on a reaction pathway diagram

Change observed	Change to system
Sharp increase in concentration of one substance	Increase in concentration of one substance
Sharp decrease in concentration of one substance	Decrease in concentration of one substance

Changes in pressure

The position of equilibrium is affected if the pressure of the closed system is altered when a system is in a state of equilibrium.

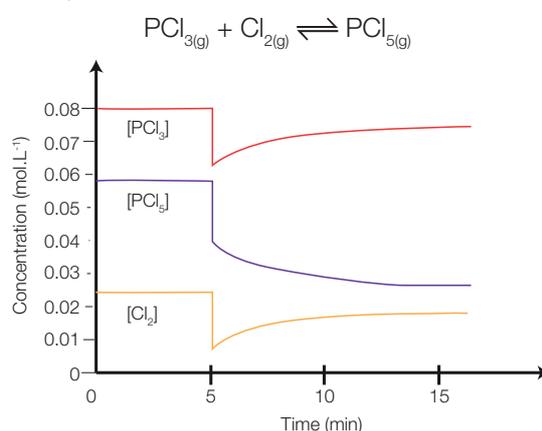
If the pressure of a system is increased by reducing the volume of the reaction vessel, the system will counteract the introduced change placed on the equilibrium mixture by attempting to reduce the pressure of the system. Le Châtelier's principle states that the reduction in pressure is achieved by shifting to the side of the equation which results in the formation of the least moles of gaseous particles until equilibrium is re-established.

If the pressure of a system is decreased by increasing the volume of the reaction vessel, the system will counteract the introduced change placed on the equilibrium mixture by attempting to increase the pressure of the system. Le Châtelier's principle states that the increase in pressure is achieved by shifting to the side of the equation which results in the formation of the most moles of gaseous particles until equilibrium is re-established.

If the number of moles of gaseous particles is equivalent on both sides of the reaction, there is no change to the position of equilibrium.

Worked example

The effect of a decrease in pressure can be seen in the reaction pathway diagram below representing the reaction between phosphorous trichloride (PCl_3) and chlorine gas (Cl_2), forming phosphorous pentachloride (PCl_5).



From the diagram above it can be concluded that at $t = 5$ mins the concentration of all species has decreased due to an increase in volume and therefore a decrease in pressure. According to Le Châtelier's principle the system will counteract the introduced change placed on the equilibrium mixture by attempting to increase the pressure. The increase in pressure is achieved by shifting to the side of the equation which results in the formation of the most moles of gaseous particles until equilibrium is re-established. In the reaction the left hand side has 2 moles of gas whilst the right hand side has 1 mole of gas. Therefore, the position of equilibrium would shift to the left in the backward direction as this creates the most moles of gas. Therefore, increasing the concentrations of PCl_3 and Cl_2 and decreasing the concentration of PCl_5 .

Summary of pressure changes to equilibrium mixtures

Introduced change at equilibrium	Effect on	Effect on the position of equilibrium
Increase in pressure of system	No change	Shifts the position of equilibrium in the direction of the production of fewer moles of gas
Decrease in pressure of system	No change	Shifts the position of equilibrium in the direction of the production of greater moles of gas

Summary of pressure changes on a reaction pathway diagram

Change observed	Change to system
Sharp increase in concentration of all gaseous species	Decrease in volume of reaction vessel Increase in pressure within reaction vessel
Sharp decrease in concentration of all gaseous species	Increase in volume of reaction vessel Decrease in pressure within reaction vessel

Changes in temperature

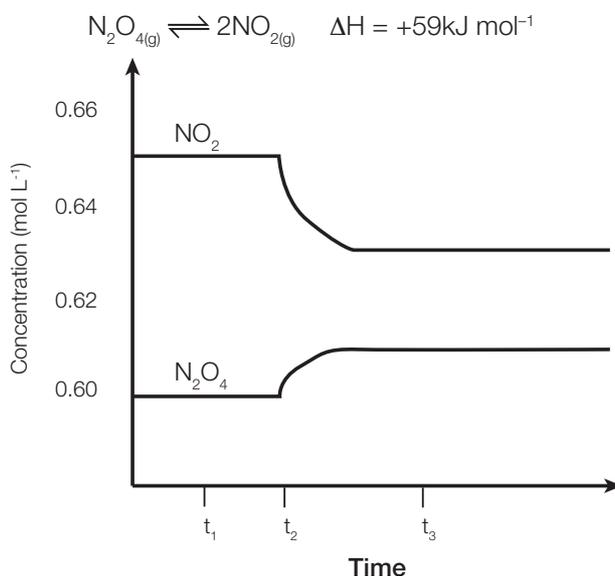
The position of equilibrium is affected if the temperature (thermal energy) of the closed system is altered when a system is in a state of equilibrium. According to Le Châtelier's principle the system will attempt to counteract the change in temperature with respect to the change that is applied. The direction in which the position of equilibrium responds is dependent on the ΔH value for the reaction. Note that the ΔH value is always in reference to the forward reaction.

If the temperature of a system is increased, the system will counteract the introduced change placed on the equilibrium mixture by absorbing the additional thermal energy. Le Châtelier's principle states that the increase in temperature leads to the position of equilibrium shifting in the endothermic (ΔH is positive) direction, absorbing the thermal energy.

If the temperature of a system is decreased, the system will counteract the introduced change placed on the equilibrium mixture by releasing thermal energy. Le Châtelier's principle states that the decrease in temperature leads to the position of equilibrium shifting in the exothermic (ΔH is negative) direction, releasing thermal energy.

Worked example

The effect of a decrease in temperature can be seen in the reaction pathway diagram below representing the dynamic equilibrium between N_2O_4 and NO_2 .



From the diagram above it can be concluded that the change that occurred resulted in the production of N_2O_4 being favoured which is the backward reaction. The enthalpy given for this reaction is positive, indicating that the forward reaction is endothermic and hence the backward is exothermic. According to Le Châtelier's principle, the exothermic reaction is favoured when the temperature of the reaction mixture is decreased. This will result in the backward reaction being favoured in order to release energy, shifting the position of equilibrium in the backward direction until equilibrium is re-established.

Effect of introduced changes to system at equilibrium on K_c value

It is important to note that the value of K_c for a given temperature is unchanged. If an introduced change to a system at equilibrium was on the concentration of species the K_c value would remain unchanged. Likewise, if the introduced change to the system at equilibrium was on the pressure of the system the K_c would also remain unchanged.

The value is only altered due to temperature changes in the system. The table below shows that as the temperature changes, the value also changes for the chemical reaction below.

Temperature ($^{\circ}\text{C}$)	K_c
25	4.64×10^{-3}
127	1.53

As the temperature decreases from 127°C to 25°C , the K_c value also decreases, indicating that the reactants N_2O_4 have the greater concentration.

Summary of temperature changes to equilibrium mixtures

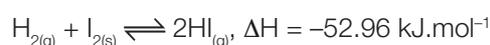
Introduced change at equilibrium	Effect on K_c	Effect on the position of equilibrium
Increase in system temperature	Changes	Shifts the position of equilibrium in the Endothermic direction
Decrease in system temperature	Changes	Shifts the position of equilibrium in the Exothermic direction

Summary of temperature changes on a reaction pathway diagram

Change observed	Change to system
Gradual changes	Increase or decrease in temperature of the system

Question

6. Hydrogen gas (H_2) reacts with iodine (I_2), forming hydrogen iodide (HI) according to the following reaction equation.



0.3 mol of I_2 is reacted with 0.5 mol of H_2 in a 100 mL vessel and at equilibrium the number of moles of HI is found to be 0.2 mol.

- (a) **Calculate** the equilibrium concentration of I_2 .

(3 marks) **KA4**

- (b) **Calculate** the K_c value for the above reaction at equilibrium.

(3 marks) **KA4**

- (c) **Explain** the effect on the position of equilibrium if the vessel is decreased to 50 mL.

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..... (3 marks) **KA1**

2.3 Optimising Production

Science understanding

Designing chemical-synthesis processes involves constructing reaction pathways that may include more than one chemical reaction.

The steps in industrial chemical processes can be conveniently displayed in flow charts.

Interpret flow charts and use them for such purposes as identifying raw materials, chemicals present at different steps in the process, waste products, and by-products.

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Industrial chemists and engineers around the world use chemical principles to identify and design the ideal reaction conditions and pathways for chemical reactions. These reaction pathways may involve multiple chemical reactions occurring. The steps involved in reaction pathways can be represented in a flow chart for a common process to show the key reactions necessary in industrial processes.

The key components of industrial chemical process flow charts are as follows:

- **Raw Materials** are added into the reaction pathway
- **By-products** are substances produced which are either reused in the reaction pathway or collected and used for another purpose.
- **Waste Products** are those which are disposed of or released into the environment.

Worked example

Blue hydrogen gas production involves using methane gas (CH_4) as the main chemical feedstock whilst green hydrogen gas production receives its energy from 100 percent renewable sources e.g. solar energy, wind energy, hydroelectric energy.

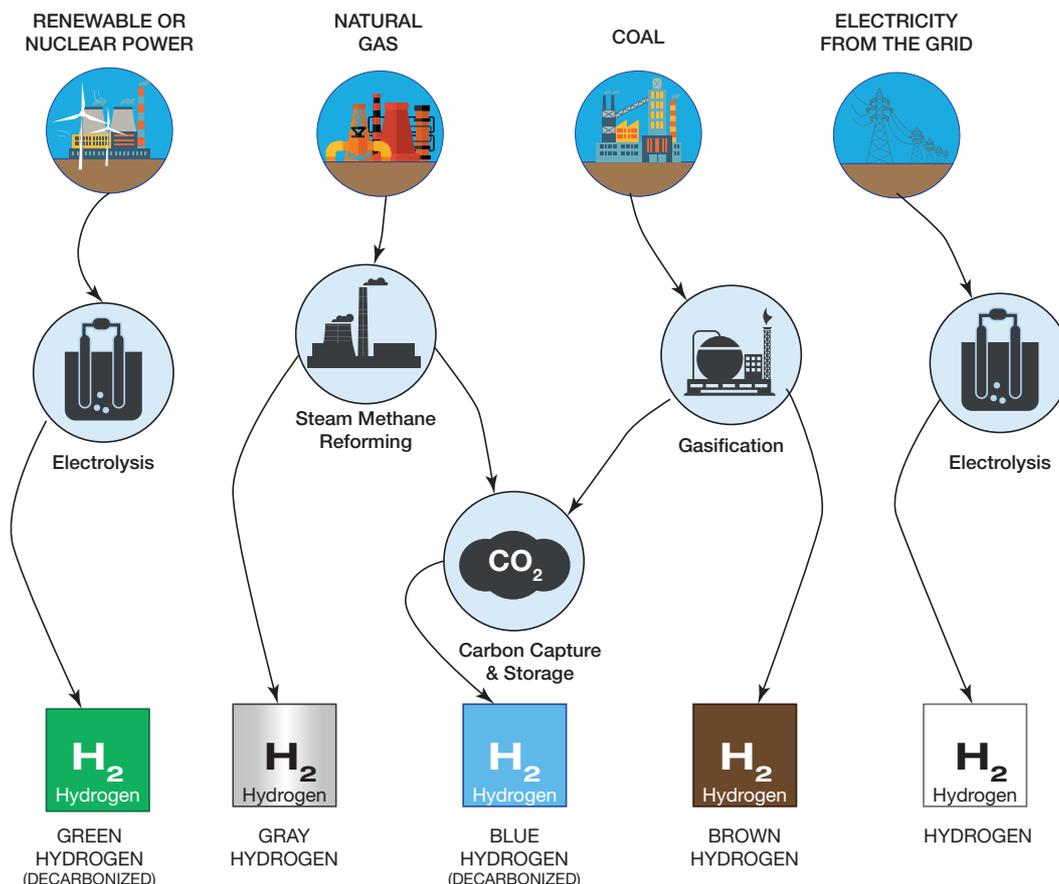
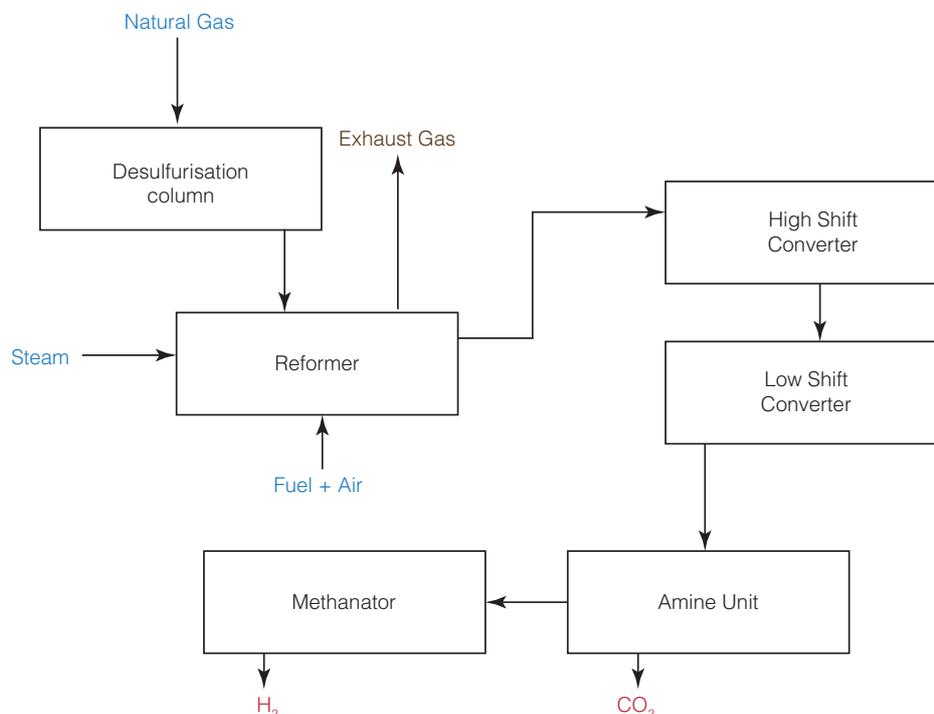


Figure 2.3.1: Non-renewable vs renewable methods of producing hydrogen gas

Blue hydrogen gas production involves using methane gas (CH_4) as the main chemical feedstock whilst green hydrogen gas production receives its energy from 100 percent renewable sources e.g. solar energy, wind energy, hydroelectric energy.

The following flow chart represents the industrial production of blue hydrogen gas.



In this reaction pathway Natural Gas (CH_4) is a raw material along with steam, fuel and air. CO_2 Rich and Exhaust Gas are classified as waste products.

Science understanding

Industrial processes are designed to maximise profit and to minimise impact on the environment.

Explain how certain reaction conditions represent a compromise that will give maximum yield in a short time.

Explain the impact of increases in temperature and pressure on manufacturing conditions and costs, and on the environment.

Explain how use of a catalyst may benefit both the manufacturer and the environment.

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In industry compromises in reaction conditions are made to balance various aspects of chemical processes. This is done to maximise profits whilst minimising the impact on the environment. If the reaction rate is high, this will ensure that the products the industry are seeking are produced in the minimum time. An example of how this could increase profits is that it would result in the product being available for the consumer sooner and less money being spent on wages for their workers.

Yield

The quantity of product formed during a process is referred to as **yield**. The yield of a chemical reaction refers to the efficiency of the reaction.

Theoretical Yield refers to the quantity of product that is expected to be obtained using stoichiometric quantities.

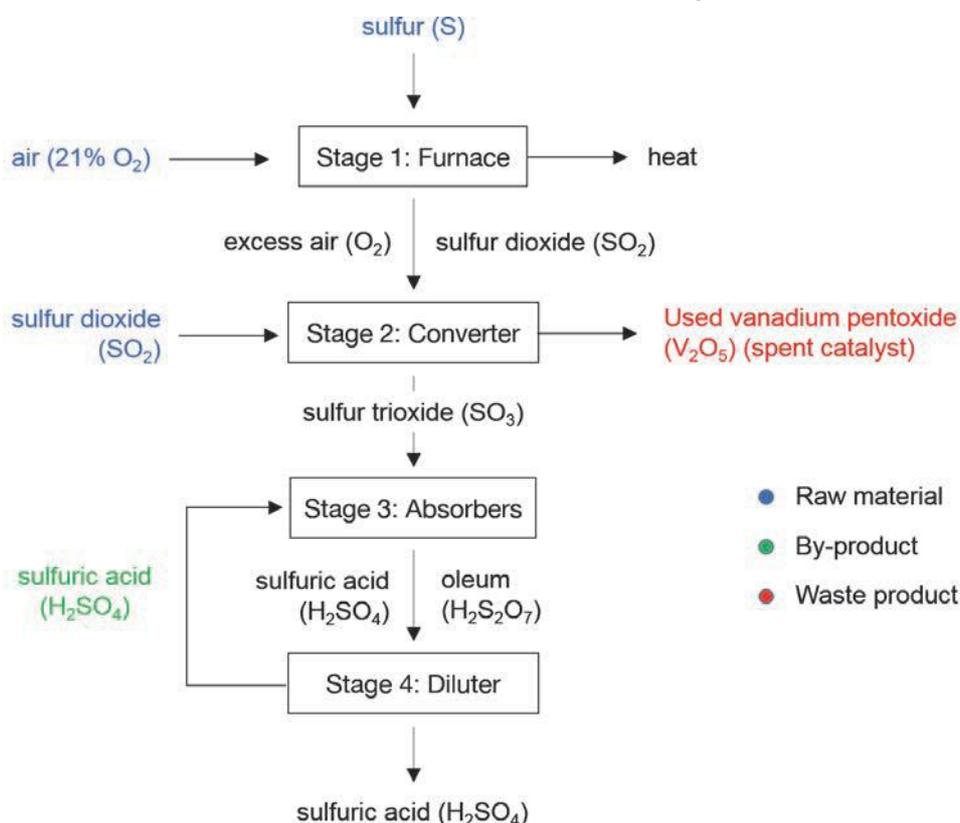
Actual Yield refers to the quantity of product that was obtained through the chemical process.

Percentage Yield is the percent ratio of actual yield to theoretical yield is calculate using the expression below.

If the actual yield of the product is high by altering the position of equilibrium for the chemical process, this would result in an increase in profits. Unfortunately, achieving the maximum reaction rate and maximum yield is not always possible and the industry has to balance both factors to achieve the maximum profit.

Worked example

Consider the industrial production of sulfuric acid as shown in the flow diagram below.



The reaction equation most influenced by rate and equilibrium changes for the above process is the reaction between sulfur dioxide (SO_2) and oxygen (O_2) to produce sulfur trioxide (SO_3).

If the temperature of the reaction mixture is increased, this results in the average kinetic energy of the sulfur dioxide and oxygen molecules increasing and exhibiting more thermal energy. Therefore, there is a larger proportion of collisions between sulfur dioxide and oxygen molecules reaching or exceeding the Activation Energy. There is an increased frequency of successful collisions occurring. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of formation of sulfur trioxide.

This reaction is an exothermic reaction as represented by the negative enthalpy value. If the temperature of the reaction mixture is increased, this would place an introduced change on the equilibrium system. According to Le Châtelier's Principle the system would attempt to counteract the introduced change by absorbing the excess energy. This is an endothermic process and so the position of equilibrium would shift in the endothermic direction, which is to the left, favouring the formation of reactants and reducing the yield of sulfur trioxide.

If the pressure of this system is increased, the system will counteract the introduced change placed on the equilibrium mixture by attempting to reduce the pressure of the system. Le Châtelier's principle states that the reduction in pressure is achieved by shifting to the side of the equation which results in the formation of the least moles of gaseous particles. Therefore, the position of equilibrium shifts to the right favouring the formation of sulfur trioxide molecules.

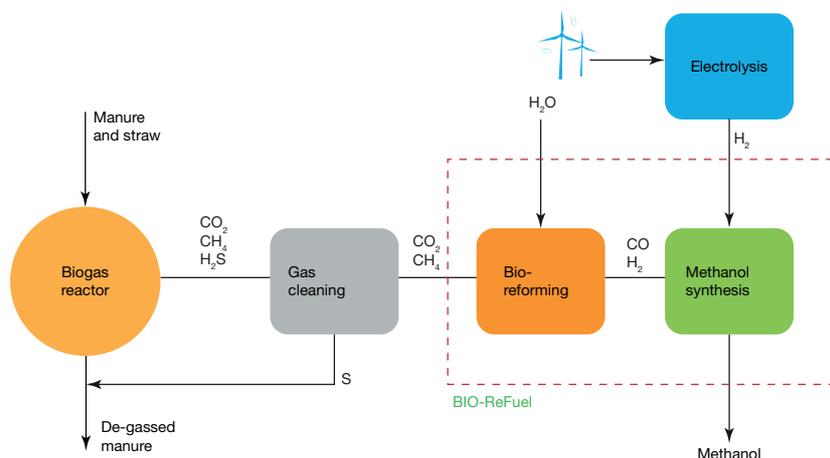
If a positive catalyst is introduced this would provide an alternative reaction pathway for the reacting particles with a lower Activation Energy. This results in a larger proportion of collisions between sulfur dioxide and oxygen molecules reaching or exceeding the Activation Energy. There is an increased frequency of successful collisions occurring. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of formation of sulfur trioxide molecules.

Theoretical conditions	Actual Conditions	Explanation
Increase temperature leading to an increased rate of formation of SO_3	Moderate temperature (450°C)	An increased temperature will lead to the favouring of the backward reaction, reducing yield of SO_3 A moderate temperature is used as a compromise between rate and equilibrium
Increase pressure leading to the formation of less moles of gaseous particles and the reaction occurring at a faster rate, favours the formation of SO_3	Atmospheric pressure (1 atm)	Reaction vessels required for high pressures are costly to the manufacturer Achieving high pressure is an energy intensive process therefore energy costs are high
Alternative reaction pathway with a lower E_a leading to an increased rate of formation of SO_3	vanadium oxide (V_2O_5) catalyst	Vanadium oxide catalyst used to reduce production costs as the SO_3 is produced in a shorter amount of time

From this example it is evident that by increasing the rate of reaction through an increase in temperature, this would result in a reduction of yield of sulfur trioxide due to equilibrium principles. Therefore, industry finds a compromise between rate and equilibrium in order to maximise yield and subsequently maximise the profits. This reaction occurs industrially at atmospheric pressure (1 atm), at a moderate temperature of 450°C in the presence of a vanadium oxide (V_2O_5) catalyst, achieving a yield of 95%.

Question

7. Methanol (CH_3OH) has many uses as a chemical or fuel and there are currently studies underway to obtain it through greener processes. The flow diagram for one of these processes is shown below.



- (a) **Identify** a raw material in this process.

..

.. .. .

(1 mark) **IAE3**

In order to form methanol, carbon monoxide (CO) and hydrogen (H_2) are reacted together at 350°C according to the following reaction equation.



- (b) **Write** the equilibrium expression for the reaction.

(1 mark) **KA4**

Summary test 2: Managing chemical processes

1. Nitrosyl chloride (NOCl) is a reagent used in the synthesis of organic compounds.
- (a) For NOCl to perform its role in the synthesis of organic compounds, the correct orientation of the molecule is essential for a successful collision to occur during the reaction.

State the other condition necessary for a successful collision.

..

.. (1 mark) **KA1**

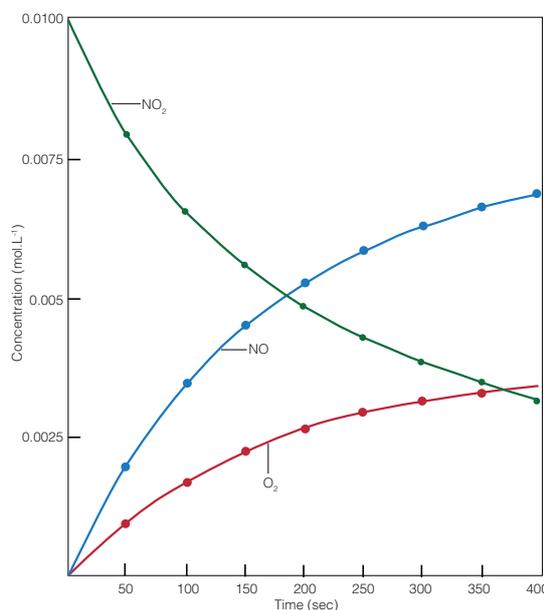
- (b) Nitrogen dioxide is involved in the production of NOCl.

Nitrogen dioxide (NO₂) can decompose forming nitric oxide (NO) and oxygen gas (O₂) according to the following equation.



In the laboratory, the concentrations of all species were recorded during the decomposition and the following graph was produced.

time (sec)	NO ₂ (mol L ⁻¹)	NO (mol L ⁻¹)	O ₂ (mol L ⁻¹)
0	0.0100	0.0000	0.0000
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035



- (i) **Identify** the independent variable for the reaction.

..

.. (1 mark) **IAE1**

- (ii) **Calculate** the instantaneous rate of NO₂ decomposition at 200 seconds.

(3 marks) **KA4**

The concentrations of the species during a reaction at 127°C were recorded at some point in time and are shown in the table below.

Chemical	NOCl	NO	Cl ₂
Concentration (mol L ⁻¹)	0.0199	0.0199	0.965

(2) **Explain** whether the reaction is in a state of equilibrium at this point in time.

..

 (3 marks) **KA4**

(iii) The reaction was repeated at by placing 0.513 mol of NOCl in a 1 L flask. The number of moles Cl₂ was measured as 0.0160 once equilibrium was reached.

(1) **Calculate** the concentration of NOCl at equilibrium. Give your answer to the correct number of significant figures.

(4 marks) **KA4**

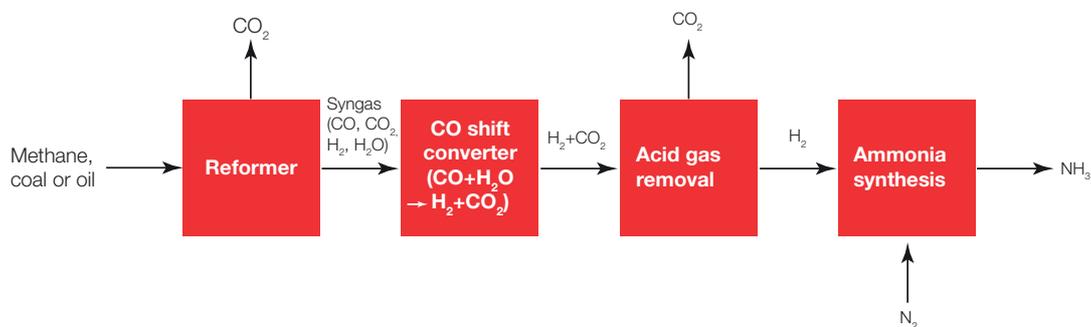
(2) **Calculate** K_c for this reaction.

(2 marks) **KA4**

(3) **State** the effect on the value of K_c if the pressure was increased.

.. (1 mark) **KA1**

- (c) The Haber-Bosch Process is one method used to industrially produce ammonia. A flow-chart representing its production is shown below.



- (i) **Identify** a raw material used in this process.

..

.. .. . (1 mark) **IAE3**

This process uses reaction conditions of approximately 450°C-500°C at a pressure of 150-200 atm in the presence of a catalyst.

- (ii) **Explain** why these reaction conditions are considered a compromise for the manufacturers.

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..... (3 marks) **KA2**

- (d) Research into alternative methods of ammonia production is ongoing, with most of the focus on the use of a catalyst.

- (i) **Explain** how the use of a catalyst increases the reaction rate for ammonia production.

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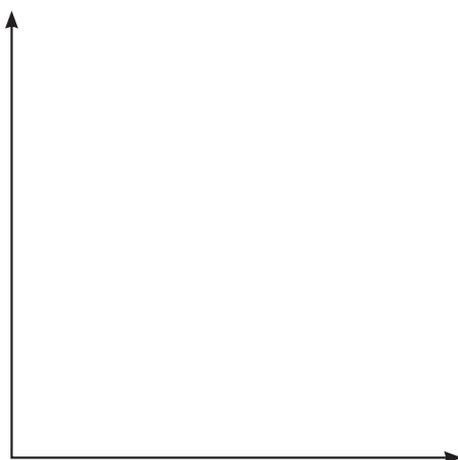
.. .. .

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.. .. .

..... (3 marks) **KA1**

- (ii) **Draw** an energy profile diagram on the axes below for the production of ammonia, both in the presence of and absence of a catalyst. Label E_a and ΔH using correct chemical conventions.



(4 marks) **KA4**

Topic 3: Organic and biological chemistry

3.1 Introduction

Science understanding

Organic compounds can be represented by molecular and structural formulae.

Organic compounds are named systematically to provide unambiguous identification.

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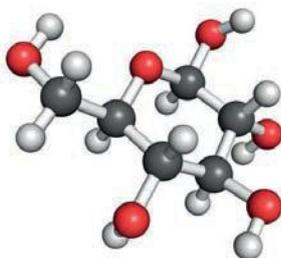
Organic chemistry is the study of covalently-bonded compounds which contain carbon, called 'organic compounds'. Carbon can form single bonds with four separate atoms, which allows for complex branching chains and rings. Consequently, there are many millions of known compounds that contain carbon and scientists are discovering and creating new ones each year.

Organic compounds are everywhere: in foods, fragrances, pharmaceuticals, cosmetics, plastics, and, of course, in our bodies.

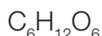


DNA

An organic polymer found in a cell's nucleus



Glucose



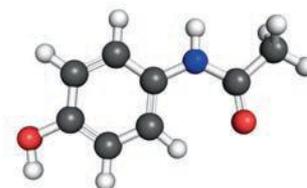
A simple sugar



Propane



A gas used as fuel



Paracetamol



A pain-relieving medicinal compound

Figure 3.01: Common organic compounds

The term "organic chemistry" once referred only to the chemistry of living things. However, in 1828, German chemist Friedrich Wöhler created urea—an organic compound found in the urine of mammals—by heating an inorganic substance. This expanded the definition of "organic chemistry" and proved that the fundamental chemistry of inanimate matter and living things was the same. Since then, scientists have developed many new carbon-containing compounds in the field of synthetic organic chemistry.



Science as a human endeavour

Food wastage

Biodegradation is nature's way of decomposing organic substances. A fallen tree in a forest will slowly decompose over the ensuing years. The number of products formed in a biodegradation reaction can be very high, depending on the type of organism being degraded. Nature uses microorganisms such as bacteria and fungi to bring about decomposition of once-living things.

Food wastage has been a major cause of concern for the environment, with Australia as a whole throwing away 7.3 million tonnes of edible food each year and 3.2 million tonnes ending up in landfill. Food waste rotting in landfill produces large amounts of greenhouse gases such as methane.

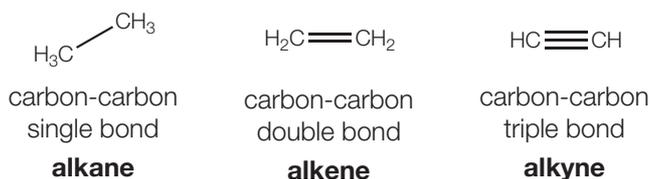
Food waste contributes approximately 3% of Australia's annual greenhouse gas emissions. As the world develops a preference for renewable energy, food waste has been identified as one such source. Large scale anaerobic bio-digesters (Figure 3.02) are being developed which allow for facilities to process mass amounts of food waste to recover energy. Through this process they are able to reduce food waste rotting in landfills. Renewable energy in the form of biogas is also produced which can potentially boost energy security.



Figure 3.02: Bio-digesters are finding success in countries such as Cambodia.

3

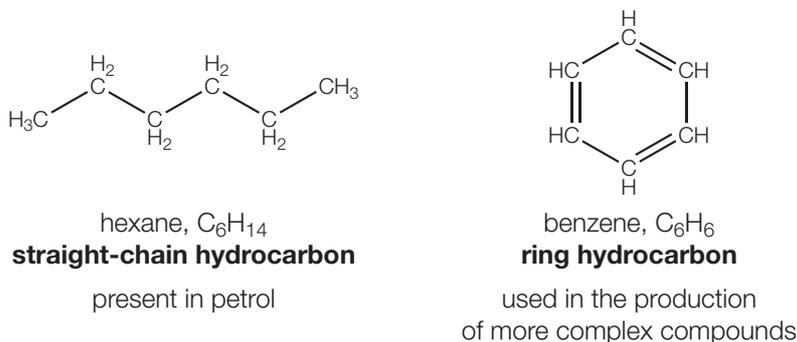
Because carbon has four valence electrons, it forms four bonds in almost all its compounds. These bonds can be single, double, or triple bonds.



The simplest class of organic compounds is composed of only carbon and hydrogen – these are the **hydrocarbons**. Hydrocarbons are classified into three general types: alkanes, alkenes, and alkynes.

Alkanes are hydrocarbons that contain only single bonds between carbon atoms. They are called **saturated** hydrocarbons because they contain the largest number of hydrogen atoms per carbon atom. **Alkenes** are hydrocarbons that contain double bonds between carbon atoms, and **alkynes** contain triple bonds between carbon atoms. Alkenes and alkynes are **unsaturated** hydrocarbons.

Carbon atoms can be arranged in straight chains or rings. Straight-chain hydrocarbons are classified as **aliphatic** while *some* rings are classified as **aromatic**.



As there are so many compounds of carbon, they have been organised into families based on their similarities and named systematically.

Naming Hydrocarbons

The systematic naming of organic compounds was established by the International Union of Pure and Applied Chemistry (IUPAC). The basic name of an organic compound has two parts:

- The prefix: the first half of the name indicates how many carbons are in the longest continuous carbon chain
- The suffix: the second half of the name indicates to which family, or *homologous series*, this compound belongs.

The prefix **alk-** refers to any non-specific hydrocarbon. When naming a specific compound, the prefix in the base name is based on the longest continuous carbon chain. Table 3.01 below shows the prefixes associated with continuous carbon chains up to a length of 10.

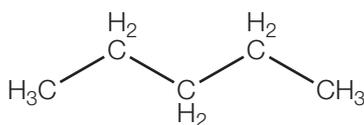
Number of carbons	Prefix
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-
9	non-
10	dec-

Table 3.01: Organic chemistry prefixes

Hydrocarbons with only single bonds take the suffix **-ane** (hence the name 'alk-ane' for this class of compounds).

Example

An alkane molecule has the structure:

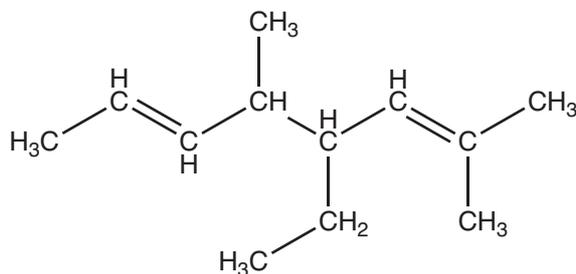


- The longest continuous chain is made up of 5 carbon atoms, so its name begins with the prefix *pent-*.
- The compound is a hydrocarbon with only single bonds, so its name ends with the suffix *-ane*.
- Therefore, the name of this compound is **pentane**.

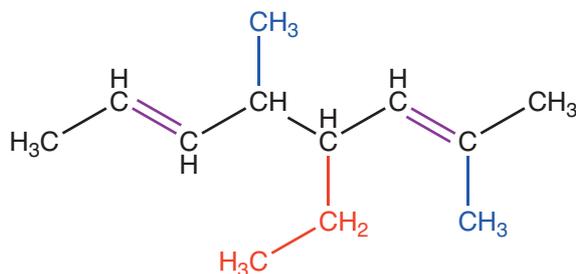
Hydrocarbons with carbon-carbon double-bonds take the suffix **-ene**, and hydrocarbons with carbon-carbon triple bonds take the suffix **-yne**.

Alkenes and alkynes containing four carbons or more require a number to be added before the base name to indicate the position of the multiple bond. When there is more than one double- or triple-bond in a compound, the prefixes **di-**, **tri-**, **tetra-** and so on are added to indicate this. *The naming of hydrocarbons is covered in detail in Topic 3 of the Stage 1 course.*

Example



- The longest continuous carbon chain is made up of 8 carbon atoms, so the base prefix is *oct-*.
- There is at least one double-bond in the molecule, so the base suffix is *-ene*.
- There are two double-bonds in the molecule, at positions 2 and 6, so the base name becomes *2,6-octadiene*.
- There are methyl substituents on carbons 2 and 5, so the prefix *2,5-dimethyl* is added.
- There is an ethyl substituent on carbon 4, so the prefix *4-ethyl* is added.
- Substituents are listed in alphabetical order (ignoring di-, tri-, and so on); ethyl comes before methyl.
- The compound is named **4-ethyl-2,5-dimethyl-2,6-octadiene**.



4-ethyl-2,5-dimethyl-2,6-octadiene

Formulae

Organic compounds can be represented by different types of formulae.

- The **molecular formula** gives the exact number and type of atoms present.
- The **empirical formula** gives the simplest ratio of atoms present.
- The **complete structural formula** shows all the atoms and how they are connected by bonds.
- The **condensed structural formula** can show the carbon-carbon bonds, but hydrogens and other atoms are simplified.
- The **skeletal structural formula** does not show the carbons and hydrogens in the carbon chain. This leaves a carbon “skeleton” with functional groups shown. Carbon atoms which appear to have fewer than four bonds in a skeletal structural formula have **implied hydrogens**.

Example

Consider straight-chain decane

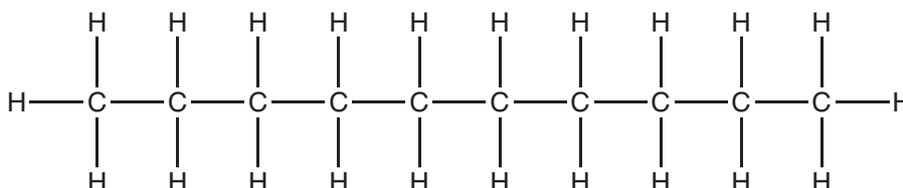
Molecular formula



Empirical formula

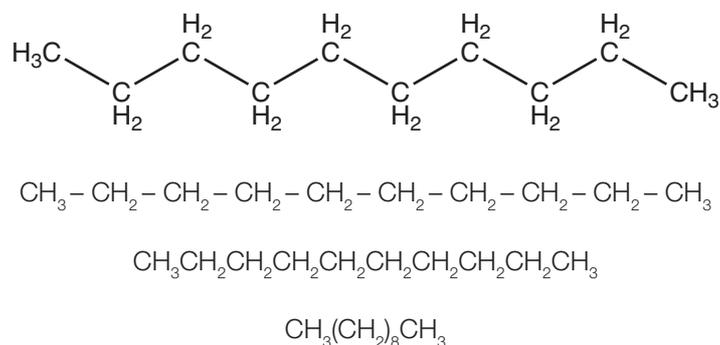
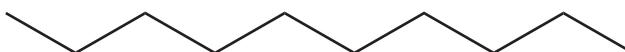
The simplest ratio of atoms for $\text{C}_{10}\text{H}_{22}$ is C_5H_{11} .

Complete structural formula

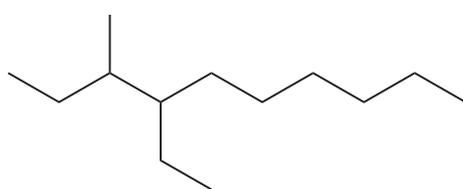


Condensed structural formula

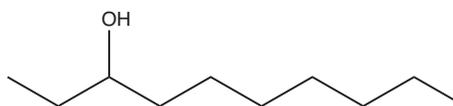
There are several ways this can be represented:

**Skeletal structural formula**

Each point on the “skeleton” represents a carbon atom. Skeletal structural formulas *must* show a ‘corner’ for each carbon. Atoms other than the hydrocarbon “skeleton” are still shown.

Example

4-ethyl-3-methyldecane



decan-3-ol

**Science as a human endeavour****Fiery ice**

Large amounts of methane gas are stored around the world trapped as solid methane hydrate. Although methane hydrate looks like regular ice, it has one significant difference: it burns as shown in Figure 3.03.

This fiery ice results from the trapped methane being released from the lattice as the ice begins to melt. Arctic regions hold large reserves of methane hydrate both on the surface and deep in oceans where low temperatures and high pressures trap methane. Anaerobic decomposition of organic material by bacteria is responsible for the production of methane which is subsequently trapped within the ice. Methane hydrate and its molecular structure are shown in Figure 3.04.

There are concerns that rising ocean temperatures may cause the deposits of methane hydrate throughout the oceans to melt, releasing large amounts of methane into the atmosphere. Methane is a potent greenhouse gas, and its presence in the atmosphere accelerates global warming.



Figure 3.03: Methane hydrate combusting

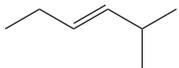
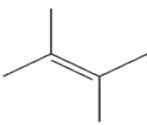


Figure 3.04: Structure of methane hydrate

Questions

1. Hydrocarbons are the principal constituents of petroleum and natural gas. They serve as **fuels** and **lubricants** as well as raw materials to produce plastics, fibres, rubbers, solvents, explosives, and industrial chemicals. They are named and drawn systematically.

(a) Complete the table below

Name	Molecular formula	Empirical formula	Complete structural formula	Condensed structural formula	Skeletal structure
				$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	
2-methylpentane					
					
3-ethyl-3-methylhexane					
					

25 marks (KA4)

- (b) The following compounds have been named incorrectly. Draw their structural formulas from the incorrect name, and provide the correct name.

Compound	Correct name	Structural formula
3-ethylbutane		
1-methyl-4-propylhexane		
3-methyl-3-butene		

12 marks (KA4)

Science understanding

The physical properties of organic compounds are influenced by the molar masses of the molecules, and the number and polarity of functional groups.

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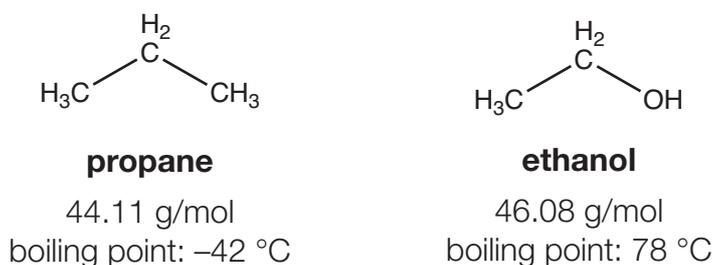
Physical properties of compounds include melting point, boiling point, miscibility, volatility, and solubility. Trends in these properties can be explained by:

- Intermolecular forces occurring between molecules
- Molecular mass

Melting point and Boiling Point

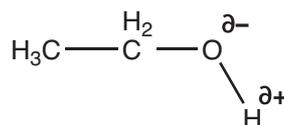
Intermolecular forces

Propane is used for water heaters and cooking. It has a molar mass of 44 g mol^{-1} and is a gas at room temperature. Ethanol has a similar molar mass of 46 g mol^{-1} but is a liquid at room temperature. The differences in the physical properties of these molecules can be explained through intermolecular forces.

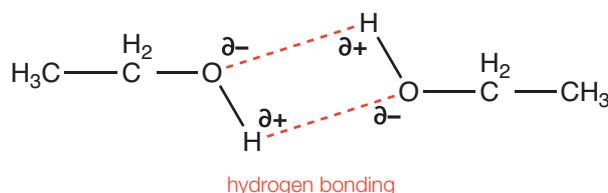


Propane is a non-polar molecule that experiences only dispersion forces between it and other propane molecules. Dispersion forces are the weakest intermolecular force and do not require a lot of energy to overcome; hence, propane has a low boiling point.

Ethanol has a hydroxyl (-OH) functional group, which is polar. Oxygen is more electronegative than hydrogen and has a δ^- charge, while hydrogen has a δ^+ charge (δ charges are partial charges, less than a whole $1+$ or $1-$). As ethanol has a small carbon chain, the molecule is polar overall.



The intermolecular forces that occur between ethanol molecules are hydrogen bonds.

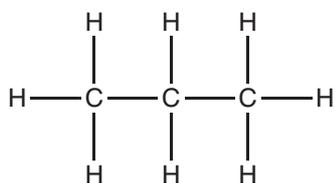


As hydrogen bonding is the strongest intermolecular force, it takes more thermal energy to separate ethanol molecules.

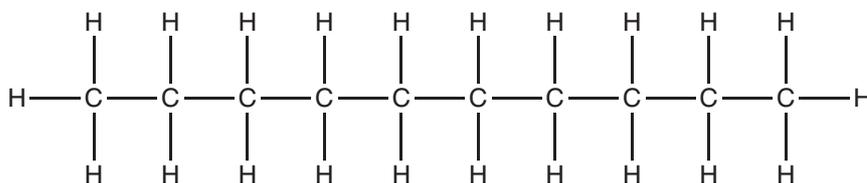
Molar mass

As the carbon chain length and the mass of the molecule increase, the effect of an individual hydroxyl group on the overall polarity of the molecule decreases.

Propane is non-polar and experiences only dispersion forces between molecules. It is a gas at room temperature. Decane is also non-polar and experiences only dispersion forces between molecules; however, it is a liquid at room temperature.

**propane**

44.11 g/mol
boiling point: $-42\text{ }^{\circ}\text{C}$

**decane**

142.32 g/mol
boiling point: $174\text{ }^{\circ}\text{C}$

The difference in boiling point is due to the difference in the molar masses of the compounds. Larger molecules experience greater dispersion forces, so melting points and boiling points increase with molar mass as more thermal energy is required to overcome these forces. This trend is shown below in Table 3.02.

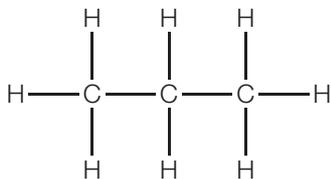
Alkane	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)
methane	-183	-162
ethane	-183	-89
propane	-187	-42
butane	-138	-1
pentane	-130	36
hexane	-95	69
heptane	-90	98
octane	-57	126
nonane	-54	151
decane	-30	174

Table 3.02: melting points and boiling points of alkanes

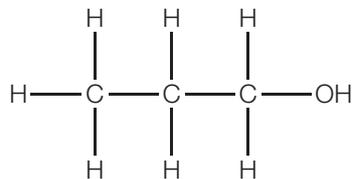
Solubility

Organic compounds are more soluble in water if they experience stronger intermolecular forces with water. Therefore, the size of the molecule and the number of polar functional groups greatly affect how soluble the compound is.

Non-polar hydrocarbons will not dissolve in a polar solvent such as water; instead, they form two layers. There is hydrogen bonding between water molecules, but only dispersion forces between hydrocarbon molecules. The hydrogen bonds in water are too strong for non-polar molecules to penetrate, so hydrocarbons and water are unable to form a homogenous solution. Put another way, water molecules are much more strongly attracted to each other than to hydrocarbon molecules, and do not allow hydrocarbon molecules to mingle with them.

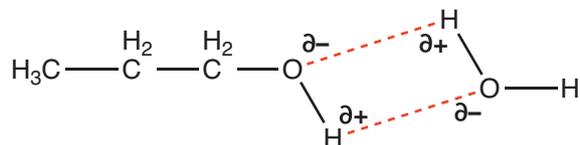
**propane**

Solubility:
47 mg/L

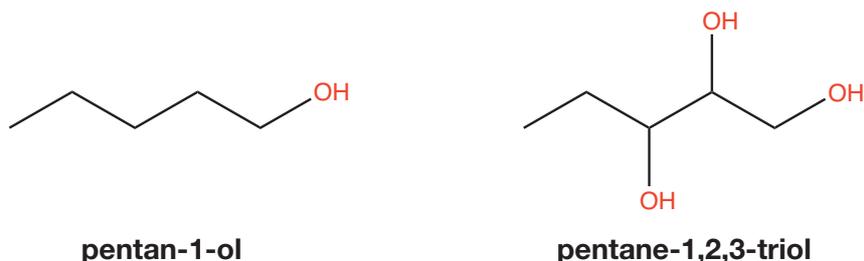
**propan-1-ol**

Solubility:
miscible

Propan-1-ol is a small, polar molecule. It can form hydrogen bonds with the polar water and is therefore miscible. (Recall that **miscible** substances can mix in any proportion; this represents maximum solubility).



As the number of polar functional groups on a hydrocarbon increases, so does solubility.

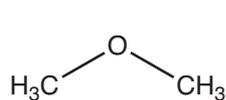


Pentan-1-ol has a polar hydroxyl group which can form hydrogen bonds with water. However, it also has a long non-polar carbon chain which makes it harder for the water molecules to surround it and fully dissolve it. Pentane-1,2,3-triol, with its three polar hydroxyl groups, has multiple sites for hydrogen bonding to occur with water molecules; it is therefore more soluble.

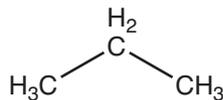
Questions

2. The boiling point of organic compounds can give important information about their physical properties and structural characteristics. Boiling point helps identify and characterise a compound.

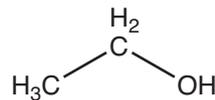
(a) Place the following compounds in order of increasing boiling points, numbering them 1 to 3.



diethyl ether
(methoxymethane)



propane



ethanol

(3 marks) KA1

- (b) Explain your reasoning.

.. .. .

.. .. . (3 marks) KA1

- (c) Butan-1-ol has a boiling point of 117.7°C whereas pentane has a boiling point of 36.1°C. Explain the differences in these boiling points.

.. .. .

.. .. . (3 marks) KA1

- (d) With reference to intermolecular bonding, predict and explain which molecule from a) would have the greatest solubility in water.

.. .. .

.. .. . (3 marks) KA1

(e) Explain the following general trends:

(i) Alcohols are soluble in water.

.....
.....
..... (2 marks) KA1

(ii) Solubility decreases as the hydrocarbon chain of an alcohol increases in length.

.....
.....
..... (2 marks) KA1

3.2 Alcohols

Science understanding

Alcohols are classified as primary, secondary, or tertiary.

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Alcohols are an important part of chemical and industrial processes. An alcohol is a compound that has a **hydroxyl functional group (-OH)** attached to a carbon atom. Commonly-known alcohols include:

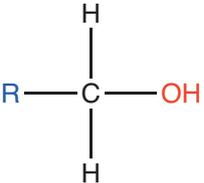
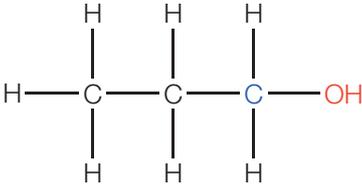
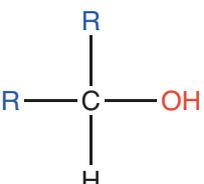
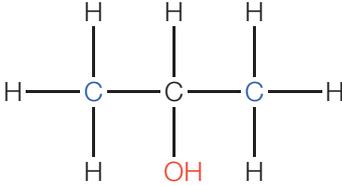
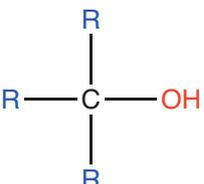
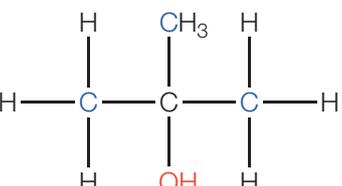
- Ethanol, which comes from the fermentation of simple sugars and is consumed recreationally
- Glycerol, which is used in the food industry, moisturisers, and detergents
- Cholesterol, a steroid present in the human body

All the above alcohols contain one or more hydroxyl functional groups in their molecular structure. Simple straight-chain alcohols have the **general formula** $C_nH_{2n+1}OH$.

Generic compounds can be written using 'R'. For example, alcohols can be represented with R-OH. "R" represents an **alkyl chain**: any substituent made up of only carbon and hydrogen.

Primary, Secondary, and Tertiary Alcohols

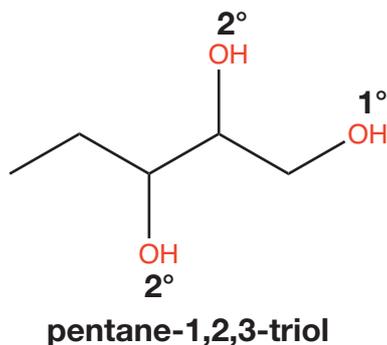
Alcohols can be classified as primary, secondary, or tertiary, depending on how many other carbons are connected to the same carbon as the hydroxyl group.

Primary (1°)		<p>The carbon connected to the hydroxyl group is connected to one hydrocarbon chain (or none, in the case of methanol).</p> <p><u>Example</u></p>  <p>propan-1-ol</p>
Secondary (2°)		<p>The carbon connected to the hydroxyl group is connected to two hydrocarbon chains.</p> <p><u>Example</u></p>  <p>propan-2-ol</p>
Tertiary (3°)		<p>The carbon connected to the hydroxyl group is connected to three hydrocarbon chains.</p> <p><u>Example</u></p>  <p>2-methylpropan-2-ol</p>

Sometimes, diols and triols have hydroxyl groups in primary, secondary, or tertiary positions within the same molecule.

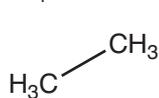
Example

Pentane-1,2,3-triol contains two secondary hydroxyl groups and one primary hydroxyl group.

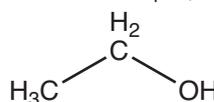


Naming alcohols

- the *-e* is removed from the parent alkane and replaced with *-ol*. For example, ethane becomes ethanol.

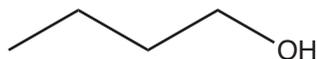


ethane

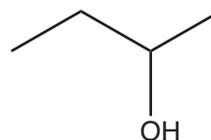


ethanol

- For all alcohols other than methanol and ethanol, it is necessary to number the position of the functional group in the name, as it can be found in different positions.

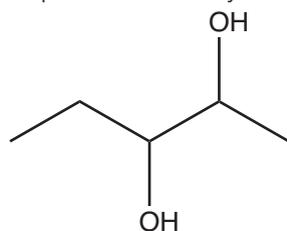


butan-1-ol

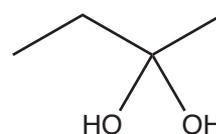


butan-2-ol

- The prefixes *di-* and *tri-* are used before *-ol* if there are two or three hydroxyl functional groups. Numbers are included to indicate the position of the hydroxyl groups. The *-e* is included at the end of the parent alkane.

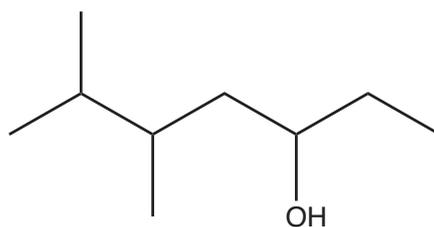


pentane-2,3-diol



butane-2,2-diol

- If there are branches, ensure the functional group (in this case, the hydroxyl) is assigned the lowest possible number.



5,6-methyl-heptan-3-ol
(not 2,3-methyl-heptan-5-ol)

Questions

3. Alcohols are used as sweeteners and in making perfumes, are valuable intermediates in the synthesis of other compounds, and are among the most abundantly produced organic chemicals in industry.

(a) Systematically name each of the following alcohols.

(i) $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---}\overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}}\text{---}\overset{\text{CH}_3}{\text{C}}\text{---CH}_2\text{---CH}_3$	(ii) $\text{CH}_2=\text{CHCH}_2\text{OH}$
(iii) $\begin{array}{c} \text{HO} \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C---C---C---CH}_2\text{---CH}_3 \\ \quad \\ \text{OH} \quad \text{CH}_3 \end{array}$	(iv) $\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{HO---CH}_2\text{---C---CH}_2\text{---OH} \\ \\ \text{OH} \end{array}$

(8 marks) KA4

- (b) Circle each of the hydroxyl groups in (a) and identify them as primary, secondary, or tertiary.

(4 marks) KA3

(c) Draw the structural formula of:

(i) propan-2-ol	(ii) 3-methyl butan-1-ol
(iii) 2,3-dimethyl-pentan-3-ol	(iv) pentane-2,2-diol

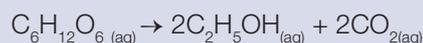
(8 marks) KA4



Science as a human endeavour

Champagne

The production of alcohol involves a **chemical reaction** called **fermentation** in which the glucose is broken down to **ethanol** by the action of enzymes in the yeast. Champagne and wine are made by the fermentation of glucose ($C_6H_{12}O_6$) obtained from grapes. Ethanol and carbon dioxide are formed:



When a carefully selected mixture of grapes is fermented in bottles to make champagne, the ethanol and some carbon dioxide dissolve in the aqueous solution. Due to the sparkle of the carbon dioxide that is required in the final product, the yeast must be removed from the bottles very carefully while keeping the carbon dioxide in solution.

When it is time to remove the yeast from the fermented champagne solution, the bottle is inverted and the yeast is frozen in the neck of the bottle (Figure 3.05). The stopper and yeast are then removed quickly and the stopper is replaced.



Figure 3.05: Trapped yeast in inverted champagne bottles

3

Science understanding

Primary, secondary, and tertiary alcohols behave differently with oxidising agents.

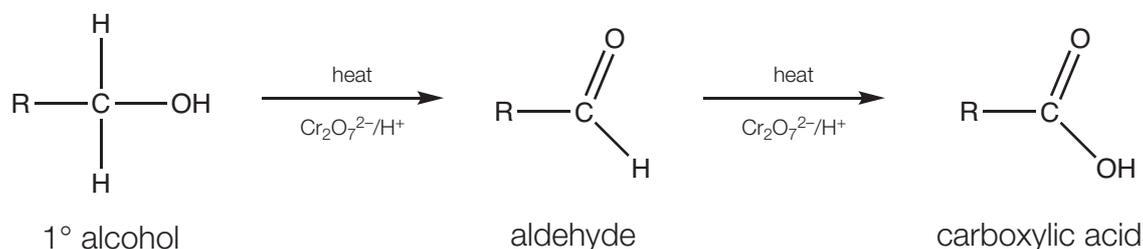
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Alcohols can be converted into many compounds, including aldehydes, ketones, carboxylic acids, and esters.

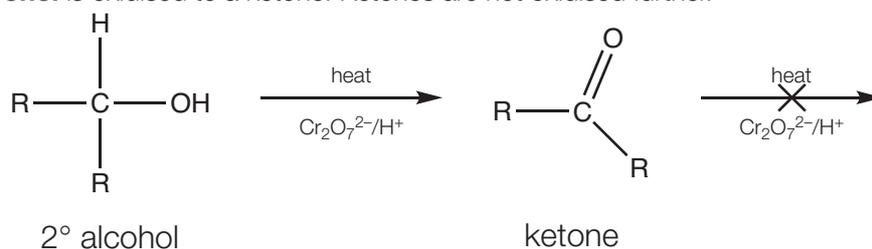
The position of the hydroxyl group can determine what type of compound the alcohol is converted to when it reacts with an oxidising agent such as acidified potassium dichromate, $Cr_2O_7^{2-}/H^+$.

Oxidation of Alcohols

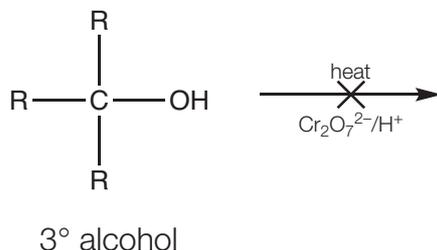
A **primary alcohol** is oxidised first to an aldehyde. If there is an excess of the oxidising agent, the aldehyde is then converted to a carboxylic acid.



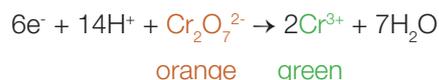
A **secondary alcohol** is oxidised to a ketone. Ketones are not oxidised further.



Tertiary alcohols cannot be oxidised without breaking a carbon-carbon bond.



The primary and secondary alcohols undergo oxidation; therefore, the dichromate solution will undergo reduction. The half-equation for the reduction of dichromate to chromium(III) ions is as follows:

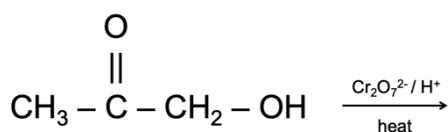
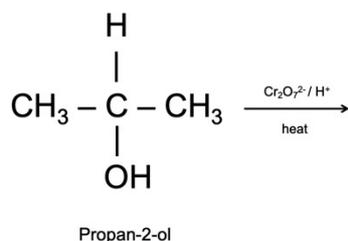


When dichromate ions are reduced to chromium(III) ions, the colour of solution changes from orange to green. Hence, primary and secondary alcohols can be distinguished from tertiary alcohols as the mixture will change colour from orange to green when acidified dichromate is added. The tertiary alcohol mixture will remain orange. *Note that it is not the alcohol itself, nor the oxidised product, that is coloured.*

The oxidation of alcohols in the presence of acidified dichromate is slow at room temperature, so the reaction is often heated to speed up the process.

Questions

4. Alcohols may be oxidised to give ketones, aldehydes, and carboxylic acids. These functional groups are useful for further reactions.
- (a) Draw the structures of the organic products when the following compounds are oxidised with acidified dichromate solution:



(6 marks) KA4

- (b) Two unmarked bottles were left in the laboratory. One contains 2-methylpropan-2-ol and the other contains 2-methylpropan-1-ol.
- (i) Draw the structures of each of these compounds.

3.3 Aldehydes and Ketones

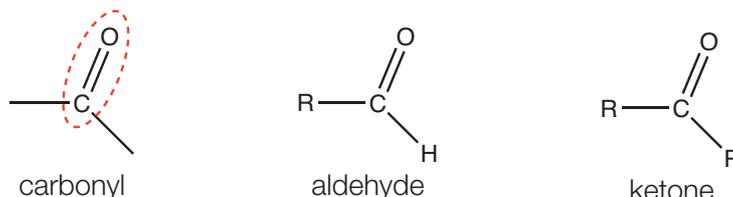
Science understanding

Aldehydes and ketones are produced by the oxidation of the corresponding primary and secondary alcohols respectively.

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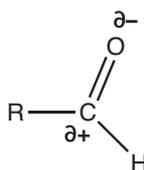
Aldehydes and ketones are found widely in fragrances and flavourings. Commonly known examples include spearmint, lemongrass, vanilla, and cinnamon.

Aldehydes and ketones each contain the **carbonyl** functional group (C=O). However, for an aldehyde, the carbonyl group is **terminal** (at the end of a chain), and for a ketone, the carbonyl group is **non-terminal** (linked to two other carbons).



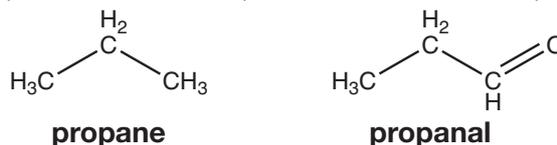
Aldehydes

Aldehydes are prepared by the oxidation of primary alcohols. They have an **aldehyde functional group**. This functional group is polar.

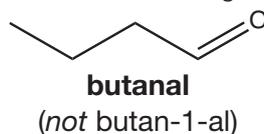


When **naming** aldehydes:

- the -e is removed from the parent alkane and replaced with -al. For example, propane becomes propanal.



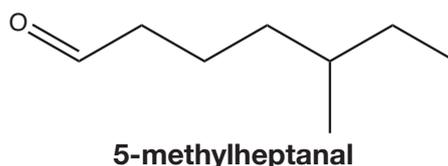
- It is not necessary to number the position of the functional group in the name, as it is always terminal.



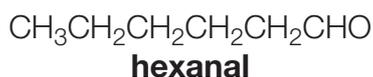
- The prefix *di-* is used before -al if there are two aldehyde functional groups. The -e is included in the name of the parent alkane.



If there are branches, always begin numbering from the functional group.



The condensed structural formula for aldehydes is written as **-CHO**.



Questions

6. Aldehydes are the key flavour components in whiskey. When oxygen diffuses into casks of whiskey, the ethanol is oxidised to an aldehyde. Draw the aldehyde product.

(2 marks) KA4



Science as a human endeavour

Mystery of the eye: Conversion of Vitamin A into Cis-Retinal

In 1967, Georges Wald was awarded a share of the Nobel Prize for Physiology and Medicine for his work with pigments in the retina. He discovered that vitamin A (retinal) was critical to our vision and investigated the way in which it absorbs light

Our vision begins when molecules of retinol absorb a small packet of light called a photon. This absorption causes the *cis* form of retinal to be converted to the *trans* form (Figure 3.06), changing the shape of the retinal molecule.

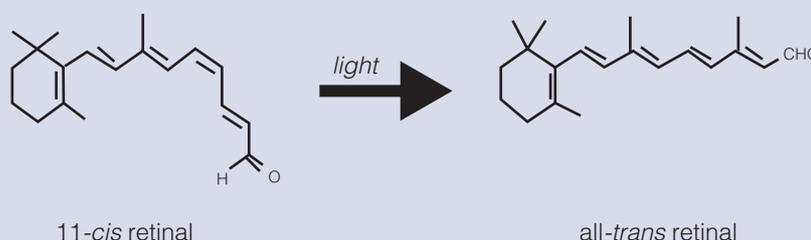


Figure 3.06: *cis* and *trans* isomers of retinal.

cis-trans isomers exhibit a type of isomerism where the atoms have different spatial arrangements in three-dimensional space.

The *cis* form of retinal is able to bond tightly to the protein opsin in our eyes. After it has absorbed light and been converted to the *trans* form, it is no longer able to sit closely within the protein, as its shape has changed. This causes the opsin protein itself to change shape, which begins a signalling pathway that sends an impulse along the optic nerve to the brain. This is how the light that enters our eyes is converted to vision in our brains.

Aldehyde preparation

Aldehydes are prepared by the *controlled* oxidation of primary alcohols. Specific apparatus is used, as shown in Figure 3.07.

An oxidising agent (often acidified dichromate) is added, drop by drop, into the alcohol mixture once heating begins.

The primary alcohol will oxidise to form an aldehyde. The aldehyde has a lower boiling point than its parent alcohol because it exhibits dipole-dipole interactions between its molecules, compared to the stronger hydrogen bonds between the alcohol molecules. The newly formed aldehyde will immediately boil off as it forms, which prevents further oxidation to a carboxylic acid. The ice bath around the receiving flask prevents loss from evaporation.

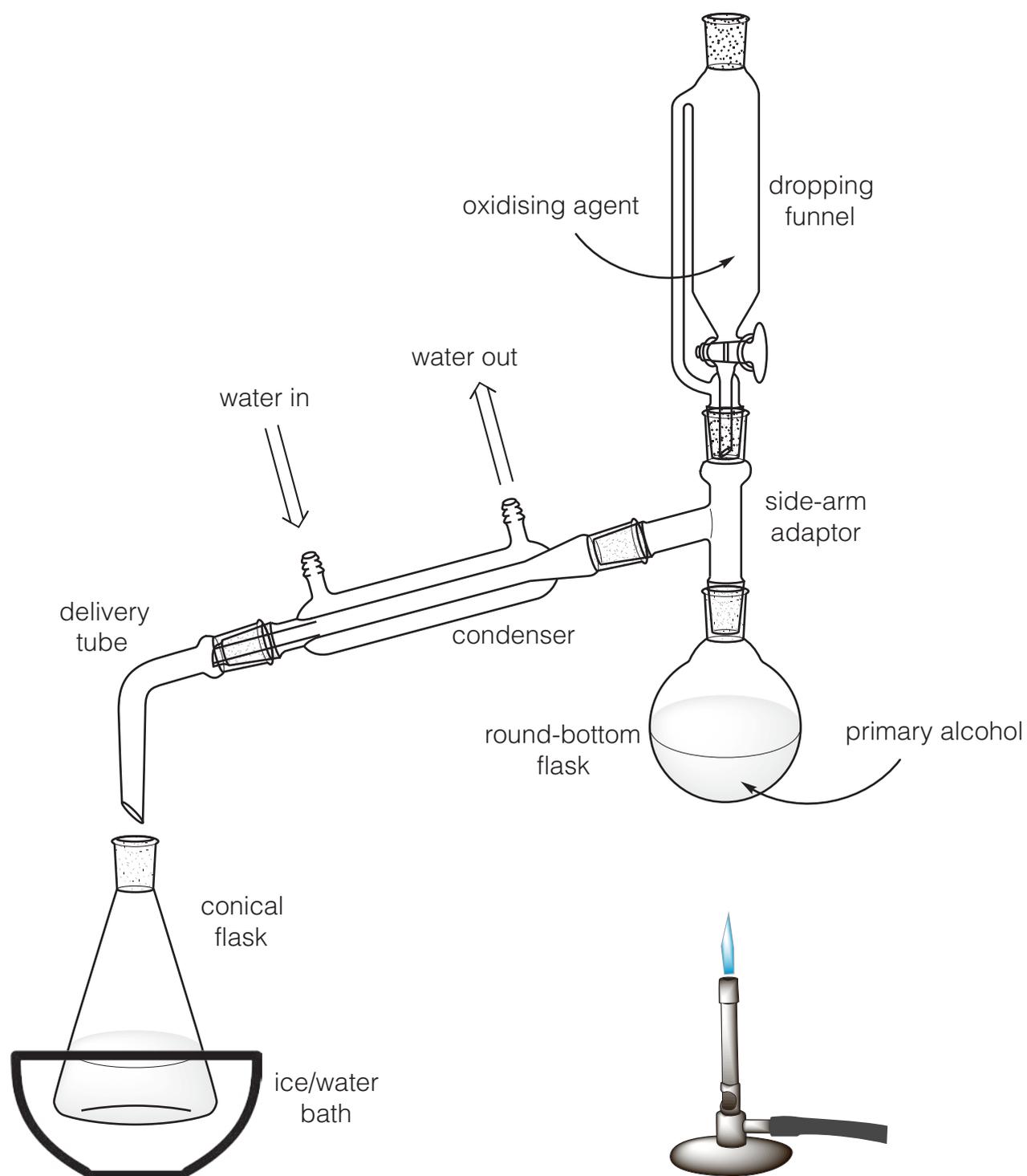
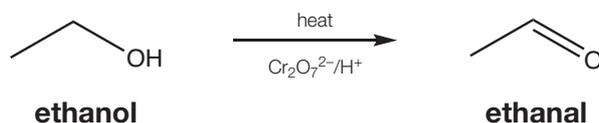


Figure 3.07: preparation of an aldehyde using distillation

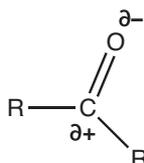
Example

Ethanol can be converted into ethanal by the controlled addition of acidified dichromate:



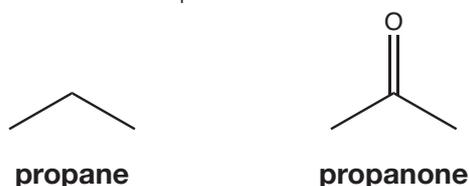
Ketones

Ketones are prepared by the oxidation of secondary alcohols. They have a **ketone functional group**. This functional group is polar.

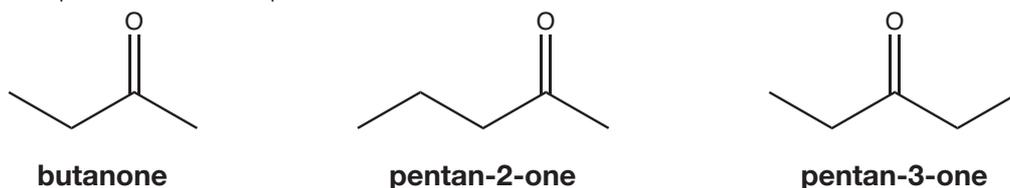


When **naming** ketones:

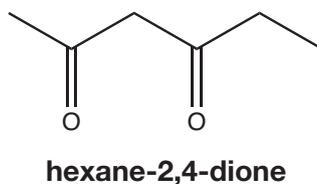
- the -e is removed from the parent alkane and replaced with *-one*. For example, propane becomes *propanone*.



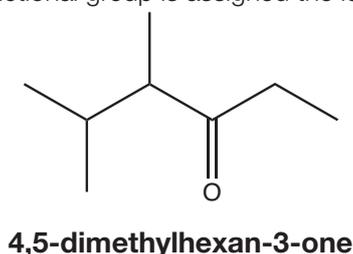
- After butanone, it is necessary to number the position of the functional group in the name, as it is non-terminal and can be placed in different positions.



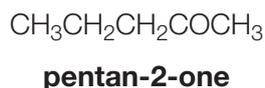
- The prefixes *di-* or *tri-* are used before *-one* if there are two or three ketone functional groups. Remember to include the numbers to indicate the position of the ketone groups. The -e is included in the name of the parent alkane.



- If there are branches, ensure the functional group is assigned the lowest number.



- The condensed structural formula for ketones is written with **-CO-** in the middle to represent the functional group.



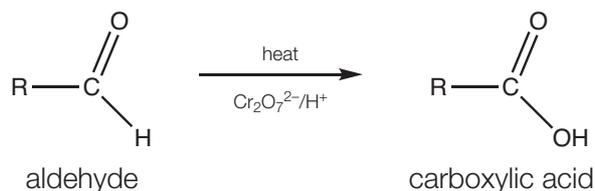
Science understanding

Aldehydes can be readily oxidised; ketones cannot.

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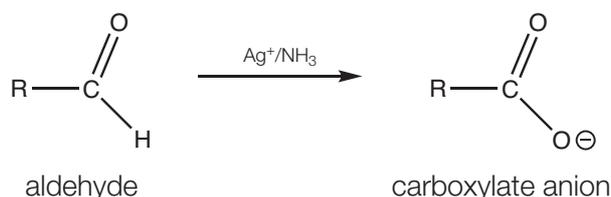
Distinguishing between an aldehyde and a ketone

Aldehydes can undergo oxidation while ketones cannot. Earlier in the chapter we looked at how aldehydes can be oxidised to give carboxylic acids with acidified dichromate. This is oxidation under **acidic conditions**.



Aldehydes can also undergo oxidation under **alkaline conditions**. Tollens' reagent (ammoniacal silver nitrate solution, Ag^+/NH_3) oxidises the aldehyde and is itself reduced to solid silver. A silver mirror forms on the inside surface of the reaction vessel.

The alkaline conditions are due to the presence of ammonia in the solution. This means protons (H^+) are scarce in solution, rather than abundant. The **carboxylate anion** is formed instead of the carboxylic acid.



Hence, an aldehyde and a ketone can be distinguished by using either acidified dichromate or Tollens' reagent. An aldehyde will be oxidised and the reaction mixture will show a colour change or silver mirror; a ketone will not be oxidised.

Acidic vs Alkaline Oxidation of Aldehydes

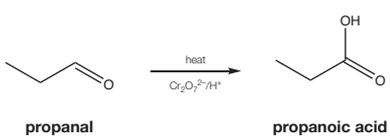
Acidified dichromate can oxidise aldehydes, primary alcohols, and secondary alcohols. However, Tollens' reagent will oxidise aldehydes only. This is useful for distinguishing alcohols from aldehydes. These reactions are summarised in Table 3.03.

<p>Acidified dichromate will oxidise...</p> <ul style="list-style-type: none"> Aldehydes <p>and also</p> <ul style="list-style-type: none"> Primary alcohols Secondary alcohols 	<p>Tollens' reagent will oxidise...</p> <ul style="list-style-type: none"> Aldehydes
<p><u>Observations</u></p> <ul style="list-style-type: none"> Solution turns from orange to green 	<p><u>Observations</u></p> <ul style="list-style-type: none"> Silver mirror forms on surface
<p><u>Oxidation Equations</u></p> $ \begin{array}{ccc} \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \\ \text{1}^\circ \text{ alcohol} \end{array} & \xrightarrow[\text{Cr}_2\text{O}_7^{2-}/\text{H}^+]{\text{heat}} & \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \\ \text{H} \\ \text{aldehyde} \end{array} & \xrightarrow[\text{Cr}_2\text{O}_7^{2-}/\text{H}^+]{\text{heat}} & \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \\ \text{OH} \\ \text{carboxylic acid} \end{array} \\ \\ \begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R} \\ \text{2}^\circ \text{ alcohol} \end{array} & \xrightarrow[\text{Cr}_2\text{O}_7^{2-}/\text{H}^+]{\text{heat}} & \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \\ \text{R} \\ \text{ketone} \end{array} \end{array} $	<p><u>Oxidation Equation</u></p> $ \begin{array}{ccc} \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \\ \text{H} \\ \text{aldehyde} \end{array} & \xrightarrow{\text{Ag}^+/\text{NH}_3} & \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \\ \text{O}^\ominus \\ \text{carboxylate anion} \end{array} \end{array} $
<p><u>Reduction Equation</u></p> $6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	<p><u>Reduction Equation</u></p> $\text{e}^- + \text{Ag}^+_{(\text{aq})} \rightarrow \text{Ag}_{(\text{s})}$

Table 3.03: The oxidation of organic compounds by acidified dichromate and Tollen's reagent.

Example

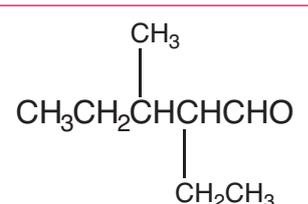
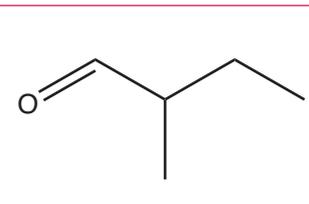
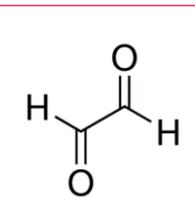
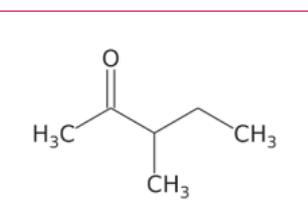
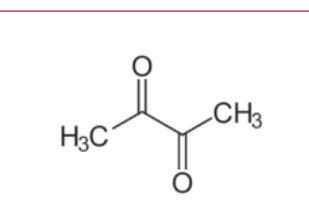
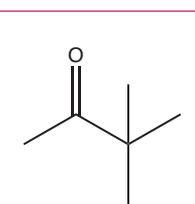
Describe and explain the chemical tests that could be performed to distinguish between propanal and propanone.

Propanal	Propanone
<p>Adding $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$</p> <p>Propanal is oxidised to propanoic acid.</p>  <p>Mixture changes colour from orange to green due to reduction of dichromate to chromium(III).</p>	<p>Adding $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$</p> <p>Propanone will not oxidise.</p> <p>Mixture remains orange.</p>
<p>Adding Tollens' reagent</p> <p>Propanal is oxidised to propanoate ion.</p>  <p>Silver mirror forms in reaction vessel.</p>	<p>Adding Tollens' reagent</p> <p>Propanone will not oxidise.</p> <p>Mixture remains colourless.</p>

Questions

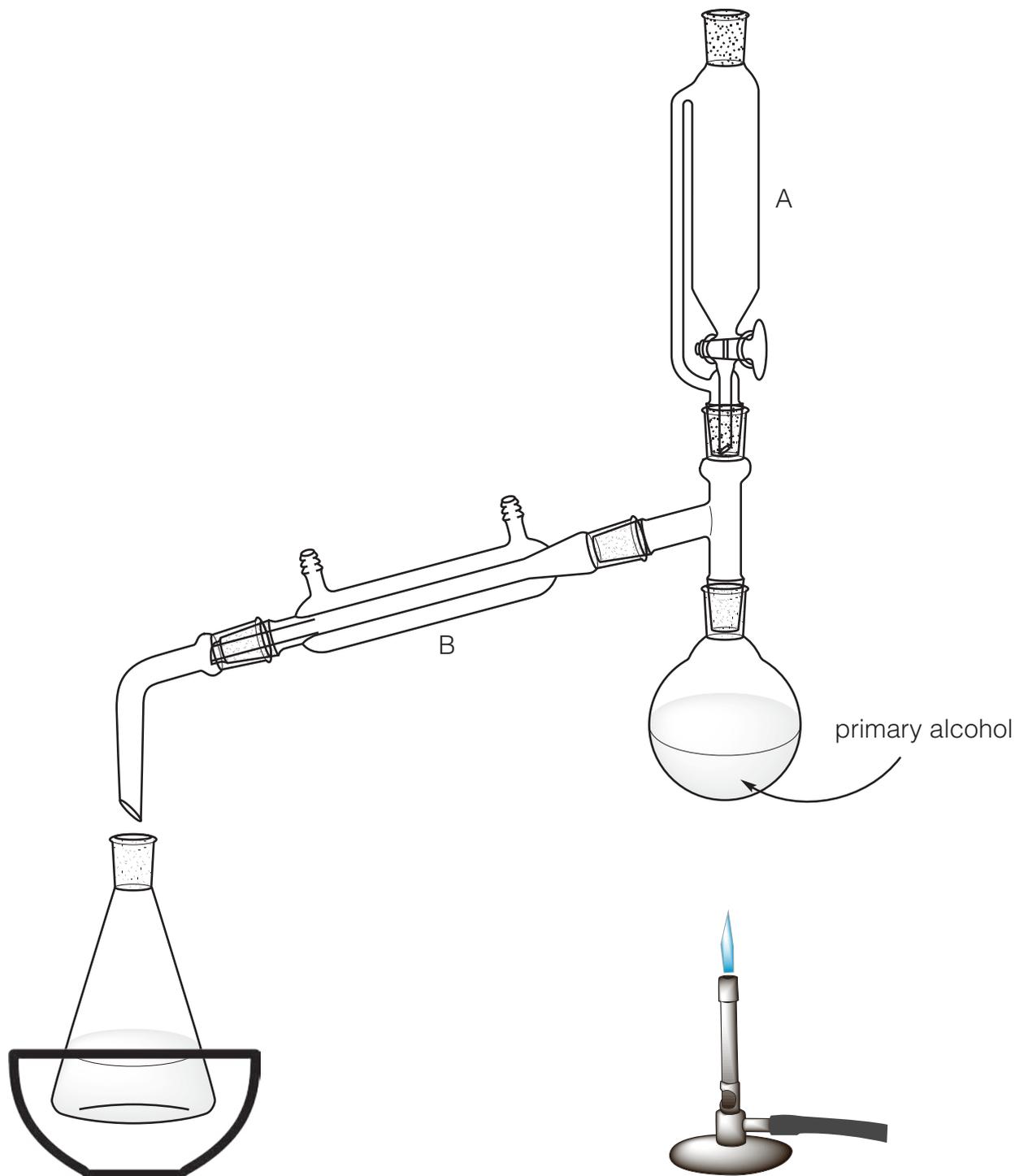
7. **Aldehydes** are versatile compounds that can help make resins, dyes, and organic acids, as well as perfumes for cologne, detergents, and soaps. Ketones are most widely used as solvents, especially in industries manufacturing explosives, lacquers, paints, and textiles. Ketones are also used in tanning, as preservatives, and in hydraulic fluids.

(a) Name the following aldehydes:

(i)		(ii)		(iii)	
(iv)		(v)		(vi)	

(12 marks) KA4

(e) An aldehyde can be prepared from an alcohol using the apparatus shown below:



(i) Name the pieces of glassware labelled **A** and **B**.

..... (2 marks) KA1

(ii) On the diagram above, show the direction of the water flow on the glassware labelled **B**.

(1 mark) KA1

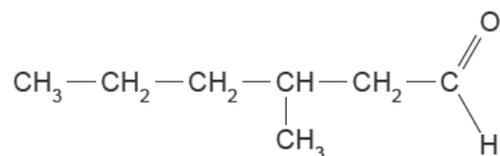
(iii) The glassware labelled **A** contained acidified dichromate ($\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$). When it reacted with the alcohol, the $\text{Cr}_2\text{O}_7^{2-}$ ions converted to Cr^{3+} ions. Write the half-equation for this conversion.

..... (2 marks) KA1

(iv) Name the functional group that would be formed if the alcohol, acidified dichromate ($\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$) and H_2SO_4 were refluxed together rather than reacted in the apparatus shown.

..... (1 mark) KA1

- (f) The structural formula of one aldehyde is shown below:



- (i) Give the systematic name of the aldehyde shown above.

..... (1 mark) KA4

- (ii) Draw the structural formula of a ketone that is an isomer of the aldehyde shown above

(2 marks) KA4

- (iii) When oxidised using Tollens' reagent, the ketone drawn in (ii) produces a carboxylate anion. Describe the solubility of the produced anion in comparison to that of its parent ketone.

.....

 (3 marks) KA1

3.4 Carbohydrates

Science understanding

Carbohydrates are naturally occurring sugars and their polymers. They are defined as either polyhydroxy aldehydes or polyhydroxy ketones, or substances that form these compounds on hydrolysis.

Disaccharides and polysaccharides are produced by the condensation of monosaccharide units linked in chains by covalent bonds.

In aqueous solution there is an equilibrium between a ring form and a chain form of glucose.

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Carbohydrates are one of the most abundant types of naturally occurring organic compounds. They perform many functions, including storing chemical energy and building the physical structure of plants.

All carbohydrates contain carbon, hydrogen, and oxygen, and have the general formula $C_x(H_2O)_y$. They are formally defined as **polyhydroxyaldehydes** (an aldehyde with multiple hydroxyl group substituents, also called an **aldose**), **polyhydroxyketones** (a ketone with multiple hydroxyl group substituents, also called a **ketose**), or compounds that yield either of these when hydrolysed.

The members of the carbohydrate family with the lowest molar masses are called “saccharides” or, more commonly, sugars. (‘Saccharin’ comes from the Greek word *sakkharon*, meaning sugar.) Saccharides can be classified as monosaccharides, disaccharides, or polysaccharides, depending on how many simple sugar units make up the molecule.

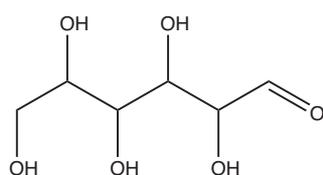
Monosaccharides

Molecular formula: $C_6H_{12}O_6$

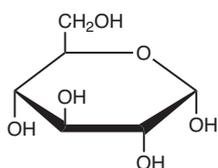
Empirical formula: CH_2O

Monosaccharides are the monomers that make up more complex carbohydrates, such as disaccharides and polysaccharides. Common monosaccharides include glucose and fructose.

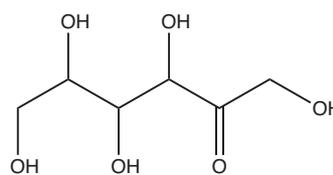
In an aqueous solution, monosaccharides exist in an equilibrium between a chain form and a cyclic (ring) form. The equilibrium lies very much in favour of the cyclic (ring) form; only 0.02% of molecules are in chain form at any one time. Notice that the ring forms do not contain aldehyde or ketone functional groups; these are the “compounds that yield polyhydroxyaldehydes or polyhydroxyketones when hydrolysed” in the definition of carbohydrates.



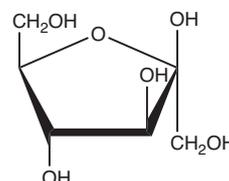
glucose
(chain form)



glucose
(ring form)



fructose
(chain form)



fructose
(ring form)

Glucose and fructose are **functional group isomers**: they have the same molecular formula ($C_6H_{12}O_6$), but different functional groups in their structures.

Physical properties

Monosaccharides are colourless crystalline solids. They have many polar hydroxyl groups per carbon atom (ratio is almost 1:1) which can form extensive hydrogen bonds with water. Hence, they are very soluble in water.

Monosaccharides also have high melting and boiling points due to the hydrogen bonding between the hydroxyl groups in the crystalline structure. The melting points of glucose and tridecane (a non-polar hydrocarbon with similar molar mass to glucose) are compared in Table 3.04 below.

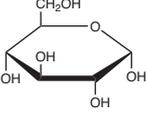
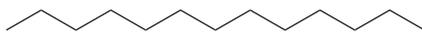
Compound	glucose	tridecane
Structure		
Molar Mass (g/mol)	180.18	184.41
Melting Point (°C)	146	-5

Table 3.04: Comparing glucose and tridecane

Disaccharides

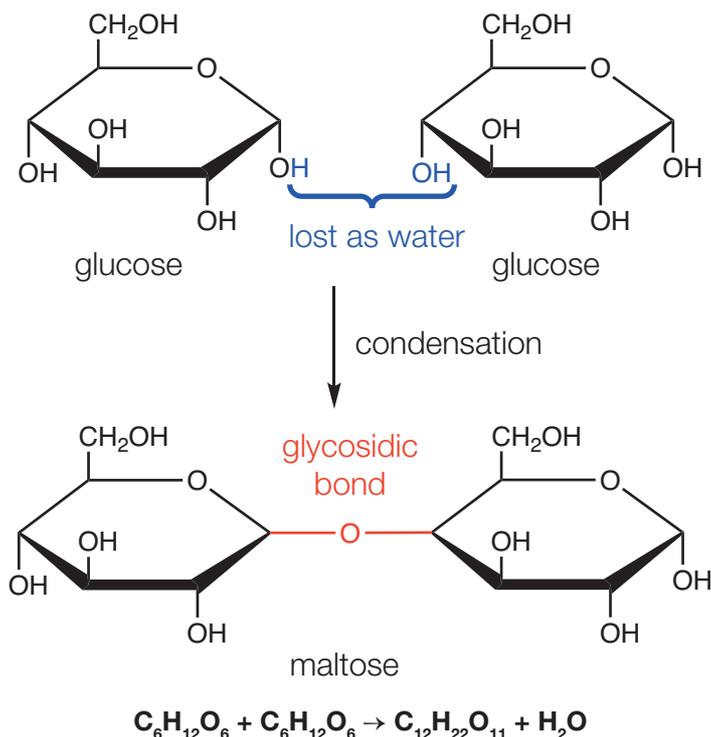
Molecular formula: $C_{12}H_{22}O_{11}$

Most carbohydrates in nature contain more than one monosaccharide unit. **Disaccharides** contain two monosaccharide monomers joined by covalent bonds. The individual atom that bridges the two monomers, and its associated bonds, are together called a **glycosidic bond**.

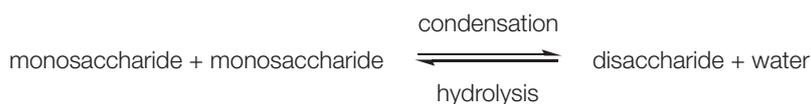
When two molecules combine to form a higher-mass product and release a molecule of water in the process, this is called a **condensation reaction**. The reverse reaction (decomposition of one molecule into two via the addition of water) is termed **hydrolysis** ('hydro' = water, 'lysis' = separation).

Example

Two units of the monosaccharide glucose can combine via a condensation reaction to form the disaccharide maltose. For each glycosidic bond that forms, one molecule of water is also produced.



The general reaction takes the form:

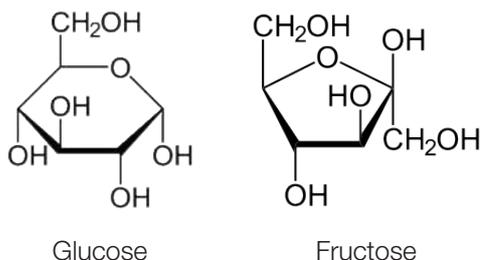


Physical properties

Like monosaccharides, disaccharides have high melting and boiling points due to the hydrogen bonding between the hydroxyl groups in the molecular structure. Many (but not all) are crystalline and soluble in water, although their solubility is in general lower than monosaccharides due to their higher molar masses.

Questions

8. Sucrose (common sugar) is a disaccharide formed from the condensation reaction between glucose and fructose.



(a) State one piece of evidence to support that glucose is a carbohydrate.

..... (1 mark) KA1

(b) Glucose and fructose are *functional group isomers*. Explain what is meant by this term.

..... (2 marks) KA1

(c) Draw the structure of sucrose.

(2 marks) KA4

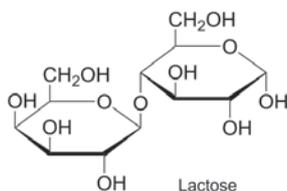
(d) Name the type of reaction that produces sucrose.

..... (1 mark) KA1

(e) Glucose can exist in both ring form (pictured) and as a straight chain. Describe how straight-chain glucose could be distinguished from a sample of ring-form glucose.

..... (3 marks) KA1

(f) Another disaccharide, lactose, is the sugar found in animal-based milk products.



Individuals who are “lactose intolerant” are unable to consume many dairy products, so the food industry has been developing low-lactose or lactose-free products using hydrolysis. The enzyme lactase hydrolyses lactose into two monosaccharides.

(i) State the molecular formula of lactose.

..... (1 mark) KA1

- (ii) Draw the monosaccharides which undergo condensation to form lactose.

(4 marks) KA4

Polysaccharides

General formula: $(C_6H_{10}O_5)_n$

Polysaccharides are polymers consisting of many monosaccharide units joined together by covalent glycosidic bonds. Commonly-known polysaccharides include starch (energy storage in plants), cellulose (found in plant cell walls), and glycogen (carbohydrate reserves in animals).

Starch

Starch is the most common carbohydrate in human diets, and is abundant in staple foods such as wheat, rice, and potatoes. It can be **malted** to produce sugars or **fermented** to produce alcohol.

The word 'starch' refers to a mixture of two types of molecules: **amylose** and **amylopectin**. Both are long polysaccharides consisting of repeating glucose units joined by glycosidic bonds. Amylose is a straight chain made up of approximately 300–3000 glucose units, while amylopectin is a branched chain made up of 2000–200,000 glucose units.

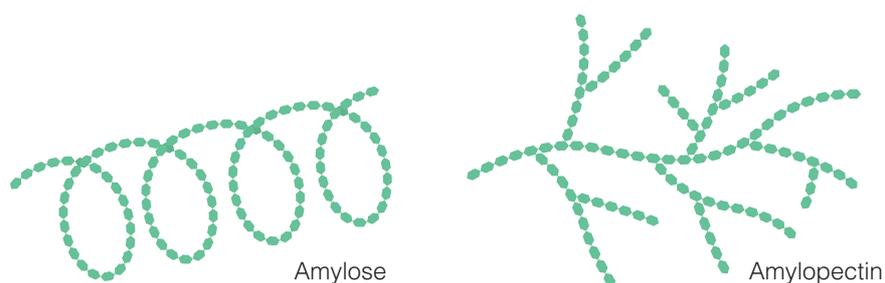
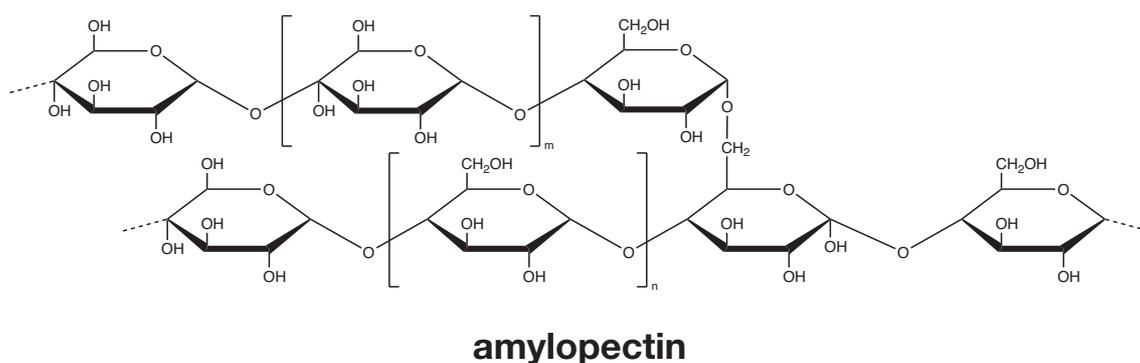
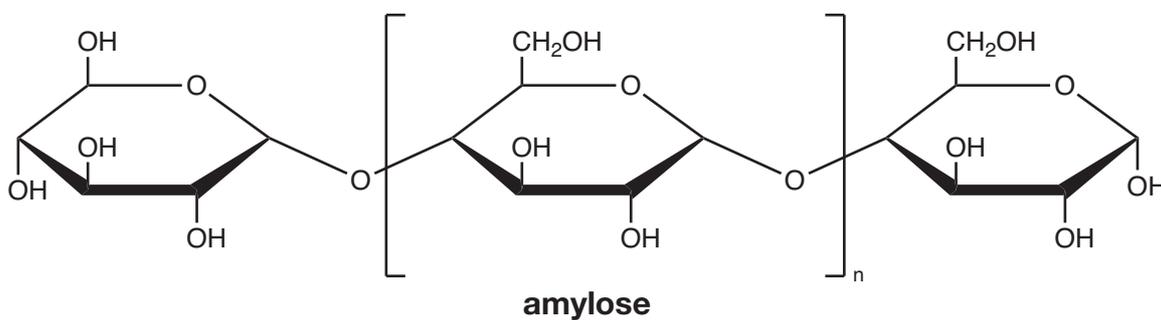


Figure 3.08 - Macromolecular structure of the components of starch

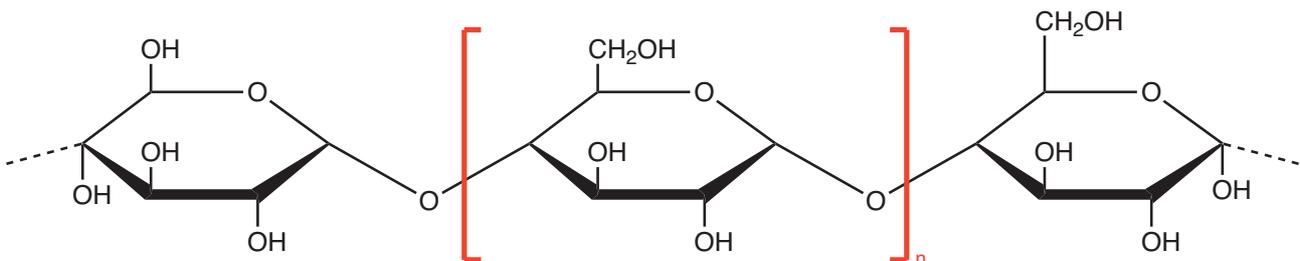
Physical properties

Due to their large molecular size, polysaccharides are insoluble in water. The polymer chains are densely tangled and form strong hydrogen bonds with each other, so water molecules cannot completely separate them. However, hydrogen bonding between polysaccharide chains and water molecules does occur; hence, polysaccharides can *absorb* significant amounts of water.

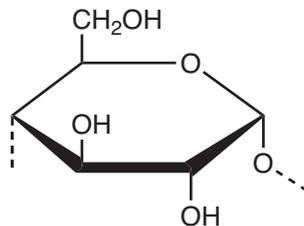
Heat can disrupt the polymer chains, so some polysaccharides can dissolve in boiling water. This is why foods that contain starch are usually only edible when cooked.

Repeating Units and Monomers

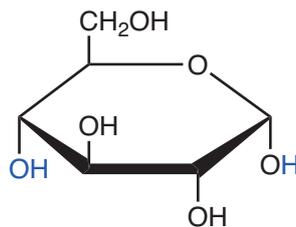
To find the repeating unit in a polysaccharide, look for the glycosidic bond that links the monomers together (the $-O-$ link). Draw square brackets around one of these, ensuring that only one glycosidic oxygen is included.



To draw the monomer from the repeating unit, transcribe the section of the repeating unit identified above.

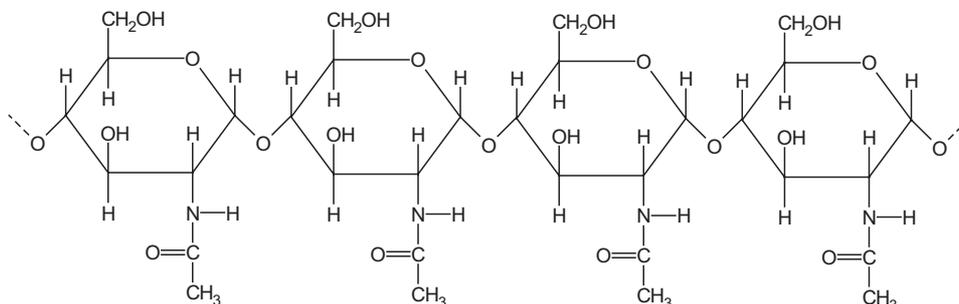


Then replace the H and OH that was lost as H_2O .



Questions

9. The following polymer represents part of the structure of chitin (pronounced /'kɪtɪn/, KY-tin). Chitin is one of the most important biopolymers in nature. It is mainly produced by fungi, arthropods, and nematodes. In insects, it functions as scaffold material.



- (a) On the structural formula above, use brackets to indicate one repeating unit.

(1 mark) KA1

(b) Draw the monomer from which chitin is formed.

(2 marks) KA4

(c) State whether chitin can be classified as a monosaccharide, disaccharide or polysaccharide.

..... (1 mark) KA1

3.5 Carboxylic acids

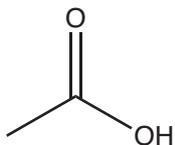
Science understanding

Carboxylic acids can be produced by the oxidation of aldehydes or primary alcohols.

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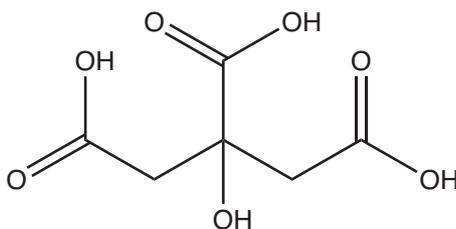
Carboxylic acids are weak organic acids found in nature. Commonly known examples include:

- Acetic acid (systematic name: ethanoic acid), the main component of vinegar
- Citric acid, found in citrus fruits
- Lactic acid, found in sour milk and also produced by our muscles during anaerobic metabolism



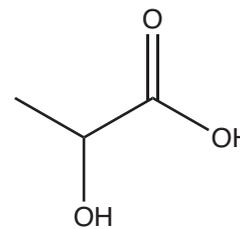
acetic acid

ethanoic acid



citric acid

2-hydroxypropane-1,2,3-tricarboxylic acid

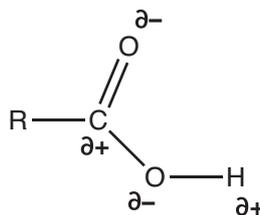


lactic acid

2-hydroxypropanoic acid

Carboxylic acids are also a very important part of the production of the polymers that make fibres and paints.

The functional group of carboxylic acids is the **carboxyl** group, named as such because it is made up of a **carbonyl** group (C=O) and a **hydroxyl** group (-OH). The carboxyl functional group is extremely polar.

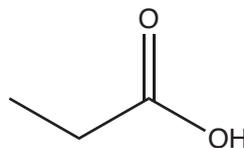


carboxylic acid

Carboxylic acids have the **general formula** $C_nH_{2n+1}COOH$. Carboxylic acids can also be written as $R-COOH$, or $R-CO_2H$, where "R" represents the alkyl chain component.

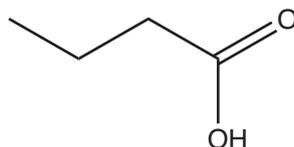
When **naming** carboxylic acids:

- the -e is removed from the parent alkane and replaced with *-oic acid*. For example, propane becomes *propanoic acid*.



propanoic acid

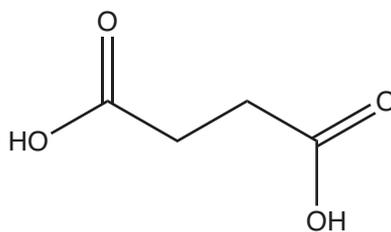
- It is not necessary to number the position of the functional group, as it is always terminal.



butanoic acid

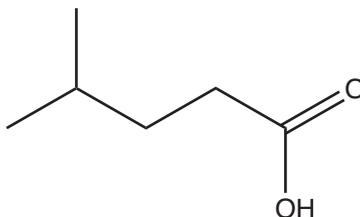
(not butan-1-oic acid)

- The prefix *di-* is used before *-oic acid* if there are two carboxyl functional groups. The *-e* is included in the name of the parent alkane.



butanedioic acid

- If there are branches, always begin numbering from the functional group.



4-methylpentanoic acid

Carboxylic acids are produced by the complete oxidation of primary alcohols and aldehydes.

Physical properties of carboxylic acids

Due to high potential of the carboxyl group to form hydrogen bonds, carboxylic acids have significantly higher melting and boiling points than other organic compounds with similar molecular masses. They are also more soluble in water than other polar organic compounds with similar molecular masses due to the many sites where hydrogen bonding can occur.

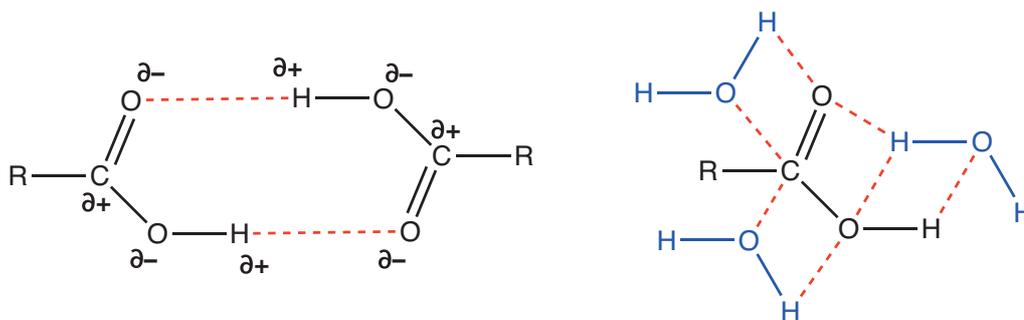


Figure 3.09: Carboxyl groups can form multiple hydrogen bonds

Compound	butanoic acid	pentan-1-ol	pentanal
Structure			
Molar Mass (g/mol)	88.1	88.1	86.1
Boiling Point (°C)	163	137	103
Solubility (g/L water)	miscible	32.7	14.8

Table 3.05: boiling points and solubility of alcohols, aldehydes, and carboxylic acids.

Carboxylic acids up to butanoic acid are very soluble in water; however, solubility decreases as the carbon chain length increases. This is because the hydrocarbon chain is non-polar and **hydrophobic**. As the carbon chain becomes longer, it becomes harder for the polar water molecules to surround and interact with the carboxylic acid to dissolve it.

Acid	Solubility (g/L water)
methanoic acid	miscible
ethanoic acid	miscible
propanoic acid	miscible
butanoic acid	miscible
pentanoic acid	50
hexanoic acid	11
heptanoic acid	2.4
octanoic acid	0.68
nonanoic acid	0.3
decanoic acid	0.15

Table 3.06: Solubility of carboxylic acids

3

Science understanding

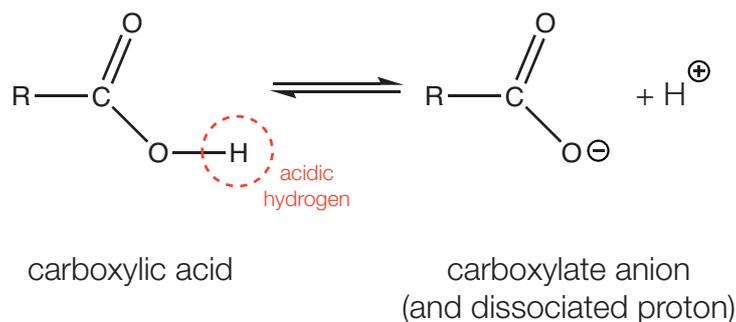
Carboxylic acids are weak acids and, to a small extent, ionise in water.

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Reactions of carboxylic acids

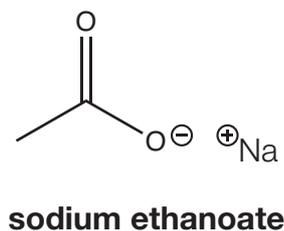
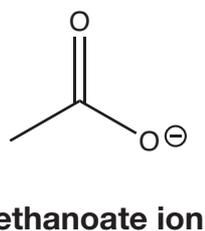
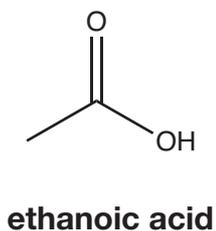
Carboxylic acids are acidic due to the acidic hydrogen in the hydroxyl group. The hydrogen can be lost as H^+ , which then bonds to water to form the hydronium ion, H_3O^+ . The anion that is formed when the carboxylic acid loses its H^+ is called the **carboxylate anion**.

Carboxylic acids are **weak acids**, meaning they do not completely dissociate in water. Typically, fewer than 5% of the molecules are dissociated at any one time.



Salts of carboxylic acids are named in the same way as the salts of inorganic acids. First, the cation is named. The name of the carboxylate anion is generated by replacing *-ic acid* with *-ate*.

Example

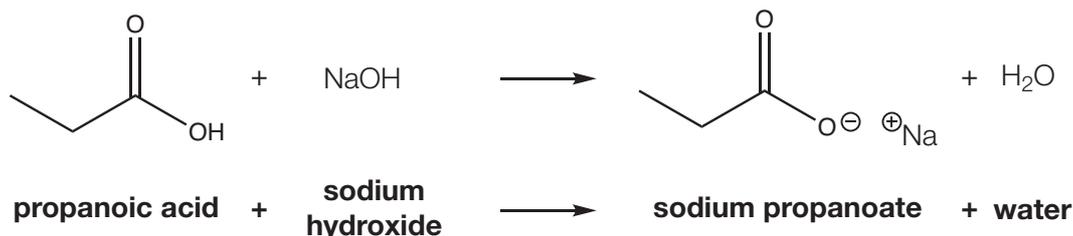


Carboxylic acids undergo typical acid reactions, generally at a much lower rate than inorganic acids.

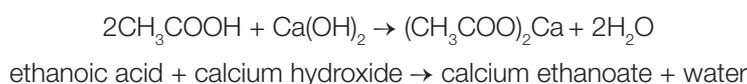
Reaction with metal hydroxides

All carboxylic acids, whether soluble or insoluble in water, react with strong bases to form water-soluble salts.

Example



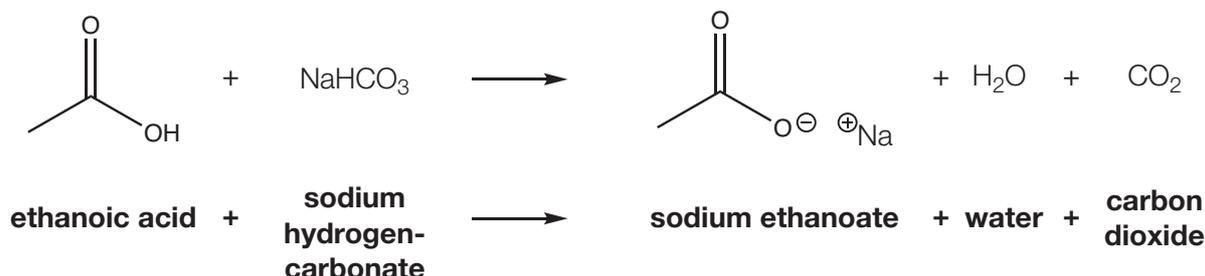
Example



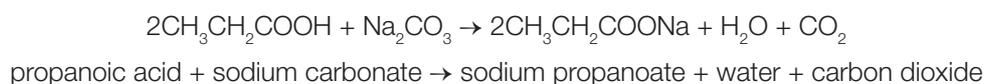
Reaction with carbonates and hydrogen-carbonates

Carboxylic acids react with carbonates and hydrogen-carbonates to produce water-soluble salts, water, and carbon dioxide gas. These reactions effervesce due to the production of gaseous carbon dioxide.

Example



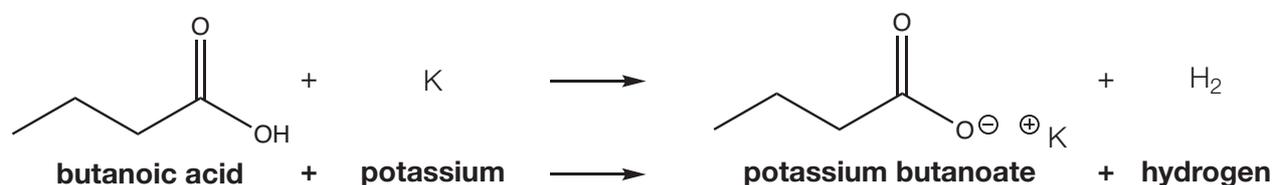
Example



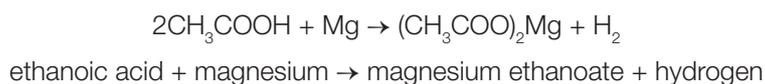
Reaction with metals

Carboxylic acids react with the more reactive metals to produce a salt and hydrogen gas.

Example



Example



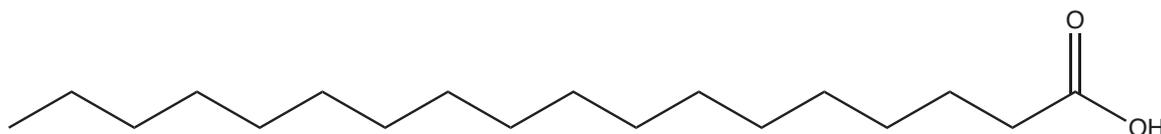
Solubility of carboxylate salts

Sodium and potassium carboxylate salts are *always soluble in water*, regardless of the solubility of the parent carboxylic acid.

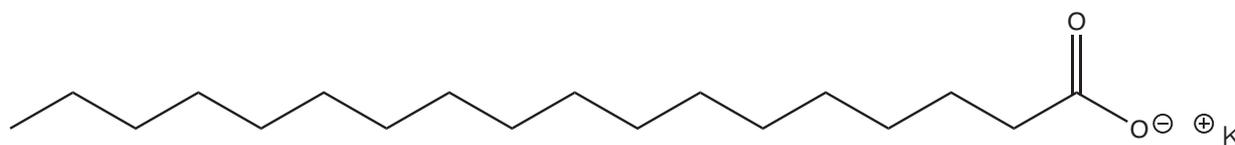
Carboxylic acids have *partial* charges on the polar hydroxyl group, which allows them to form hydrogen bonds with polar water. However, the solubility due to this hydrogen bonding decreases as the carbon chain length increases. When a carboxylate salt dissociates in water it forms the carboxylate anion, which has a *full* negative charge. The full charge on the ion allows for stronger ion-dipole interactions with water, and hence increased solubility.

Example

Stearic acid is a waxy, solid fatty acid. It is a long-chain carboxylic acid with 18 carbon atoms and is insoluble in water. However, its sodium salt (sodium stearate) is soluble.



stearic acid
(octadecanoic acid)
insoluble

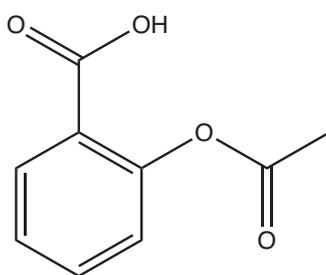


sodium stearate
(sodium octadecanoate)
soluble

Many pharmaceuticals contain carboxyl functional groups. However, because of their complex structures, they are insoluble in water and bodily fluids. Converting the drug to its carboxylate salt form allows it to dissolve and be more effective in the body.

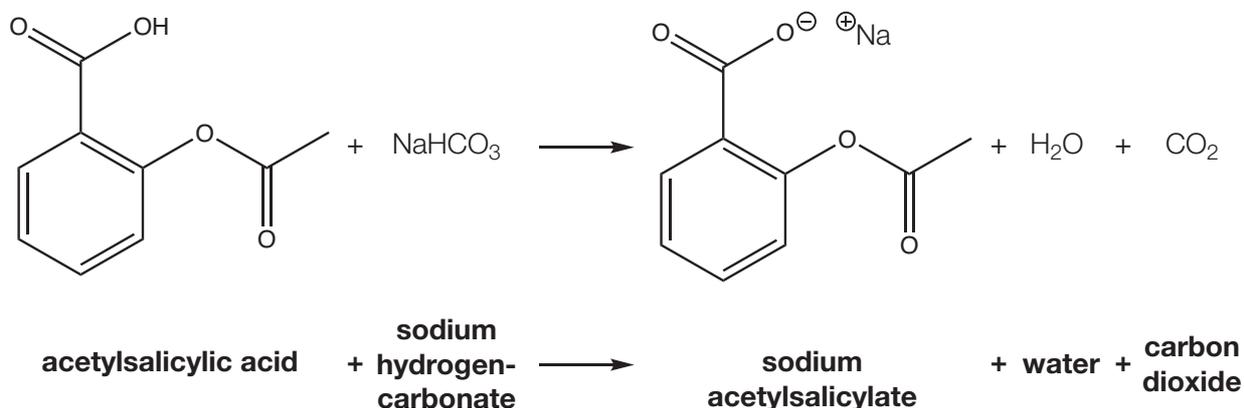
Example

Aspirin (acetylsalicylic acid) has the structure shown below. It is not very soluble in water or in the acids present in the stomach.



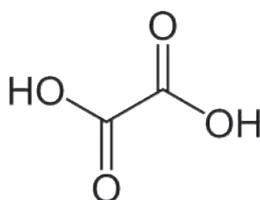
acetylsalicylic acid
(aspirin)
(2-acetoxybenzoic acid)

Sometimes aspirin is sold as “soluble aspirin”, which also contains sodium hydrogencarbonate (NaHCO₃). As the tablet dissolves, the aspirin and sodium hydrogencarbonate react to form the sodium salt of the aspirin, sodium acetylsalicylate. Like all sodium carboxylate salts, the sodium salt of aspirin is soluble in blood and other bodily fluids, as it will form strong ion-dipole interactions with water molecules.



Questions

10. Rhubarb is a pink vegetable commonly used to make tart-flavoured pies, jams, and sauces. The stalks are the only edible part of the rhubarb plant, as the leaves contain poisonous *oxalic acid*. The structural formula of oxalic acid is below:



- (a) Name oxalic acid systemically.

..... (2 marks) KA4

- (b) State the molecular formula of oxalic acid.

..... (2 marks) KA4

- (c) Predict what would be observed when each of the following procedures is carried out. Explain your prediction with the aid of equations.

- (i) Some solid oxalic acid is mixed with sodium hydroxide solution.

.....

 (3 marks) KA1

- (ii) Some solid oxalic acid is mixed with sodium carbonate solution.

.....

 (3 marks) KA1

- (d) Other carboxylic acids and their derivatives are used in the production of polymers, biopolymers, coatings, adhesives, and pharmaceutical drugs. They also can be used as solvents, food additives, antimicrobials, and flavourings.

- (i) Name the following carboxylic acids:

(1)		(2)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
		(3)	

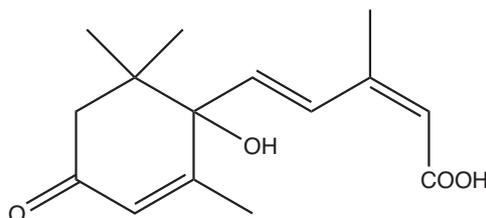
(6 marks) KA4

(ii) Draw the following carboxylic acids:

(1.)	hexanoic acid	(2.)	3-methylbutanoic acid	(3.)	octanedioic acid

(6 marks) KA4

11. Abscisic acid is a hormone found in plants that helps protect them against external stresses including drought, waterlogged soil, and pathogens. The structure of abscisic acid is shown below.



(a) Write the molecular formula of abscisic acid.

..... (2 marks) KA4

(b) Name three functional groups present in abscisic acid.

..... (3 marks) KA1

(c) A sample of abscisic acid was subjected to several chemical tests. Complete the table below by writing any observations you would expect when the reactions are complete.

Abscisic acid tested with...	Observations
Bromine water (Br ₂)	
Acidified dichromate (Cr ₂ O ₇ ²⁻ /H ⁺)	
Tollens' reagent	
Sodium bicarbonate solution (NaHCO ₃)	

(4 marks) KA1

(d) Abscisic acid was reacted with concentrated sodium hydroxide solution.

(i) Draw the structural product formed.

(2 marks) KA4

(ii) Explain why the organic product of this reaction is more soluble in water than the acid.

.....

 (3 marks) KA1

12. Read the following article:

Eggs, steak, and butter on everything – it's not like most health food diets. But the high-fat “ketogenic” diet can be an effective last resort method of reducing seizures in people with epilepsy that doesn't respond to drugs, and may even help a range of other brain conditions. Now researchers may have figured out how it works – and how to make the method more palatable.

“All the time, you're looking at getting the fat in,” says Emma Williams, whose son Matthew used to eat like this. Breakfast might be scrambled eggs with lashings of butter, followed by a lunch of steak and salad, covered in oily dressing. “If we ate out, I'd take butter and oil with me,” says Williams. According to early-stage research, the high-fat ketogenic diet may also help several other brain conditions, including Alzheimer's disease and schizophrenia. The diet seems to have slowed or even stopped cancer growth in a few people with brain tumours who started to follow it to control seizures. When given to mice with tumours, it amplified the effects of radiotherapy. The results are so intriguing that a small trial of the diet in people with brain tumours is planned for next year.

But by far the most common use is for epilepsy. The ketogenic diet has been used in children with severe epilepsy since the 1990s. Two-thirds of those who try it see their number of seizures fall by half or more. In some cases, as happened for Matthew, children can later be weaned off the diet without their epilepsy becoming worse again. Until now, the mechanism behind these effects had been a mystery. Now researchers have discovered that one of the breakdown products of fat binds to molecules on the surface of brain cells, calming the storm of electrical activity that can cause epileptic seizures.

Calm the storm

Our cells usually get their energy from glucose, which comes from the carbohydrates we eat. But when these aren't available, the liver breaks down fat into fatty **acids** and ketones, so that our cells can burn ketones for energy instead. In epilepsy, the thinking has long been that these ketones somehow make neurons in the brain less likely to fire, preventing seizures.

But there was still a puzzle: higher blood ketone levels in those following the diet don't necessarily correlate with fewer seizures. Instead, it has been suggested that a fatty **acid** called **decanoic acid** is responsible for the effect. Previous work found that directly feeding this compound to mice with a version of epilepsy reduced their seizures.

Now lab tests using frog cells have shown that **decanoic acid** directly binds to a molecule that is found on the surface of brain cells and is known to be involved in spreading electrical impulses between different neurons (Brain, DOI: 10.1093/brain/awv325). When **decanoic acid** binds to it, it reduces the flow of electrical current into the cell via this molecule. “It reduces the chance of a neuron firing,” says Robin Williams of Royal Holloway, University of London.

His team's finding could lead to easier dietary regimes that get the same result. “It's a strong theory, and if it translates into practice it could use a more acceptable diet,” says Helen Cross of Great Ormond Street Hospital for Children in London, who wasn't involved in the research. She plans to trial giving **decanoic acid** directly to people.

This could enable more people with epilepsy to benefit from the diet's effects. The ketogenic regime seems to work for adults too, but few follow it because it's so hard to stick to. In the standard version, people have to make sure around three-quarters of their food is fat. “It can be daunting,” says Emma Williams. “You have to weigh every gram of food.”

But simply adding **decanoic acid** to food won't be enough. Under a typical high-carb diet, the body would still rely on glucose for energy, and store away the **decanoic acid** as fat. To make sure that the **decanoic acid** gets into the brain, people would still need a relatively low-carb diet – but not as low as the current ketogenic diet, says Robin Williams.

For instance, in Cross's trial, due to start next year, children with epilepsy will be given **decanoic acid** twice a day, in the form of a yogurt-like drink. They won't be able to eat sugary foods, but will be able to eat plenty of carbs like wholemeal bread and pasta, which release glucose into the blood more slowly. “It's a lot more acceptable,” says Cross. “And there's no measuring involved.”

New Scientist: “How high-fat diet for epilepsy affects the brain”. Clare Wilson. 28/1/2015, Vol. 228 Issue 3049, p12-13

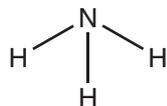
3.6 Amines

Science understanding

Amines are classified as primary, secondary, or tertiary.

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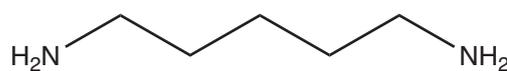
Amines are a class of organic compounds containing the **amino** functional group, which is a carbon bonded to a basic nitrogen with a lone pair. These compounds are derivatives of ammonia, NH_3 (although ammonia is not organic, as it contains no carbon). Amines are abundant in nature, and many have a characteristic unpleasant fishy odour. As their names suggest, the compounds *putrescine* and *cadaverine* are responsible for the *putrid* smell of *cadavers* (decaying animal tissue).



ammonia

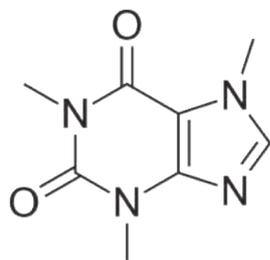


putrescine

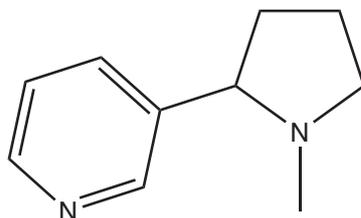


cadaverine

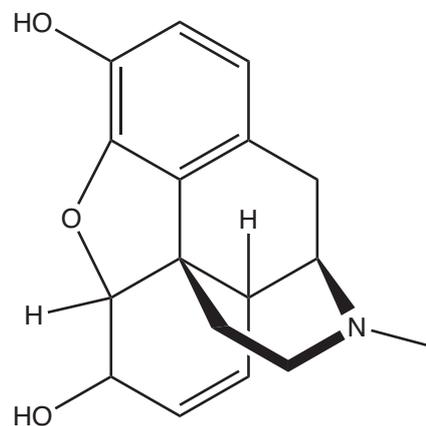
Many amines are extremely poisonous or can cause a variety of effects even in small doses. Some amines are extracted from plants, and commonly-known plant-based amines include caffeine, nicotine, and morphine.



caffeine



nicotine



morphine

Primary, secondary, and tertiary amines

Amines are classified as primary, secondary, or tertiary based on how many carbon atoms are directly connected to the nitrogen atom.

Primary (1°)		A primary amine has the nitrogen covalently bonded to <i>one</i> carbon.	 propanamine
Secondary (2°)		A secondary amine has the nitrogen covalently bonded to <i>two</i> carbons.	 N-methylethanamine
Tertiary (3°)		A tertiary amine has the nitrogen covalently bonded to <i>three</i> carbons.	 N,N-dimethylethanamine

Table 3.07: Amine classification

All amino groups have a trigonal pyramidal geometry due to the presence of the lone pair of electrons.

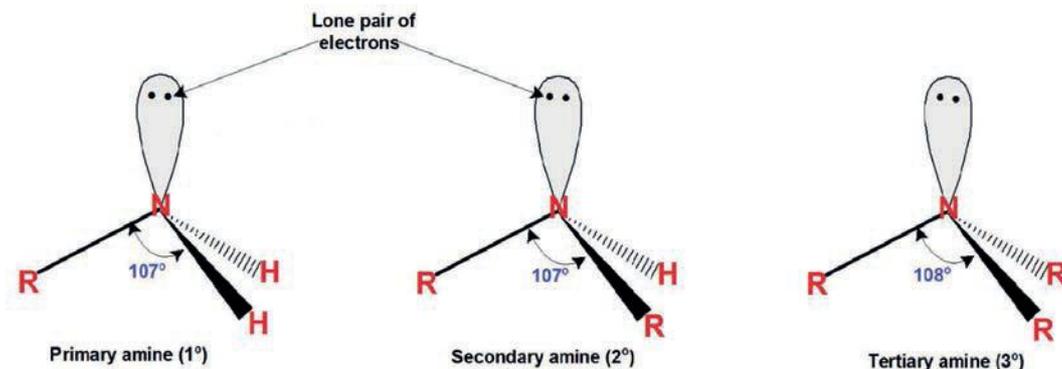


Figure 3.10: Spatial geometry of amino functional groups

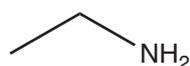
Amines have the general formula $R-NH_2$, R_2-NH , or R_3-N .

This course only requires the naming of primary amines.

- the $-e$ is removed from the parent alkane and replaced with $-amine$.

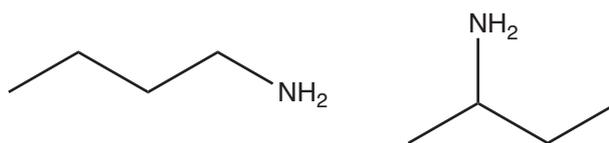
Example

Ethane becomes ethanamine.



ethanamine

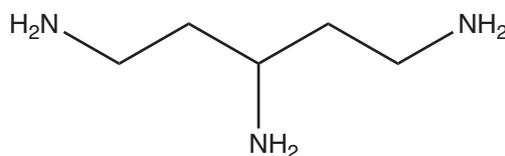
It is necessary to number the position of the functional group in the name, as it is non-terminal and can be placed in different positions.



butan-1-amine

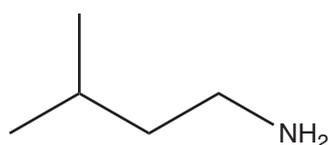
butan-2-amine

The prefixes *di-* and *tri-* are used before $-amine$ if there are two or three amino functional groups. Remember to include numbers to indicate the position of the amino groups. The $-e$ is included in the name of the parent alkane.



pentane-1,3,5-triamine

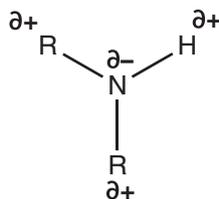
If there are branches, ensure the functional group is assigned the lowest number.



3-methylbutan-1-amine

Physical properties of amines

Both N–C and N–H bonds in amino functional groups are polar. However, because nitrogen is less electronegative than oxygen, the magnitude of the partial charges in amines is considerably less than in functional groups which contain oxygen.



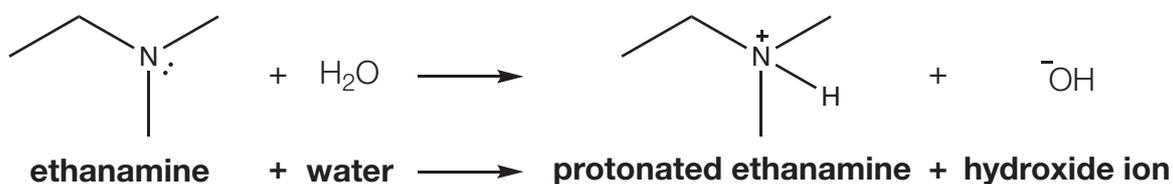
Both primary and secondary amines can form intermolecular hydrogen bonds. They have higher boiling points than alkanes of a similar molar mass, and they are soluble in water. However, as the carbon-chain length increases, the solubility of amines decreases.

Science understanding

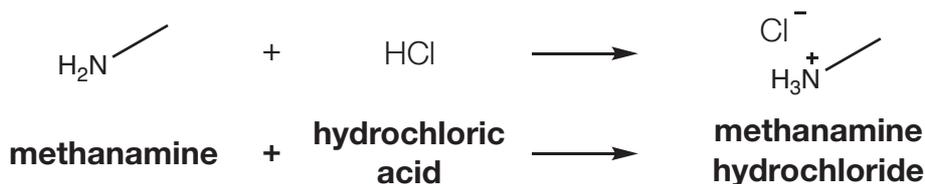
Amines act as bases.

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The most important chemical property of amines is their basicity. The lone pair on the nitrogen can accept H^+ to form a **protonated amine**. Amines are weak bases; similar to carboxylic acids, they incompletely ionise in aqueous solution.



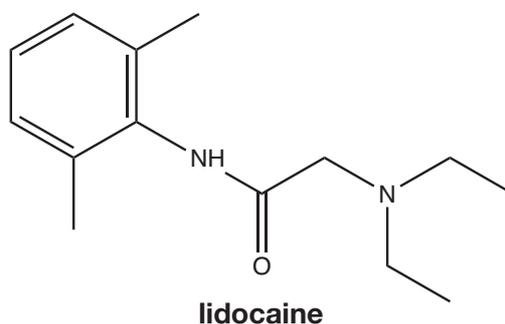
When amines react with acids, they form ionic salts. These ionic salts are water soluble.



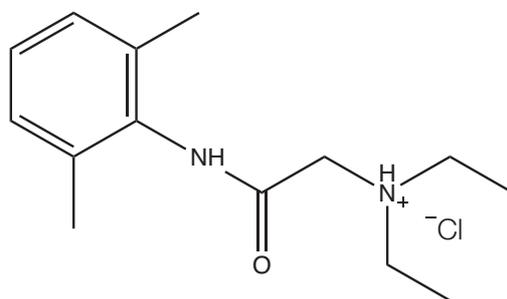
Many pharmaceutical drugs contain amino groups but are also large molecules with many non-polar components. They are administered as water-soluble salts because these amine salts can form strong ion-dipole interactions with polar water molecules. Ion-dipole interactions are stronger than hydrogen bonds; hence, the drugs dissolve more easily in bodily fluids.

Example

Lidocaine is a widely used local anaesthetic that was introduced in 1948. Its structural formula is below:



The molecule is quite big and has large non-polar sections, which makes it essentially insoluble in aqueous bodily fluids. Hence, it is administered in the form lidocaine hydrochloride (marketed under the name Xylocaine®).



lidocaine hydrochloride
(Xylocaine[®])

Questions

13. Amines play an important role in biology: they are involved in the creation of amino acids, the building blocks of proteins in living beings. Many vitamins are also built from amino acids. Amines are also widely used in the preparation of medicines.

(a) Identify the functional group of each of the amines as primary, secondary, or tertiary.

(i)		(ii)		(iii)	$\text{H}_3\text{C}-(\text{CH}_2)_5-\text{NH}_2$
(iv)	$(\text{CH}_3)_3\text{N}$	(v)		(vi)	$(\text{CH}_3)_2\text{NH}$

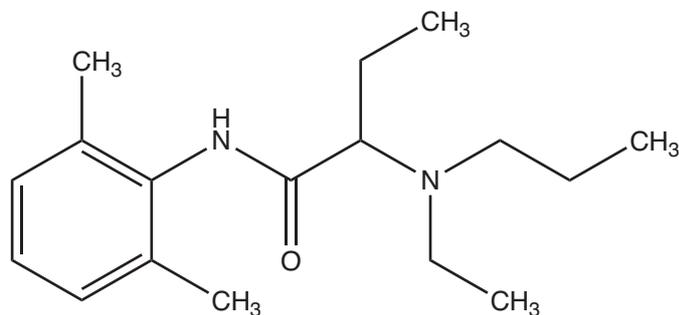
(12 marks) KA4

(b) Draw the structural formula of the following amines:

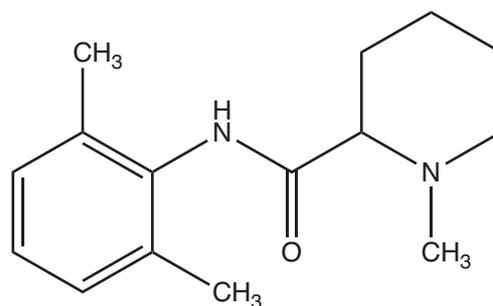
(i)	propan-1-amine	(ii)	methanamine	(iii)	ethane-1,2-diamine
(iv)	hexane-1,6-diamine	(v)	hexane-1,3,4-triamine	(vi)	butan-1-amine

(13 marks) KA4

14. Etidocaine and mepivacaine are two local anaesthetics: drugs that numb an area of the body to help reduce pain. Their structures are below.



etidocaine



mepivacaine

- (a) Circle the amino functional groups in each compound and classify them as primary, secondary, or tertiary.

(2 marks) KA1

Draw the structure of the protonated form of

- etidocaine; and
- mepivacaine.

(4 marks) KA4

3.7 Esters

Science understanding

Carboxylic acids undergo condensation reactions with alcohols to form esters.

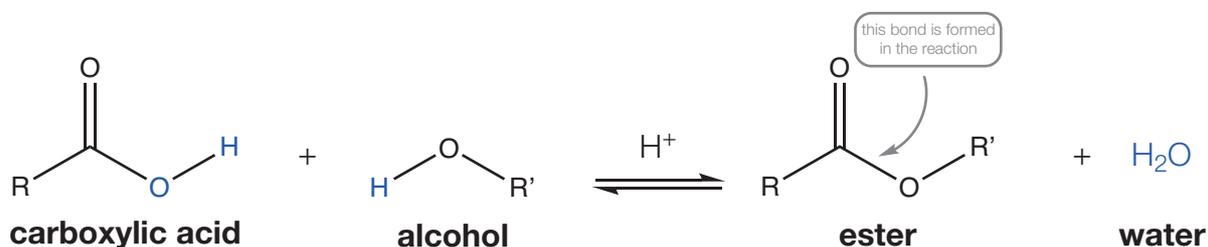
Condensation reactions occur when two organic molecules combine to form a larger molecule, also releasing another small molecule, such as water.

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Esters are organic compounds that contain the **ester** functional group. Many esters, both natural and synthetic, are encountered in everyday life. They often have a sweet smell and can be used to add flavour or scent to foods and perfumes. Esters are found in:

- Fruits such as bananas, apples, pears, and raspberries
- Artificial flavourings
- Cosmetics, like nail polish remover
- Animal fats and vegetable oils
- Rum and wine

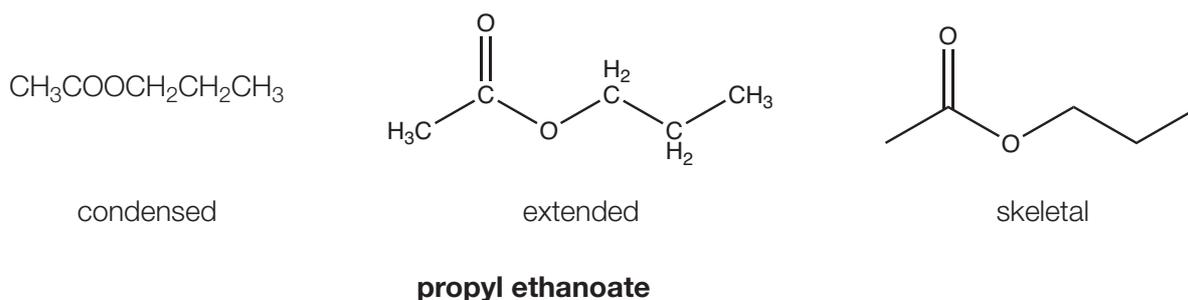
An ester can be prepared by reacting a carboxylic acid with an alcohol in the presence of an acid catalyst. It is a condensation reaction, as a water molecule is produced.



The functional group is called an **ester**. It can be written as **-COO-**.

Example

The ester that gives pears their flavouring is shown here in three different structural forms.



Science understanding

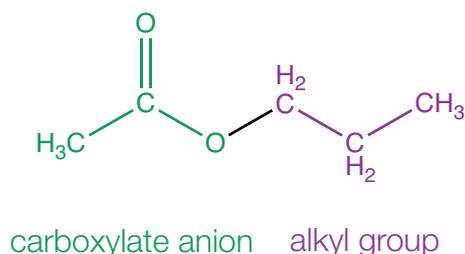
Identify, name systematically, and draw structural formulae of methyl and ethyl esters of acids containing up to eight carbon atoms in the main chain, with side chains limited to a maximum of two carbon atoms.

Draw the structural formula of the ester that could be produced by the condensation reaction between a carboxylic acid and an alcohol, given their structural formulae or vice versa.

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Naming esters

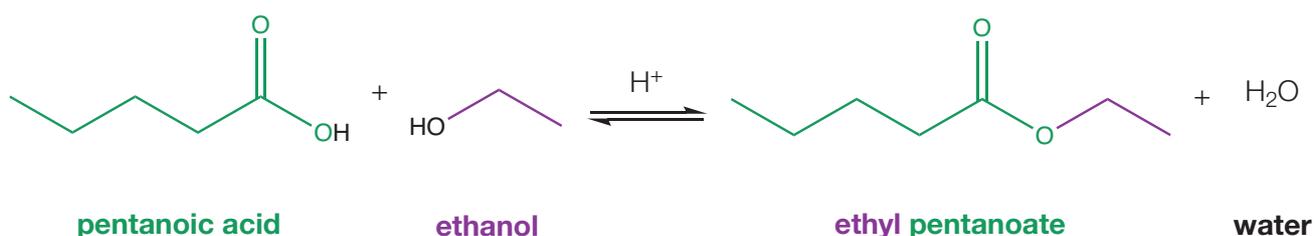
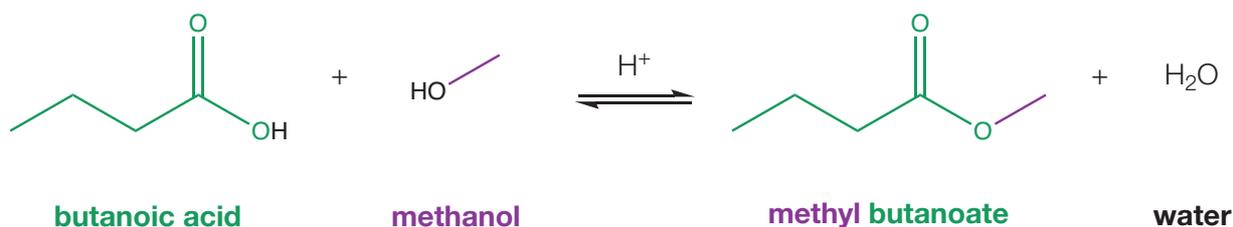
Esters are composed of two parts: the carboxylate ion and the alkyl group.



As such, there are two parts to the name of an ester.

- The first part is derived from the alkyl group. The alkane suffix *-an-* and the alcohol suffix *-ol* are removed and replaced with the ending that signifies a hydrocarbon fragment: *-yl*. For example, *methanol* becomes *methyl*, *ethanol* becomes *ethyl*, *propanol* becomes *propyl*, and so on.
- The second part of the name is simply the carboxylate anion. The carboxylic acid suffix is removed and replaced with *-oate*. For example, *methanoic acid* becomes *methanoate*, *ethanoic acid* becomes *ethanoate*, *propanoic acid* becomes *propanoate*, and so on.

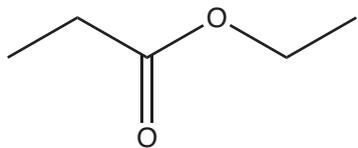
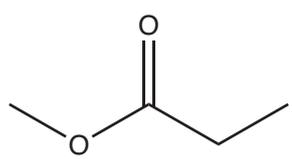
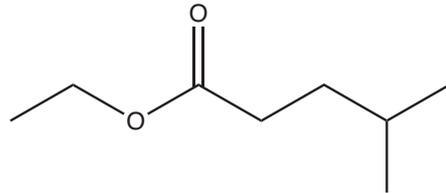
Example



Questions

15. Esters are found in food flavourings, perfumes, and in biological molecules such as triglycerides. Esters can also be used to make products such as soap and biodiesel.

(a) Name the following esters systematically and name the alcohol and carboxylic acid from which they are prepared.

i) $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_3$	ii) $\text{CH}_3\text{OOCCH}_2\text{CH}_2\text{CH}_3$
Name: Alcohol: Carboxylic acid:	Name: Alcohol: Carboxylic acid:
iii) $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	iv) 
Name: Alcohol: Carboxylic acid:	Name: Alcohol: Carboxylic acid:
v) 	vi) 
Name: Alcohol: Carboxylic acid:	Name: Alcohol: Carboxylic acid:

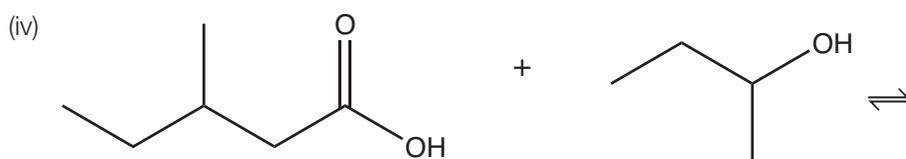
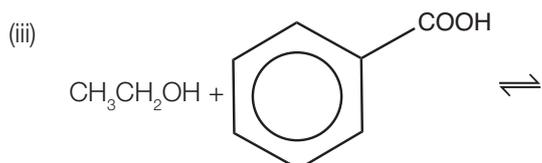
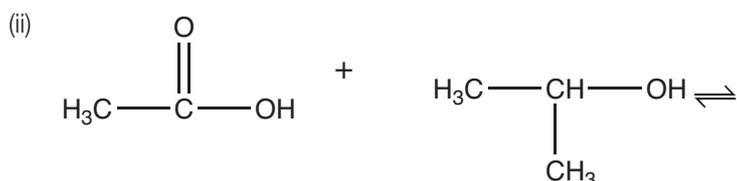
(24 marks) KA4

(b) Draw the following esters:

(i) methyl hexanoate <div style="border: 1px solid black; height: 80px; width: 100%;"></div>	(ii) 2-methylpropyl propanoate <div style="border: 1px solid black; height: 80px; width: 100%;"></div>
(iii) butyl butanoate <div style="border: 1px solid black; height: 80px; width: 100%;"></div>	(iv) propyl octanoate <div style="border: 1px solid black; height: 80px; width: 100%;"></div>

(8 marks) KA4

(c) Draw the products of the following reactions:



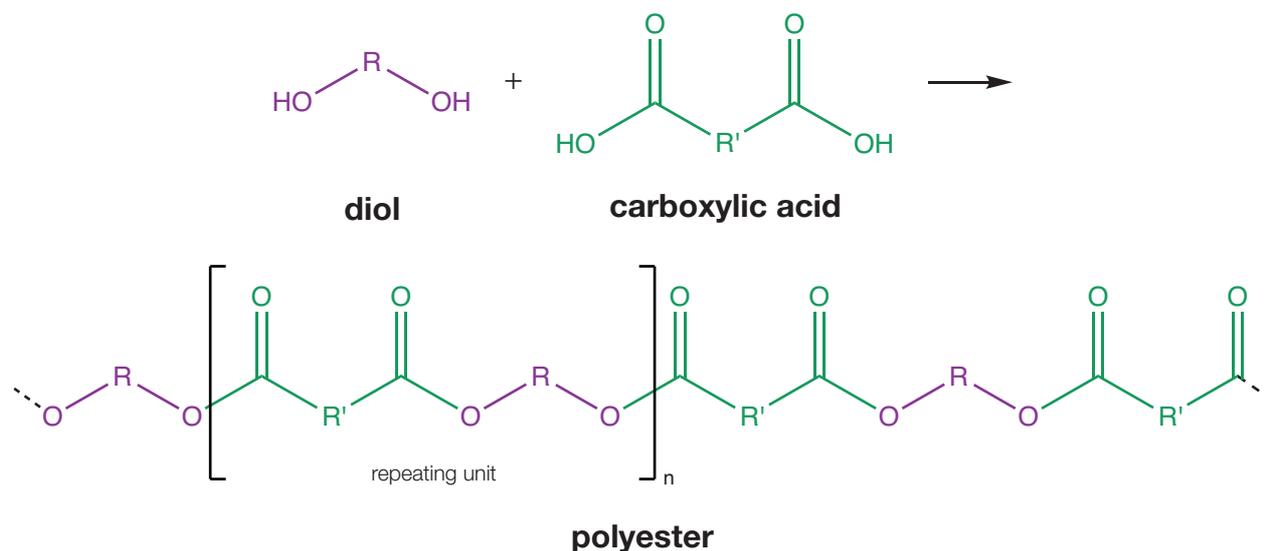
(8 marks) KA4

Science understanding

Draw the structural formula of a polyester, given the structural formula(e) of the monomer(s) or vice versa.

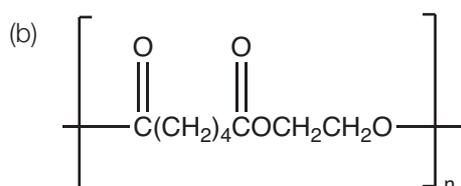
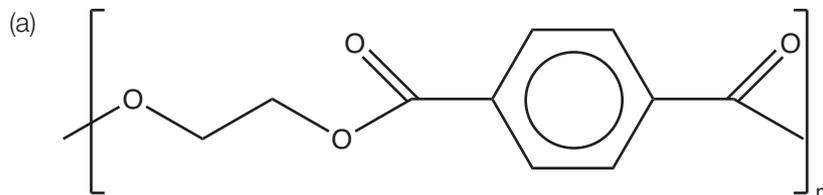
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When a diol and a dicarboxylic acid react, they form a compound called a **polyester**. Two different monomers (the diol and dicarboxylic acid) have combined to form a polymer. *Polymers are discussed in more detail in Chapter 4.*



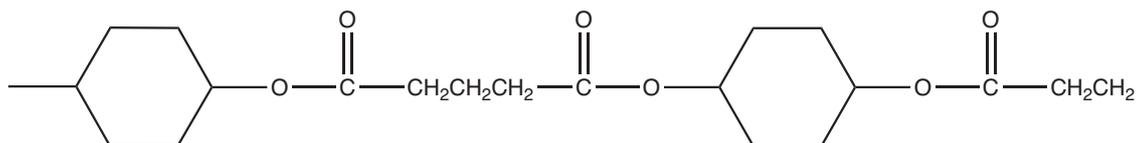
This is also a condensation reaction, as one water molecule is produced for each ester group. As there are many ester functional groups present, it is called polyester (“poly” meaning “many”).

17. For the following polyesters, draw the two monomers from which it could be made.



(4 marks) KA4

(c) The following is the structural diagram of a polyester.



(i) Draw brackets around the repeating unit.

(1 mark) KA1

(ii) Draw the structural formulae of the two monomers from which this polymer could be made.

(4 marks) KA4

Science understanding

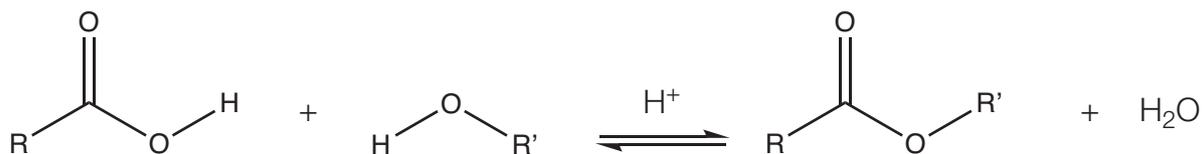
Condensation reactions are slow at 25°C.

Explain the use of heating under reflux, and the use of a trace of concentrated sulfuric acid in the laboratory preparation of esters.

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Esterification

The reaction between a carboxylic acid and an alcohol in the presence of an acid catalyst, usually concentrated sulfuric acid, is called **Fischer esterification**, after the German chemist Emil Fischer.



The Fischer Esterification

Acid-catalysed esterification is reversible and will eventually reach a state of equilibrium. The equilibrium constant (K_c) is much less than 1, meaning the equilibrium favours the backward reaction. By controlling the reaction conditions, it is possible to shift the position of equilibrium to give a higher yield of ester. According to Le Châtelier's principle, an increase in the concentration of alcohol will drive the equilibrium to favour the forward reaction. *Equilibrium and Le Châtelier's principle are discussed in detail in Topic 2.2.*

Heating Under Reflux

Ester formation is very slow at 25°C, even with a catalyst, so it is important to heat the contents of the flask. However, the reactants and products are usually volatile, and the heating needs to be *controlled*. The apparatus used for heating the reaction mixture is shown below. It is called **reflux apparatus**.

When the mixture boils, the vapours rise up from the flask and enter the **condenser**. Cold water flows up from the bottom of the water jacket of the condenser and cools the vapours, which condense and run back into the flask. The heating must be controlled so the reactants do not boil so vigorously as to escape the flask. The solution should be simmering, the flask should not be filled more than halfway, and the condensing vapours should not reach higher than halfway up the condenser.

The use of reflux apparatus allows for extended boiling without evaporative loss of the reactants or products, which are often volatile liquids.

After an extended period of heating, the contents in the flask include the original alcohol, carboxylic acid, and sulfuric acid, as well as the ester and water. Reflux is usually followed by distillation to isolate the product(s).

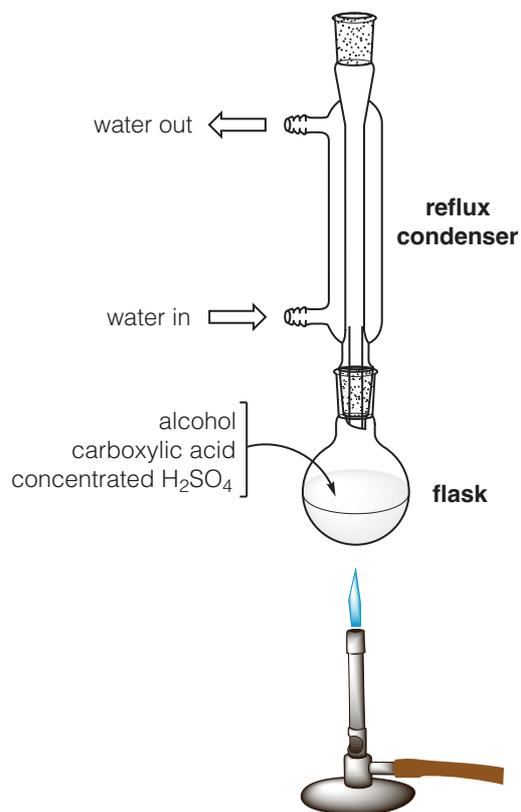
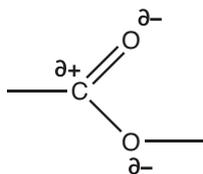


Figure 3.11: Reflux apparatus for esterification

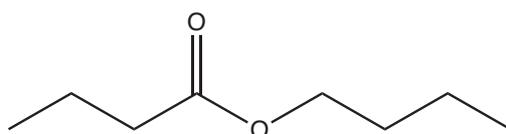
Physical properties of esters

Boiling point



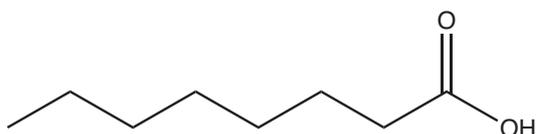
Esters have a polar functional group.

Unlike alcohols and carboxylic acids, ester molecules are unable to form hydrogen bonds between each other, instead experiencing dipole-dipole secondary interactions. This is because the carbon atom with a $\delta+$ charge is surrounded by other bulky atoms and cannot be accessed by $\delta-$ atoms in other molecules. The boiling points of esters are therefore significantly lower than carboxylic acids and alcohols with similar molar masses.



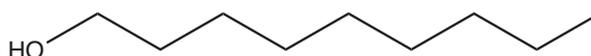
butyl butanoate

144.21 g/mol
boiling point: 77 °C



octanoic acid

144.21 g/mol
boiling point: 237 °C

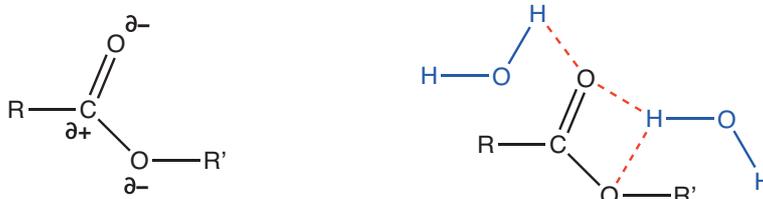


nonan-1-ol

144.26 g/mol
boiling point: 214 °C

Solubility in water

The ester functional group is polar. Hence, small esters are soluble in water as they can form hydrogen bonds with polar water molecules. However, solubility decreases with increasing carbon chain length, as the overall molecule becomes more non-polar.

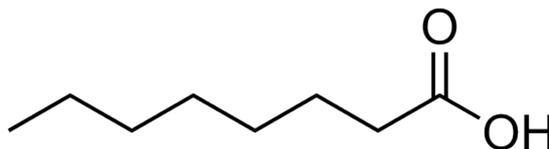


Ester	Solubility (g/L water)
ethyl methanoate	105
ethyl ethanoate	87
ethyl propanoate	17
ethyl butanoate	12
ethyl pentanoate	2

Table 3.08: Ester solubility

Questions

18. Caprylic acid is one of the acids found in coconut oil. It has some antibacterial properties and can be taken as a dietary supplement or used in cosmetics. Its structure is below.



- (a) State the systematic name of caprylic acid.
 (2 marks) KA4
- (b) Caprylic acid can be refluxed with ethanol in the presence of concentrated sulfuric acid. It produces a compound that has a pleasant apple flavour and odour.
- (i) Draw the structural formula of the new compound.
 (2 marks) KA4
- (ii) Write the systematic name of the new compound.
 (2 marks) KA4
- (iii) State the purpose of adding concentrated sulfuric acid to the reaction.
 (1 mark) KA1
- (iv) Explain why the contents of the flask are heated under reflux.
 ..
 ..
 ..
 ..
 (2 marks) KA1
- (v) Explain why ethanol is added in excess in the esterification reaction.
 ..
 ..
 ..
 ..
 ..
 ..
 ..
 ..
 (4 marks) KA1

Science understanding

Esters may be hydrolysed under acidic or alkaline conditions.

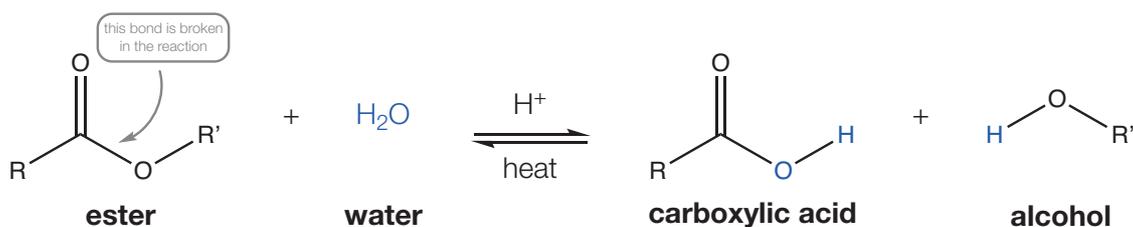
Identify the products of acidic or alkaline hydrolysis of an ester or polyester, given the appropriate structural formula.

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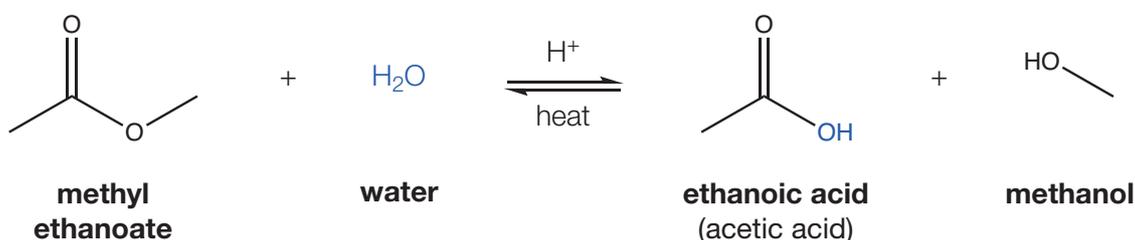
Hydrolysis is a reaction in which a chemical compound is broken down by water. Esters can be hydrolysed, but the process is very slow even in boiling water. Hydrolysis occurs more quickly when the ester is refluxed with a strong acid or alkali. The products of hydrolysis are different depending on the pH of the reaction.

Acidic hydrolysis

If an ester is refluxed with water using a strong acid catalyst, the original alcohol and carboxylic acid are reformed. Acidic hydrolysis is reversible.

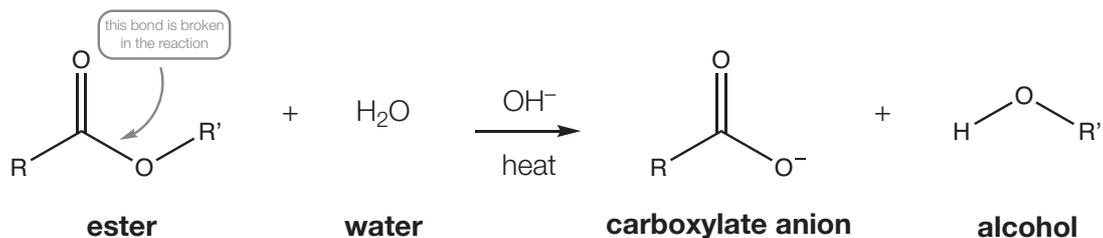


Example

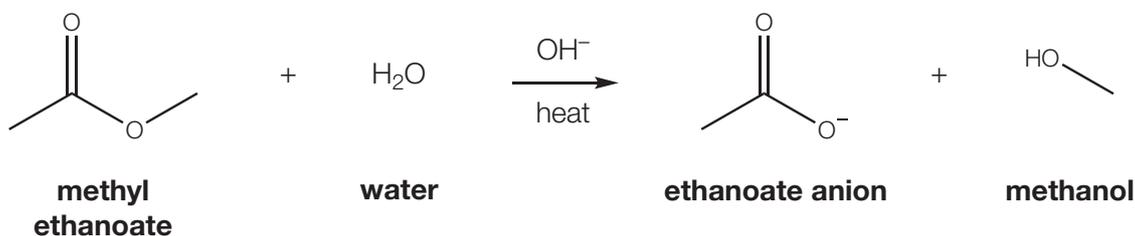


Alkaline hydrolysis

If an ester is refluxed with water using a strong alkali, such as NaOH, the original alcohol and carboxylate anion are formed. This method allows the carboxylate salt to be removed from the equilibrium reaction; due to this, the reaction is irreversible.

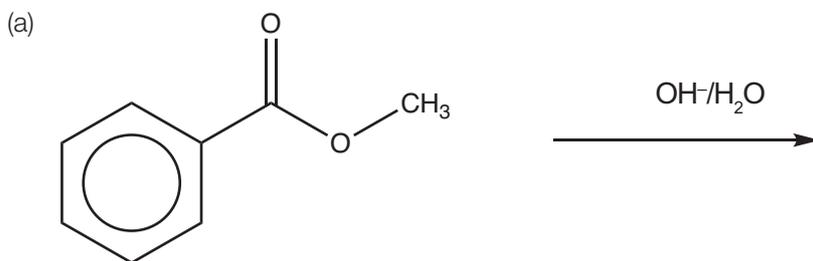


Example

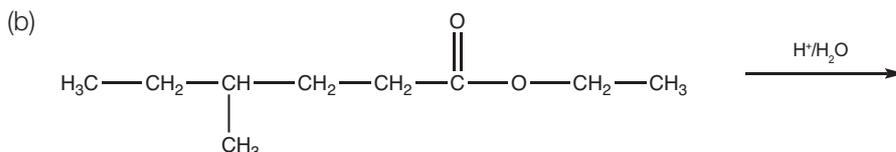


Questions

19. Complete the following ester hydrolysis reactions.



(4 marks) KA4

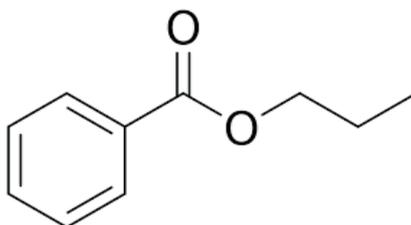


(4 marks) KA4

(i) Name the products in (b) systematically.

..... (2 marks) KA1

(c) The ester propyl benzoate is shown below.



Propyl benzoate

It can be hydrolysed with hot, concentrated sodium hydroxide solution.

(i) Draw the products below.

Carboxylate salt	Alcohol

(4 marks) KA4

(ii) Explain why the carboxylate salt is soluble in water while the original ester is not.

.....

 (3 marks) KA1

3.8 Amides

Science understanding

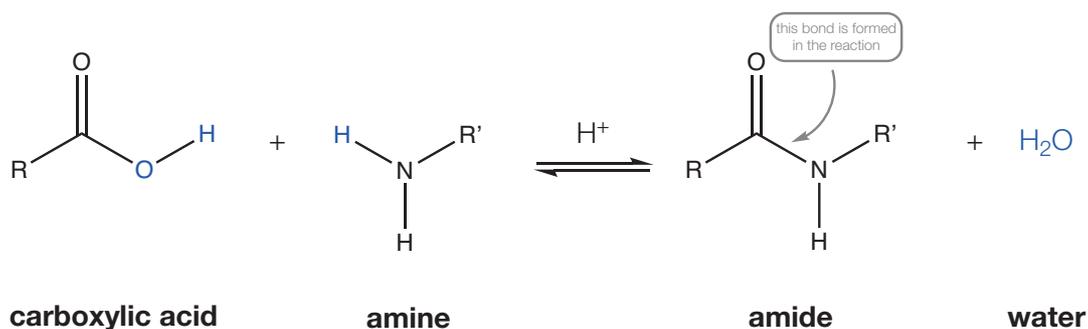
Carboxylic acids undergo condensation reactions with amines to form amides.

Draw the structural formula of the amide formed from a carboxylic acid and an amine, given their structural formulae or vice versa.

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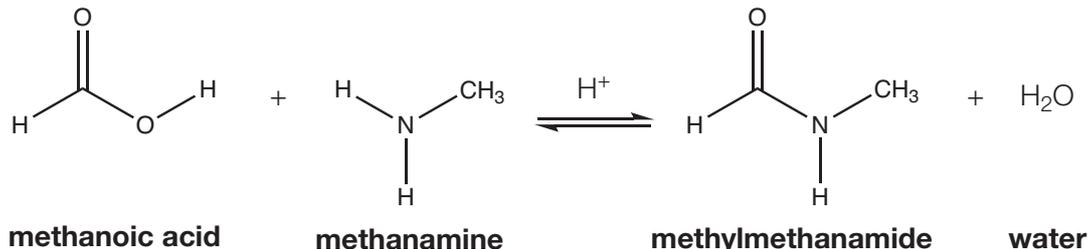
An amide is an organic compound formed by the condensation reaction between a carboxylic acid and an amine. The name of the functional group is also **amide**.

Example

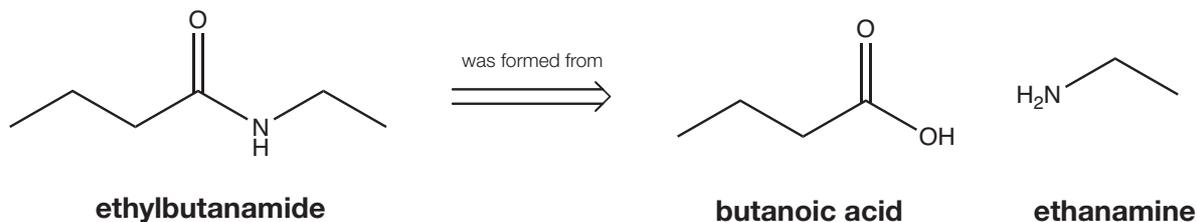


Example

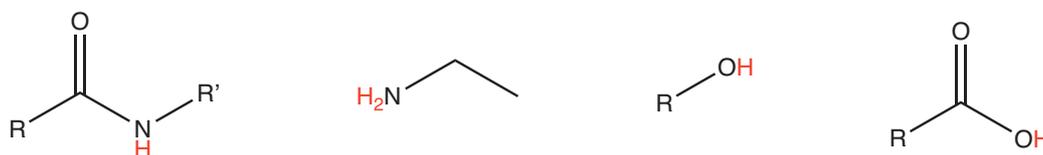
Methanoic acid reacts with methanamine to produce an amide and water.



The structural formula of the original carboxylic acid and amine can be determined from the amide.



When using skeletal formulas, only hydrogens bonded to carbon can be omitted. The hydrogen atom covalently bonded to the nitrogen within the amide functional group must always be drawn (similar to the hydrogen atom in hydroxyl groups).



Hydrogens that are not bonded to carbon are always drawn.

The naming of amides is not required for SACE Stage 2 Chemistry.

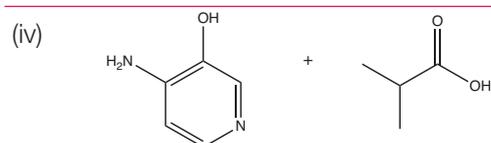
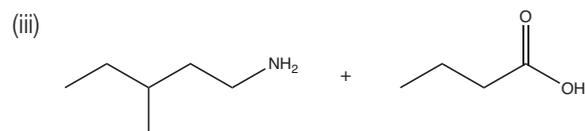
Questions

20. Amides are found in natural substances, from black pepper and caffeine to penicillin and anandamide found in chocolate.

(a) Draw the structural formulae for the amides that can be prepared from the following reagents:

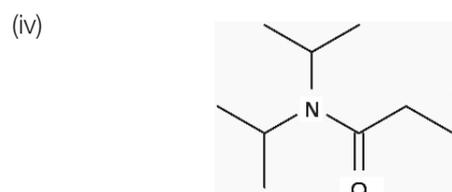
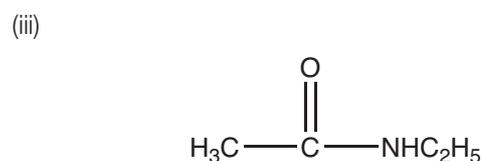
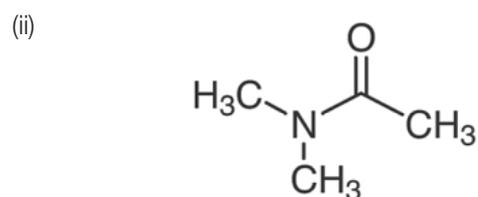
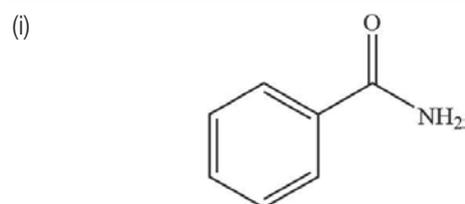
(i) Butan-1-amine and propanoic acid

(ii) Pentanoic acid and propan-2-amine



(8 marks) KA4

(b) Draw the structural formulae of the carboxylic acids and amines that react to form the amides below:



(8 marks) KA4

Primary, secondary, and tertiary amides

Amides are classified as primary (1°), secondary (2°), or tertiary (3°) based on how many carbon atoms are directly bonded to the nitrogen atom.

			Examples
Primary (1°) amide		One carbon covalently bonded to the nitrogen atom.	
Secondary (2°) amide		Two carbons directly covalently bonded to the nitrogen atom.	
Tertiary (3°) amide		Three carbons directly covalently bonded to the nitrogen atom.	

Table 3.09: Amide classification

Questions

21. Identify the following amides as primary, secondary, or tertiary.

(i).....	(ii).....	(iii).....
(iv).....	(v).....	

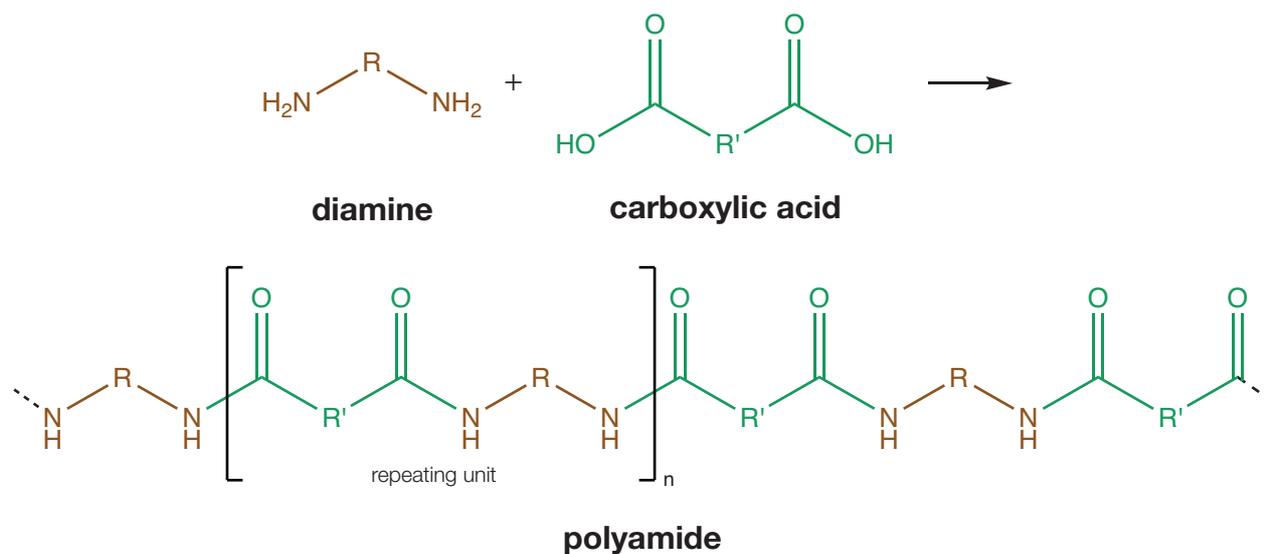
(5 marks) KA1

Science understanding

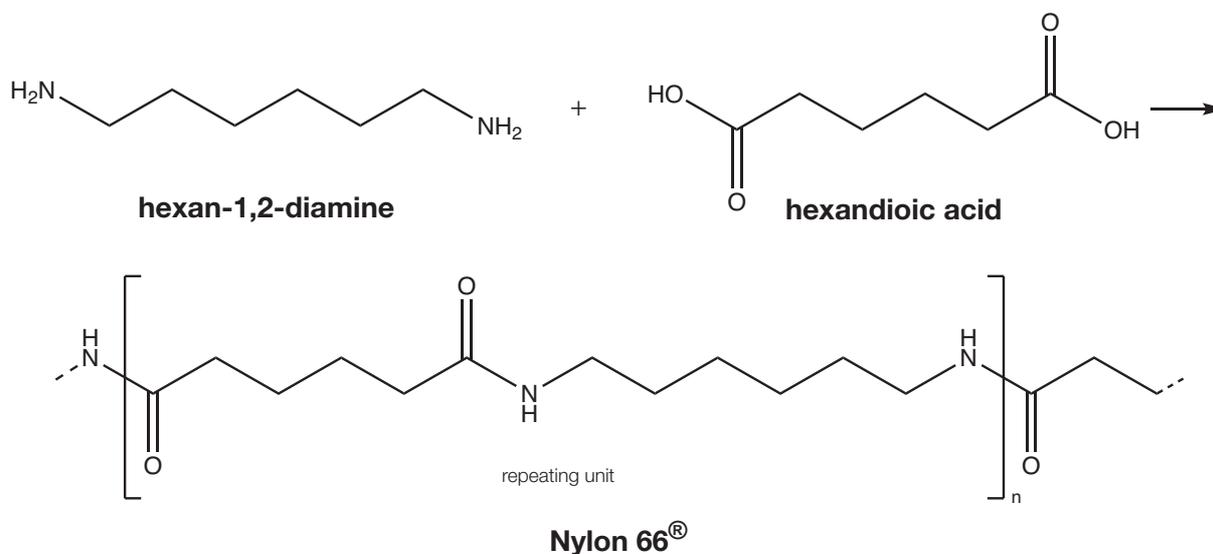
Draw the structural formula of a polyamide, given the structural formula(e) of the monomer(s) or vice versa.

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Polyamides are polymers formed in the condensation reaction between a dicarboxylic acid and a diamine.

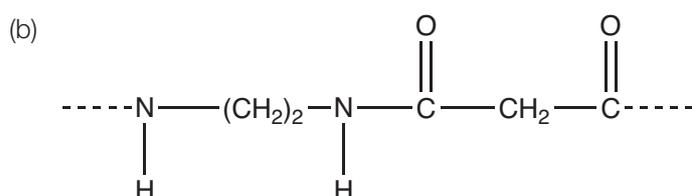
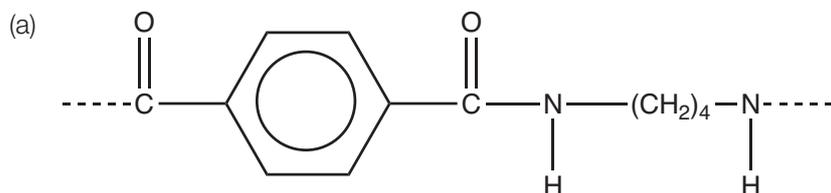


Nylon 66 is a polyamide used in fibres for textiles and carpets. It is formed from the reaction between hexan-1,6-diamine and hexandioic acid.



Questions

23. For the following polymers, draw the structural formula of the monomers.



(8 marks) KA4

(c) Draw the structural formula of the polyamides that are formed in the reactions below.

(i) Ethanediamine and propanedioic acid

(ii) Decanedioic acid and butane-1,4-diamine

(4 marks) KA4

Science understanding

Amides may be hydrolysed under acidic or alkaline conditions.

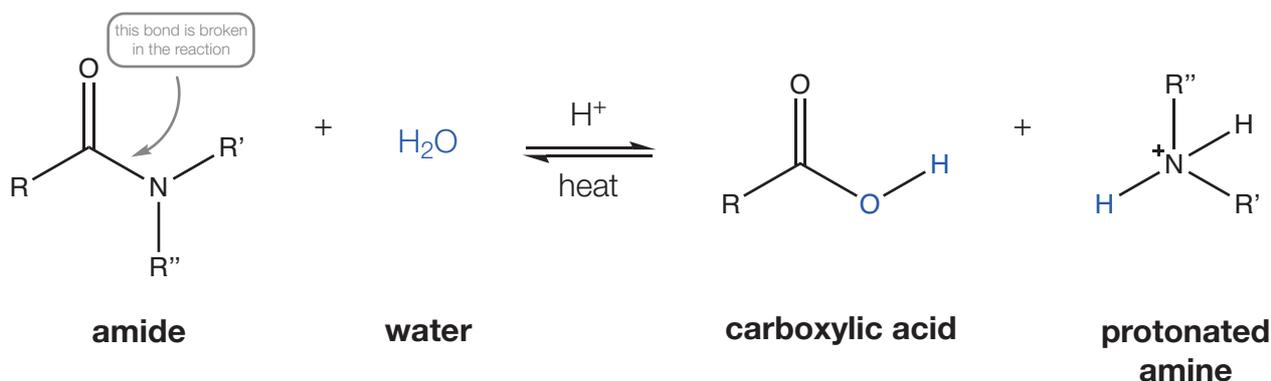
Identify the products of acidic or alkaline hydrolysis of an amide or polyamide, given the appropriate structural formula.

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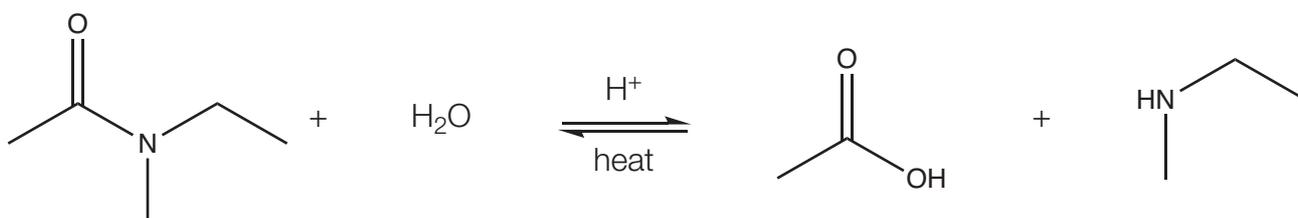
Amides can undergo hydrolysis in acidic or alkaline conditions. They require more vigorous conditions for hydrolysis than esters. The products of hydrolysis are different, depending on the pH of the reaction. Amide hydrolysis is a common reaction in biological systems; it is the initial step in the digestion of protein.

Acidic hydrolysis

If an amide is refluxed with water using a hot, aqueous acid, the products are the original carboxylic acid and a **protonated amine**. This reaction is reversible.

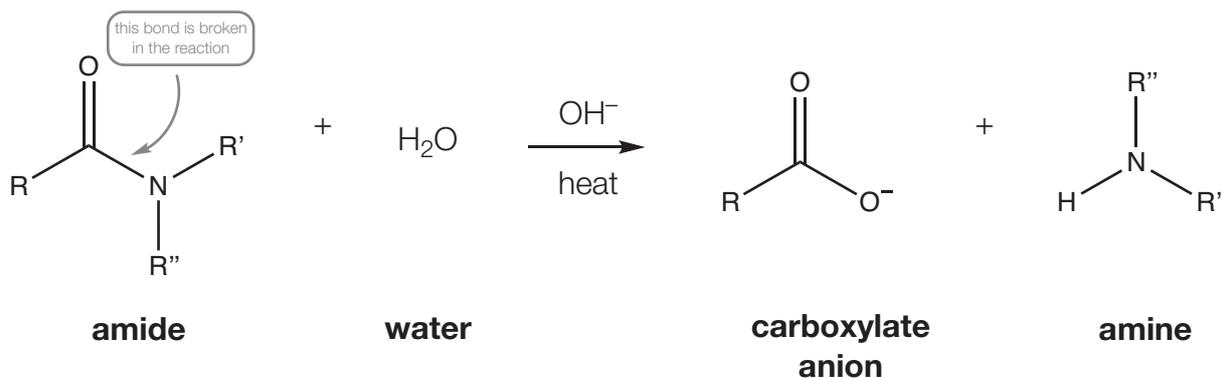


Example

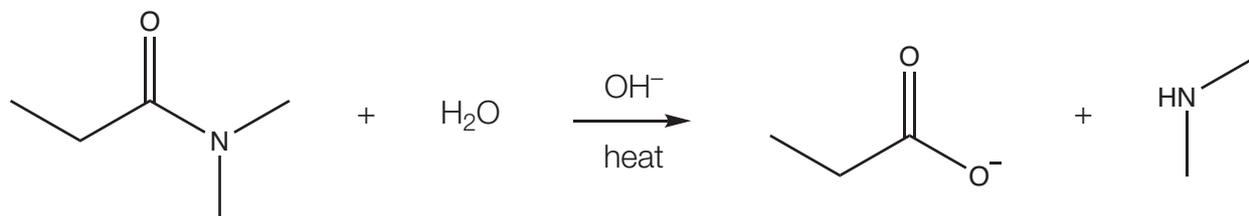


Alkaline hydrolysis

When an amide is refluxed with water using a strong base, such as NaOH, the products are a **carboxylate anion** and an amine. This hydrolysis reaction is driven to completion as the carboxylate anion forms a salt with the spectator cation from the catalytic base.

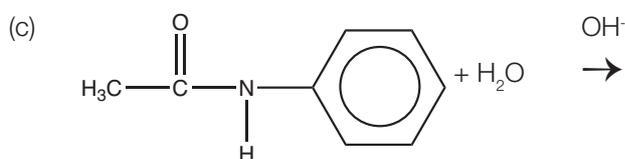
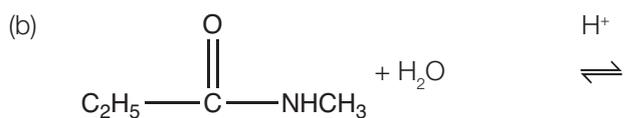
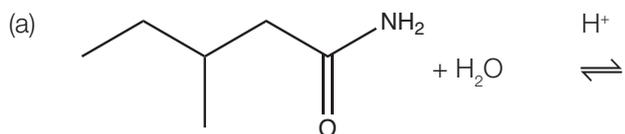


Example



Questions

24. Draw the structural formulae of the products of the following amide hydrolysis reactions.



(12 marks) KA4

3

3.9 Triglycerides

Science understanding

Edible oils and fats are esters of propan-1,2,3-triol (glycerol) and various carboxylic acids.

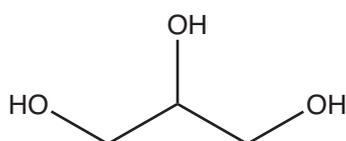
Draw the structural formula of an edible oil or fat, given the structural formula(e) of the carboxylic acid(s) from which it is derived.

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Fats and oils, like those that come from animal fats, fish oils, and vegetable oils, are naturally occurring esters. The esters are made from one molecule of propan-1,2,3-triol, called **glycerol**, and three long-chain carboxylic acids, called **fatty acids**.

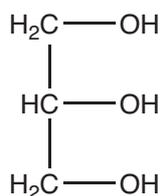
Glycerol

Glycerol is the common name for propan-1,2,3-triol, a small molecule with three hydroxyl groups.



glycerol
(propan-1,2,3-triol)

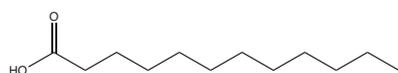
Because there are three hydroxyl groups in the glycerol molecule, three fatty acid molecules can be covalently bonded to one glycerol molecule. Glycerol is often drawn in such a way that the long-chain fatty acids can be conveniently drawn to the right.



glycerol
(propan-1,2,3-triol)

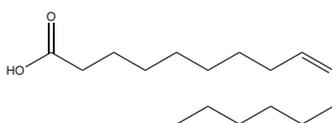
Fatty acids

Fatty acids are long-chain carboxylic acid molecules found in fats. The chains are unbranched and usually contain an even number of carbon atoms in the range 12–22. The chains can be **saturated** (only single bonds between carbon atoms) or **unsaturated** (at least one double or triple bond between carbon atoms). Unsaturated fatty acids with one double or triple bond are called **monounsaturated**. Unsaturated fatty acids with more than one double or triple bond are called **polyunsaturated**.



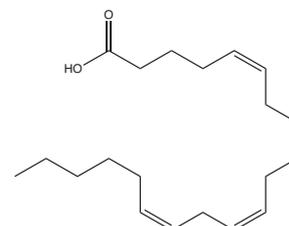
lauric acid
(dodecanoic acid)

a saturated fatty acid



palmitoleic acid
(hexadec-9-enoic acid)

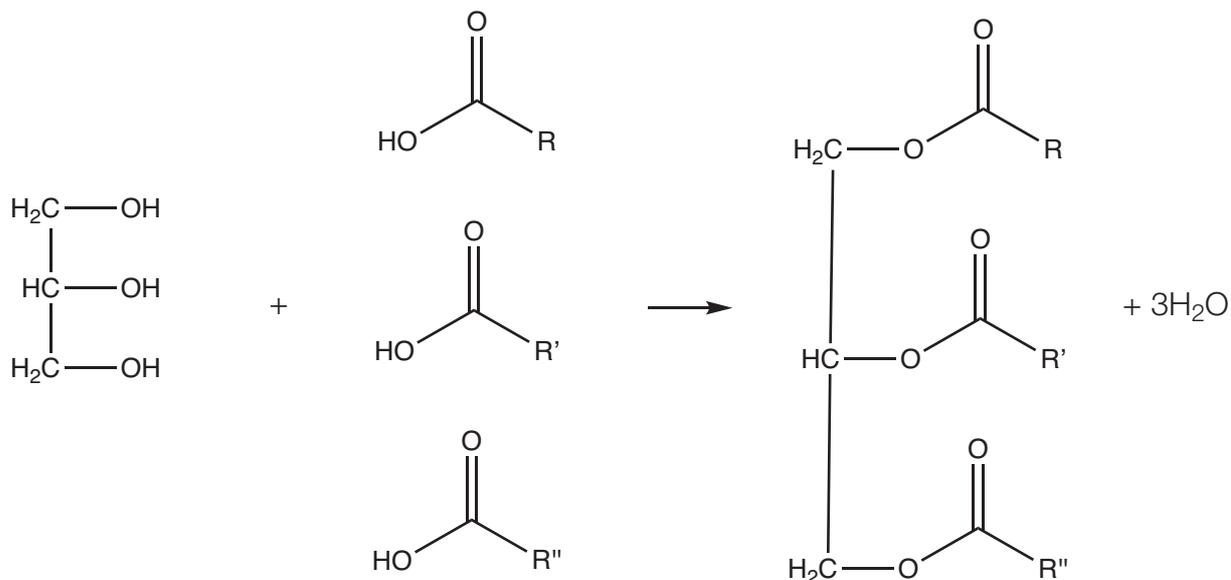
a monounsaturated fatty acid



arachidonic acid
(icosa-5,8,11,14-tetraenoic acid)

an polyunsaturated fatty acid

One molecule of glycerol reacts with three fatty acids to form a compound with three ester groups. Hence, these fats and oils are called **triesters** or **triglycerides**. As with any reaction involving an alcohol and a carboxylic acid, one molecule of water is produced for every ester group formed. For a triglyceride, three molecules of water are produced. The three fatty acids in the triglyceride are not necessarily the same.



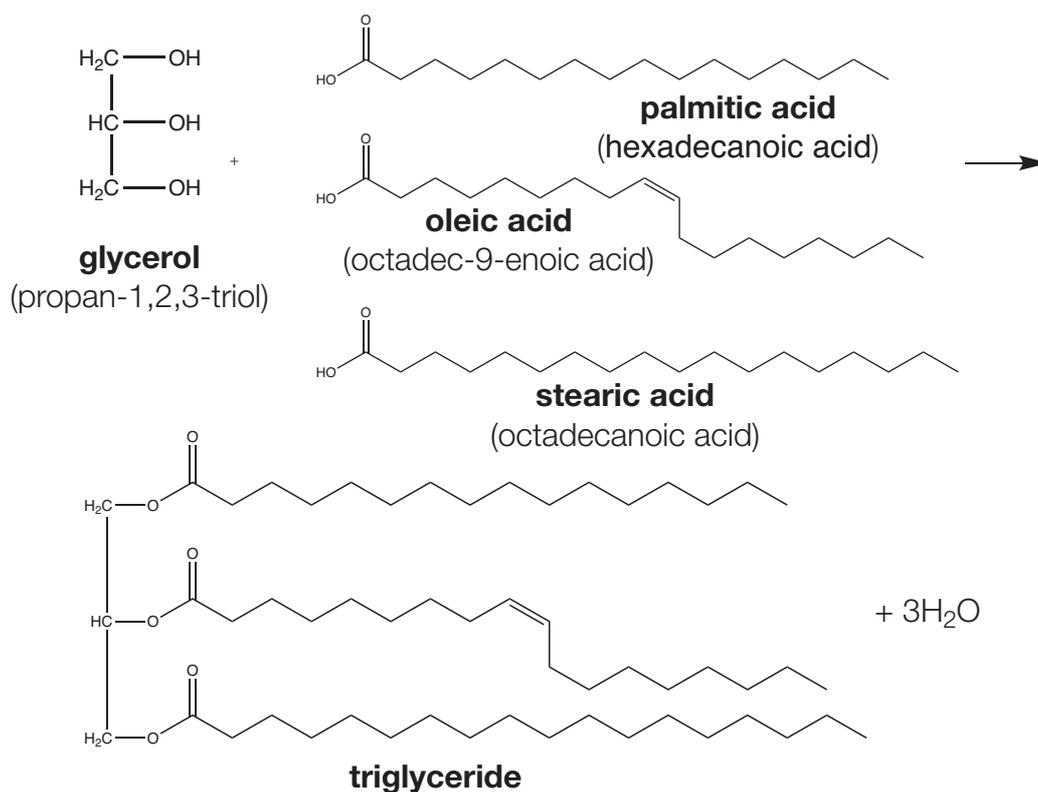
glycerol
(propan-1,2,3-triol)

three fatty acids

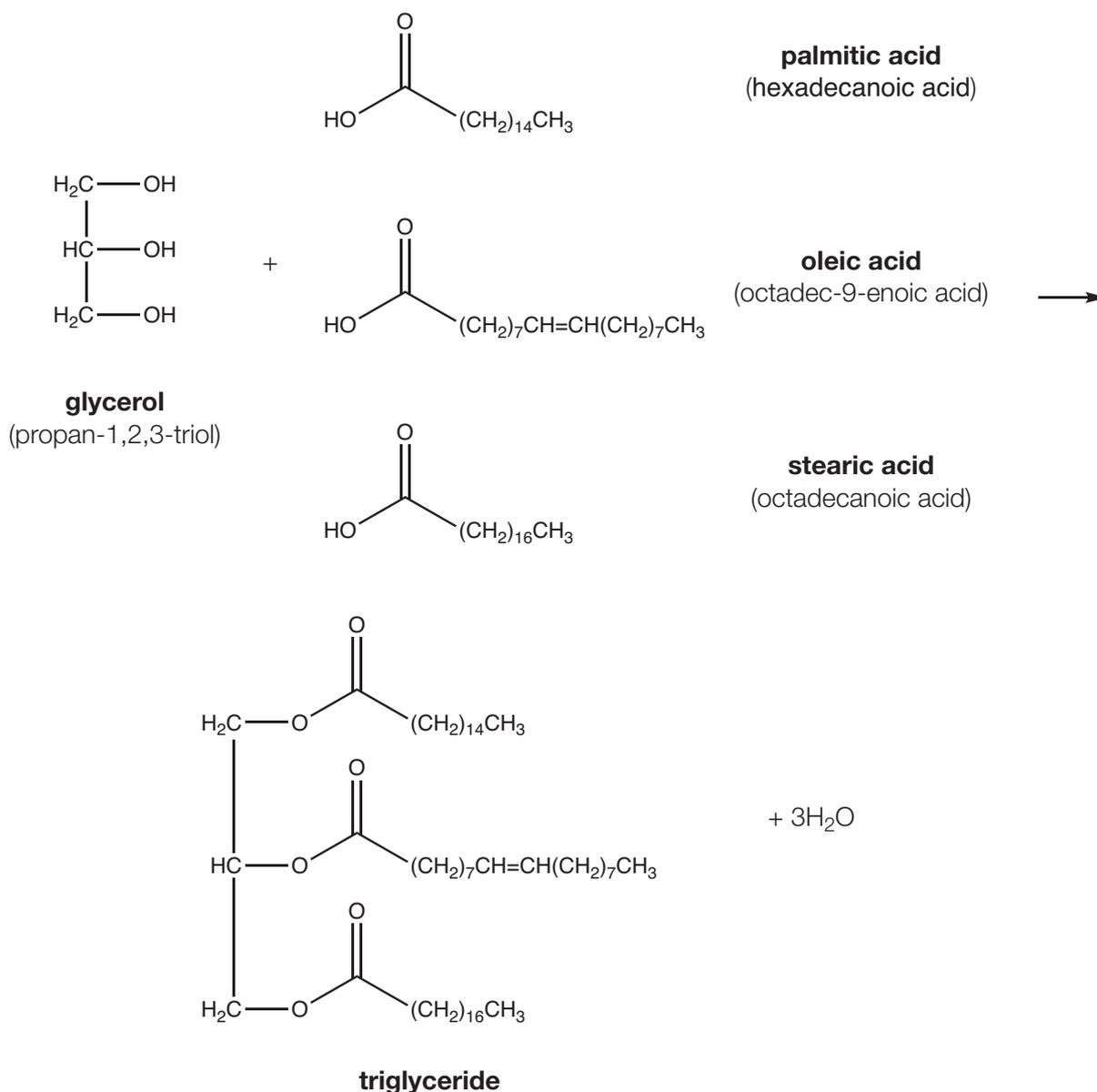
triglyceride

water

Palmitic acid, oleic acid, and stearic acid are the three most abundant fatty acids in the biological world. When one molecule of glycerol reacts with these three fatty acids, the following triglyceride is formed.



Triglycerides can also be represented using condensed structural formula, with CH=CH representing a double bond in the fatty acid molecule. The reaction above can be written as:



Science as a human endeavour

Protesting whaling with butter?

Butter is a solid triglyceride, which must be refrigerated to ensure its safe consumption. If correct storage conditions are not maintained the butter can become “rancid”. Chemically rancidity is the process by which the triglyceride hydrolyses and releases butanoic acid. Butanoic acid is the putrid smell that is present in both vomit and body odour.

In pursuit of Japanese whaling ships between 2005 and 2010, anti-whaling activists threw rancid butter onto the decks of the whaling ships (Figure 3.12).

These objects were deemed “butter bombs”, though activists claimed they were merely throwing harmless food material at the manned whaling ships.



Figure 3.12: “Butter bombs” thrown by activists onto the deck of a whaling ship.

Questions

25. Animal fat contains a high proportion of stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$. Draw the structural formula of the triglyceride formed from glycerol and three stearic acid molecules.

(2 marks) KA4

26. Draw the triglyceride formed from the three fatty acids below



(2 marks) KA4

Science understanding

Triglycerides can be hydrolysed to produce propan-1,2,3-triol and various carboxylic acids.

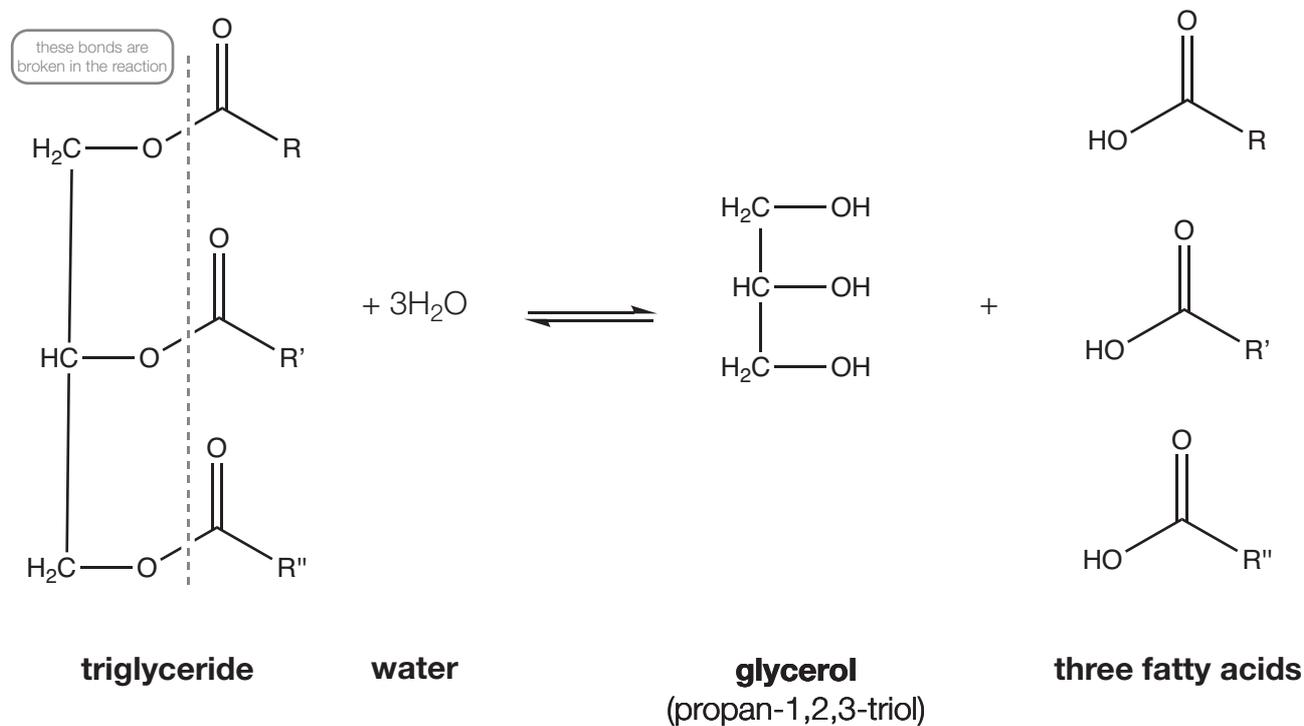
Identify and draw the structural formulae of the alcohol and acid(s) from which a triglyceride is derived, given its structural formula.

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Like other esters, triglycerides can undergo hydrolysis in acidic or alkaline conditions to recover the reactants of the condensation reaction. Hydrolysis of triglycerides occurs inside the cells of living organisms. It is catalysed by the enzyme **lipase** (triglycerides are **lipids**), which is found in saliva and digestive secretions.

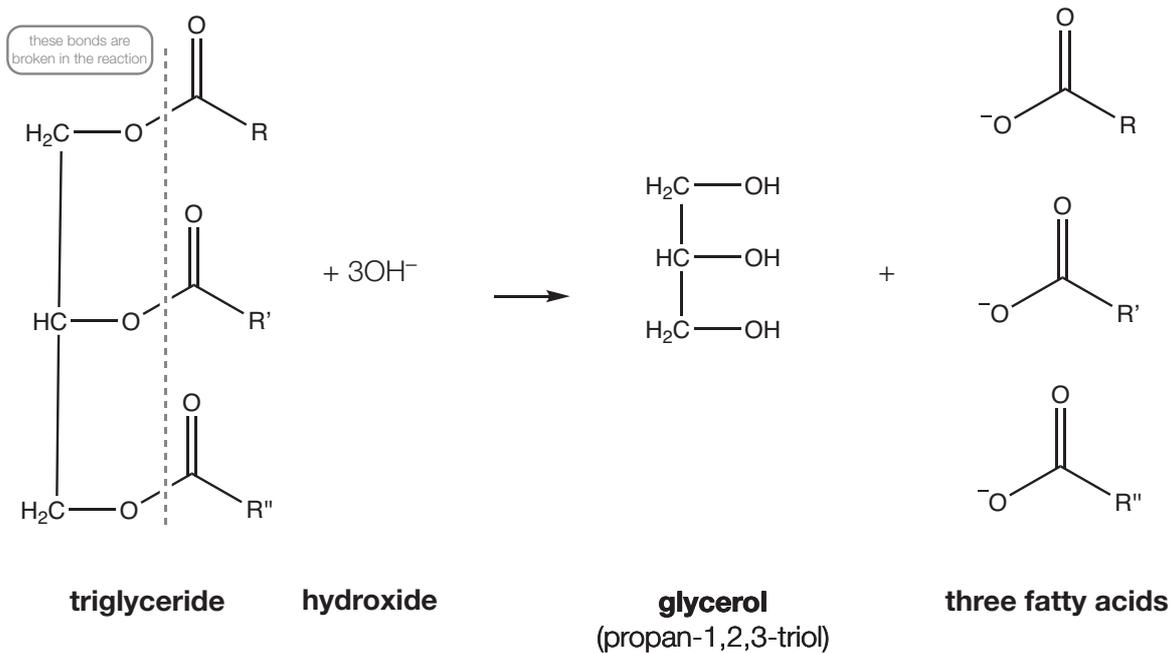
Acidic hydrolysis

In an acidic solution, triglycerides are hydrolysed to produce glycerol and free fatty acids. This process is reversible.



Alkaline hydrolysis

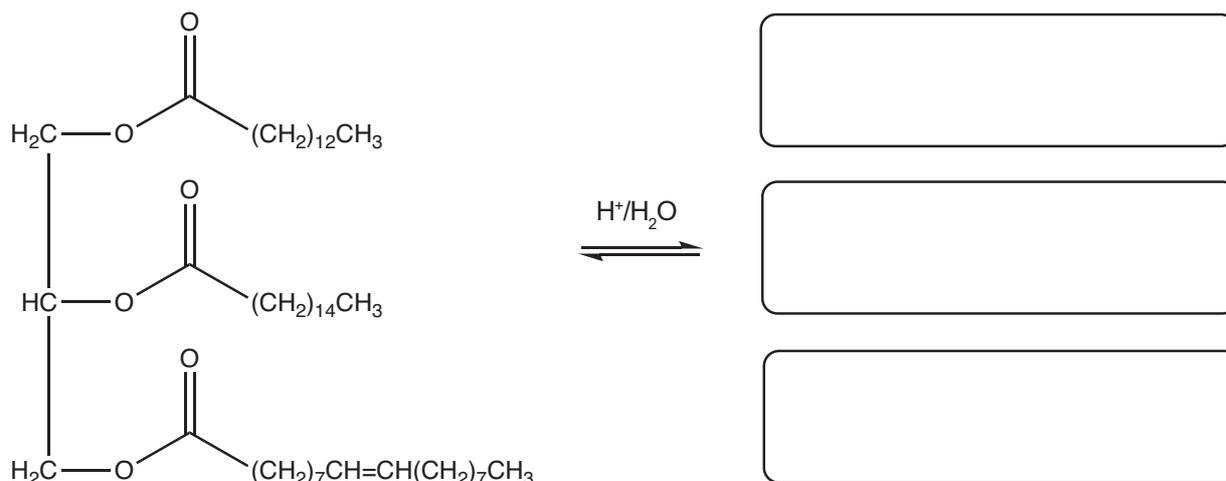
In an alkaline solution, triglycerides hydrolyse to produce glycerol and the carboxylate anions. Alkaline hydrolysis is not reversible, so the reaction is driven to completion.



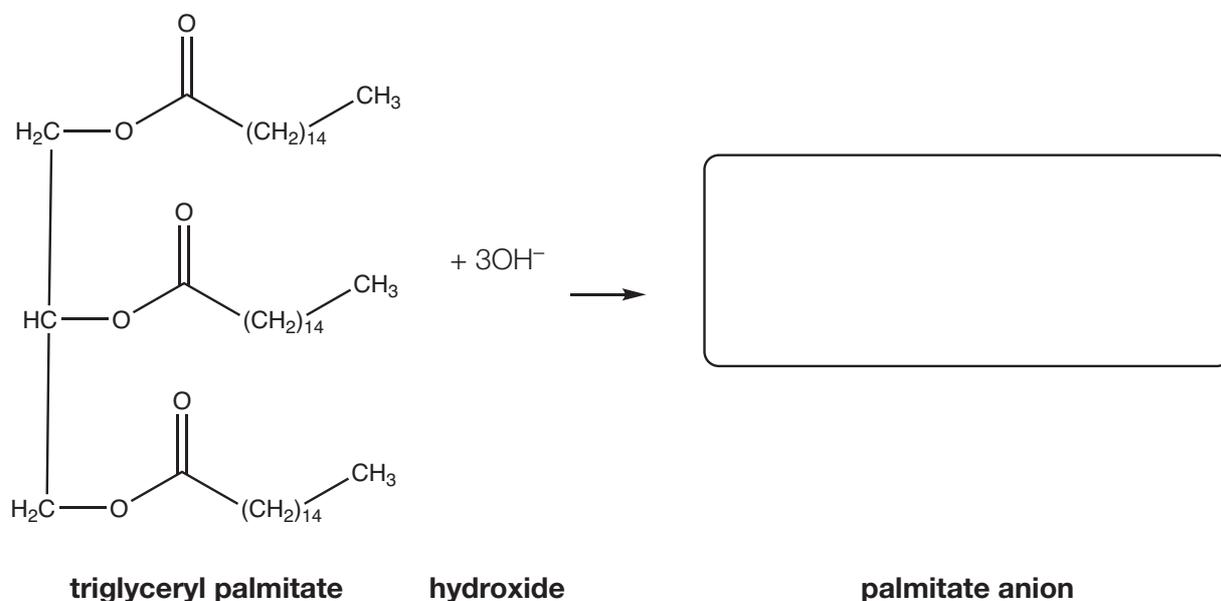
Questions

27. Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

- (a) Draw the structural formula of the three fatty acids formed from the acidic hydrolysis of the following triglyceride:



- (b) The triglyceride glyceryl tripalmitate can undergo alkaline hydrolysis to form the palmitate anion. Draw the structural formula of the palmitate anion.



Science understanding

Triglycerides may be saturated or unsaturated.

Describe and explain the use of a solution of bromine or iodine to determine the degree of unsaturation of a compound. Draw the structural formula of the reaction product.

Explain how the degree of unsaturation causes differences in the melting points of edible oils and fats.

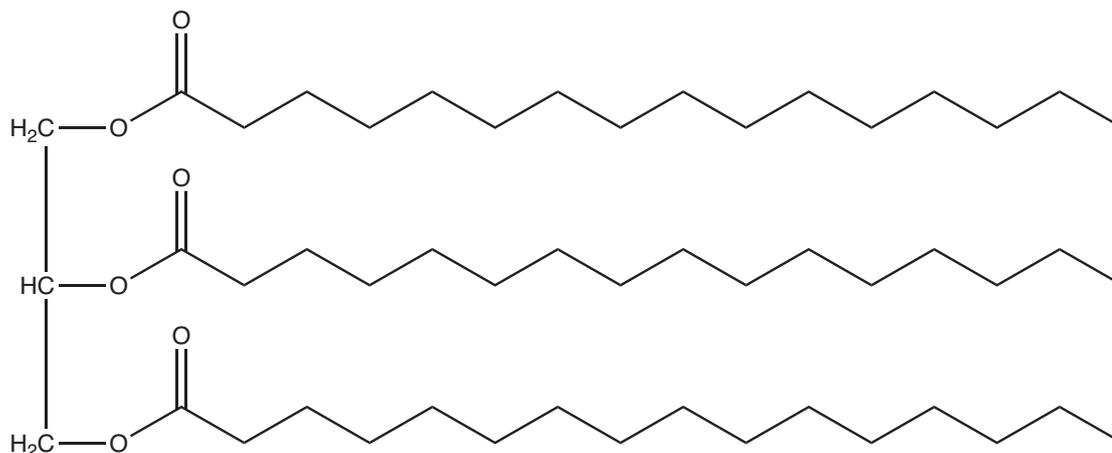
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Physical properties

The melting point of triglycerides is related to the saturated and unsaturated fatty acid components within the molecule, and the strength of the intermolecular forces.

Saturated Triglycerides

In a saturated triglyceride, the geometry around the carbon atoms in the fatty acid chain is tetrahedral. As such, the hydrocarbon chains lie parallel to each other, stacking neatly, and giving the molecule an ordered shape. This increases the strength of the intermolecular dispersion forces between the chains and thus the lattice structure of the solid is formed.

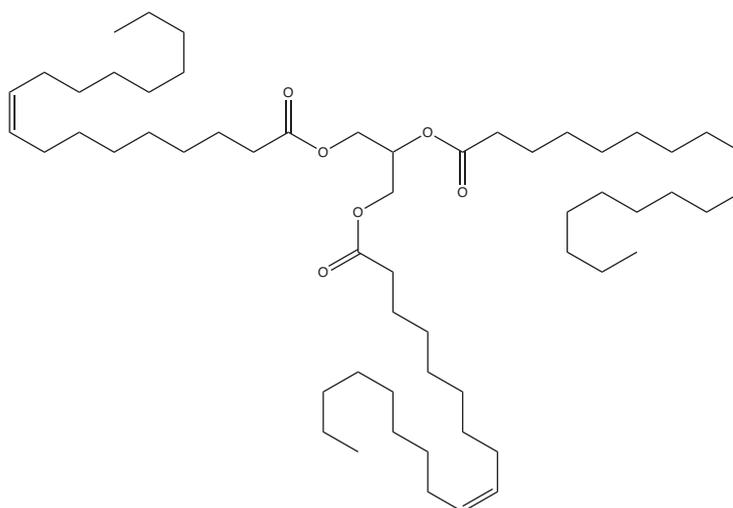


tripalmitin
saturated triglyceride

melting point: 66 °C

Unsaturated Triglycerides

In an unsaturated triglyceride, the geometry around the carbon atoms in the fatty acid chain is a combination of tetrahedral and trigonal planar. The double bonds force the carbon chains to twist at certain points. As such, the hydrocarbon chains have a less-ordered structure and do not stack as neatly or compactly together. The intermolecular dispersion forces are weaker, and thus unsaturated triglycerides have lower melting points and are usually liquids at room temperature.



triolein
unsaturated triglyceride

melting point: 5 °C

Triglycerides rich in saturated fatty acids are generally solids at room temperature and are called **fats**, while those rich in unsaturated fatty acids are liquids at room temperature and are called **oils**. Other than their state at room temperature, fats and oils are chemically indistinguishable (chemists use the word **triglycerides** to include both groups).

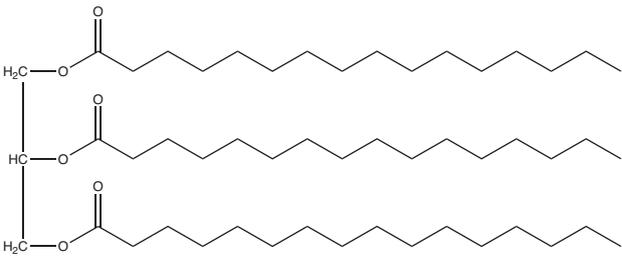
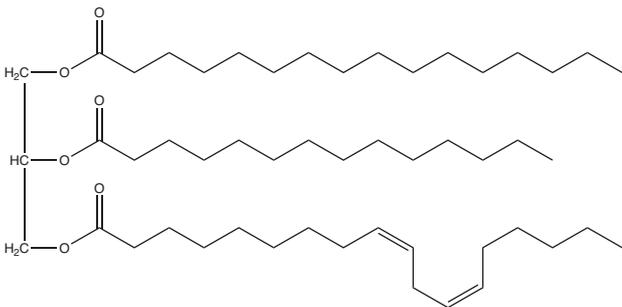
Edible fats	Edible oils
Solids at room temperature (25°C).	Liquids at room temperature (25°C).
Triglyceride molecules contain mainly saturated fatty acid substituents.	Triglyceride molecules contain one or more unsaturated fatty acid substituents.
Generally derived from land animals.	Generally derived from plants.
Fats of land animals usually contain 40-50% saturated fatty acids.	Most plant oils contain 80% or more unsaturated fatty acids.
	

Table 3.10: Properties of edible fats and oils

Table 3.11 shows the percentage of saturated and unsaturated fatty acid content of triglyceride of common fats and oils.

Derived from	Fat or oil	Saturated fatty acids (% of total fat)	Unsaturated fatty acids (% of total fat)
Animals	Beef fat	52	48
	Butter fat	66	34
Plants	Olive oil	15	85
	Sunflower oil	10	90

Table 3.11 - percentage of saturated and unsaturated fatty acid content of triglyceride of common fats and oils.

Degree of unsaturation

The general formula for a *saturated* fatty acid is $C_nH_{2n}COOH$. Given the formula of any fatty acid, this general formula can be used to determine whether it is saturated or unsaturated.

Example

Linoleic acid has the formula $C_{18}H_{32}COOH$.

If saturated, the acid would fit the formula $C_{18}H_{(2 \times 18)}COOH$, which is $C_{18}H_{36}COOH$. The acid is therefore *unsaturated*.

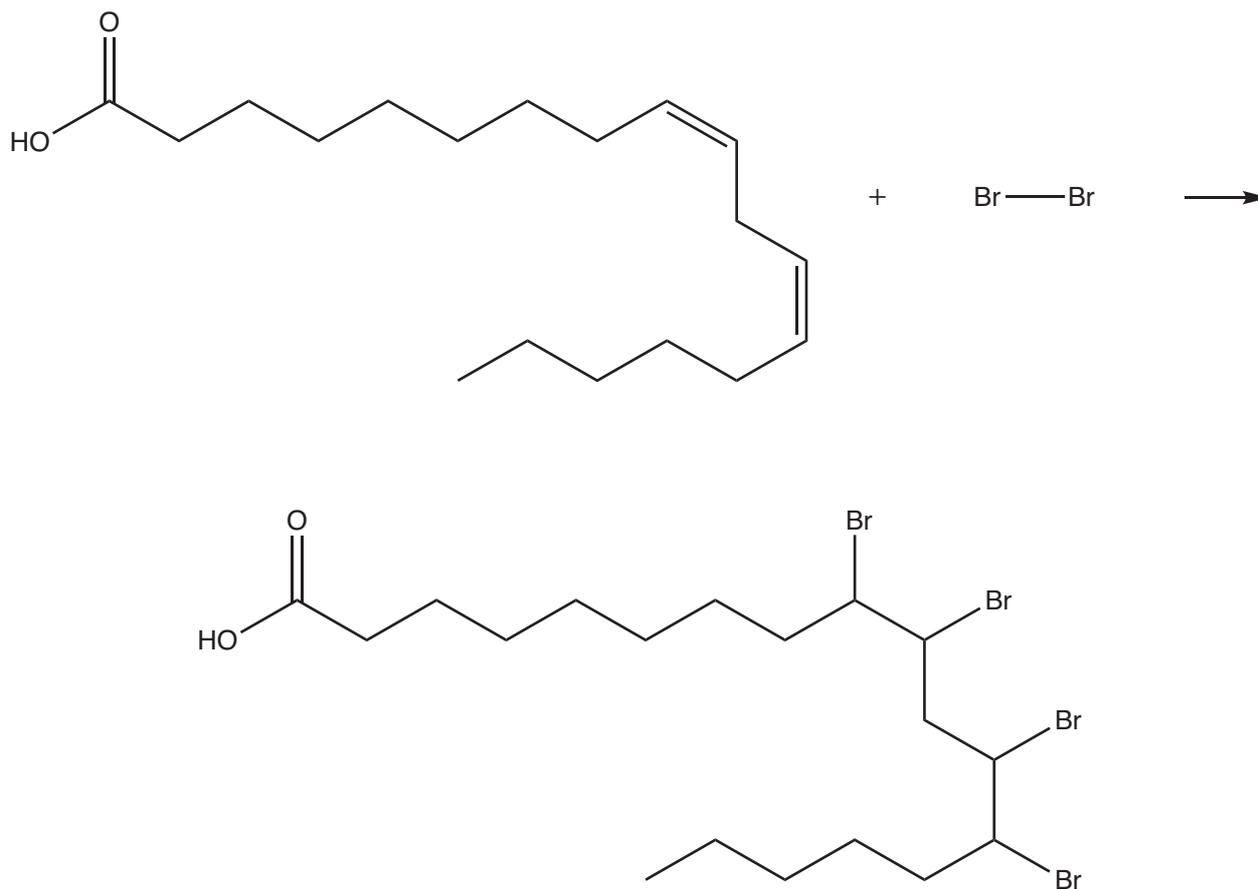
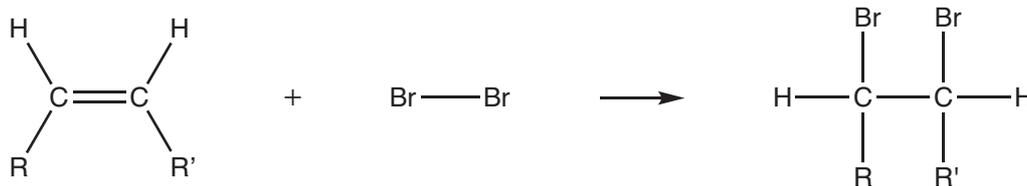
To determine how many double bonds it contains, calculate how many hydrogens are missing.

$$36 - 32 = 4$$

Linoleic acid has four fewer hydrogens than the corresponding saturated fatty acid. Each double bond displaces two hydrogens, one from each carbon in the bond, so linoleic acid has two double bonds.

Bromine / Iodine number

Alkenes are unsaturated and contain the C=C functional group. They undergo addition reactions with small diatomic halogen molecules such as bromine (Br₂) or iodine (I₂). Unsaturated fatty acids and triglycerides contain the C=C functional group and will also undergo this addition reaction.



The mass of bromine or iodine that reacts with exactly 100 g of the compound is called the **bromine number** or **iodine number**.

Example

Determining Iodine Number

Linoleic acid has an M_r of 280.5 gmol^{-1} and the formula $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ (or $\text{C}_{18}\text{H}_{32}\text{O}_2$).

One mole of linoleic acid has two double bonds; therefore, 2 mol of iodine will react.

$$\begin{aligned} M_r(\text{I}_2) &= 253.8 \text{ gmol}^{-1} \\ \text{mass}(\text{I}_2) &= n \times M_r \\ &= 2 \text{ mol} \times 253.8 \text{ gmol}^{-1} \\ &= 507.6 \text{ g} \end{aligned}$$

The mass of 1 mol of iodine is 507.6 g.

$$\begin{aligned} \text{mass}(\text{linoleic acid}) &= n \times M_r \\ &= 1 \text{ mol} \times 280.5 \text{ gmol}^{-1} \\ &= 280.5 \text{ g} \end{aligned}$$

The mass of 2 mol of linoleic acid is 280.5 g.

If 507.6 g of iodine reacts with 280.5 g linoleic acid, and x grams of iodine reacts with 100 g linoleic acid, then:

$$\begin{aligned} \frac{x}{507.6} &= \frac{100}{281} \\ x &= \frac{100}{281} \times 507.6 \\ x &= 180.6 \text{ g} \end{aligned}$$

Therefore, the iodine number of linoleic acid is 181.

Example

Determining Number of Double Bonds

2.8 g of linoleic acid will react with 5.0 g of I_2 .

1 mol of I_2 reacts with 1 mol of double bonds.

$$\begin{aligned} n(\text{I}_2) &= \frac{m}{M_r} = \frac{5.0 \text{ g}}{(2 \times 126.9) \text{ g/mol}} \\ &= 0.020 \text{ mol} \end{aligned}$$

5.0 g of I_2 is 0.020 moles.

$$\begin{aligned} n(\text{linoleic acid}) &= \frac{m}{M_r} = \frac{2.8 \text{ g}}{((18 \times 12.01) + (30 \times 1.01) + (2 \times 16.00)) \text{ g/mol}} \\ &= 0.010 \text{ mol} \end{aligned}$$

2.8 g of linoleic acid is 0.010 moles.

If 0.020 mol of iodine reacts with 0.010 mol of linoleic acid, and x mol of iodine reacts with 1 mol of linoleic acid, then

$$\begin{aligned} \frac{x}{1} &= \frac{0.020}{0.010} \\ x &= \frac{0.020}{0.010} \times 1 \\ x &= 2 \text{ mol} \end{aligned}$$

2 moles of iodine are needed for every 1 mole of linoleic acid. Therefore, linoleic acid has 2 carbon-carbon double bonds.

Questions

28. Ricinoleic acid has a molar mass of $298.46 \text{ g mol}^{-1}$ and an iodine number of 85. Determine the number of double bonds in ricinoleic acid.

(3 marks) KA4

Science understanding

Liquid triglycerides can be converted into triglycerides of higher melting point.

Explain the role of pressure, temperature, and a catalyst in the hydrogenation of liquid triglycerides to form triglycerides of higher melting point.

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Liquid oil triglycerides can be converted to solid fats by a process called **hydrogenation**, where hydrogen is added across C=C double bonds.



Science as a human endeavour

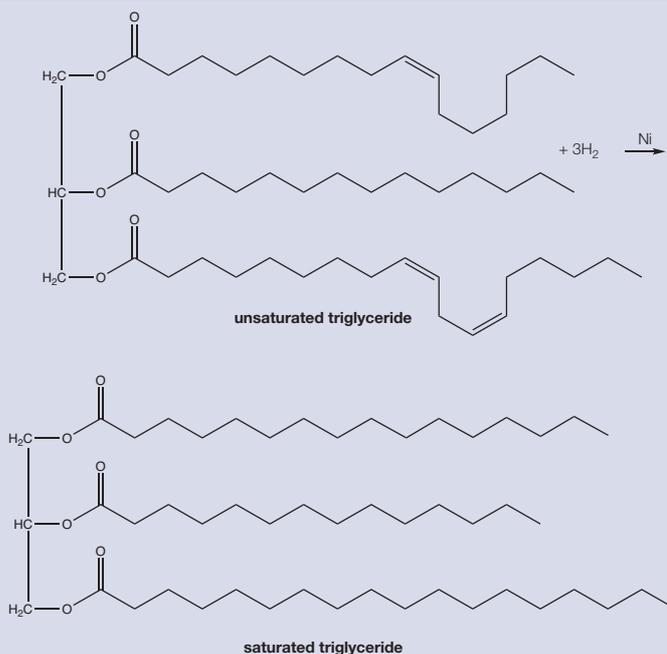
Hydrogenation

In 1869, when fats and oils were scarce in Western Europe, French chemist Hippolyte Mège-Mouriès invented margarine from animal fats. He won a prize from Emperor Napoleon III for “a satisfactory butter substitute”. Today, margarine is prepared from vegetable oils including corn, soy, and sunflower, using the hydrogenation process. The vegetable oil is heated to a high temperature with hydrogen gas under pressure in the presence of a nickel catalyst.

The hydrogens add across the double bonds to increase the degree of saturation, changing the C=C double bonds to C-C single bonds. This changes the geometry around the carbon atoms from trigonal planar to tetrahedral, allowing the chains to stack more neatly and form a product that is solid at room temperature.

The use of high temperature, high pressure, and a powdered catalyst such as nickel are all required to increase the rate of reaction.

- The catalyst provides an alternate pathway where the activation energy is lower. It is in a powdered form to increase the surface area.
- Increasing the temperature increases the kinetic energy of the particles, so more particles will have energy greater than or equal to activation energy. This leads to more successful collisions per unit time.
- Increasing the pressure increases the concentration of the gaseous hydrogen. There is less space for the particles to occupy and an increased total number of particle collisions per unit time.



(d) List the reagent required to convert flaxseed oil into margarine.

..... (1 mark) KA1

(e) List three reaction conditions required to convert flaxseed oil into margarine.

.....

 (3 marks) KA1

(f) Describe the difference in physical properties between flaxseed oil and margarine.

..... (1 mark) KA1

(g) Explain why margarine has a higher melting point than the oils from which it is prepared.

.....

 (4 marks) KA1

Science understanding

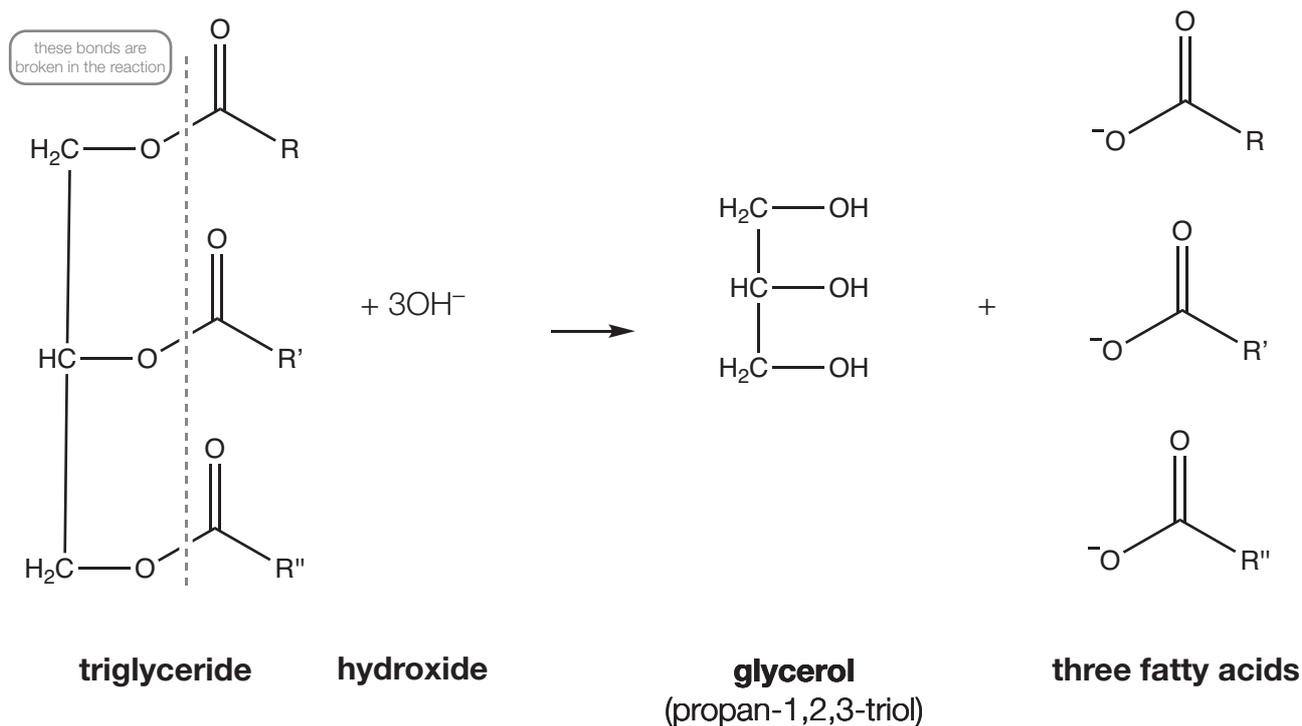
Alkaline hydrolysis of triglycerides produces carboxylate ions, which have both hydrophilic and hydrophobic regions.

Explain how such particles form micelles in solutions.

Explain how micelles can dissolve and move non-polar substances through an aqueous medium or vice versa.

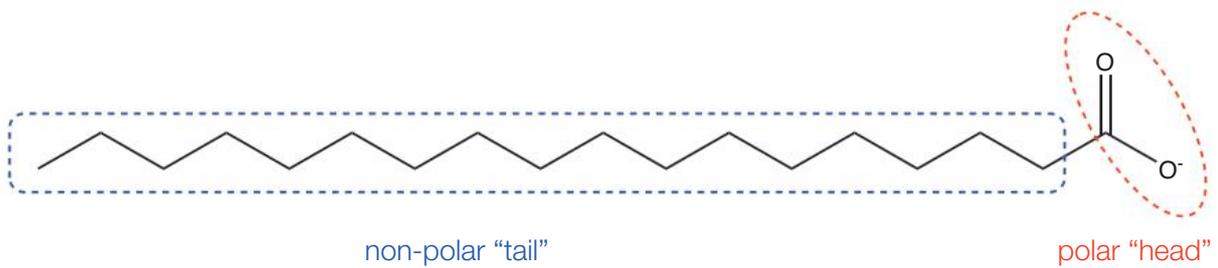
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When triglycerides undergo hydrolysis in alkaline solution, carboxylate anions are formed.



The carboxylate anions, or “fatty acid anions”, that are produced are composed of two parts:

- A non-polar “tail”. This long hydrocarbon chain is **hydrophobic** (‘water-hating’) as it cannot form secondary interactions with water.
- A polar “head”. This carboxylate functional group is **hydrophilic** (‘water-loving’) as it can form strong ion-dipole secondary interactions with water.



When these carboxylate anions are dispersed in water or aqueous solution, they form **micelles**. The non-polar hydrocarbon chains cluster in the centre of the micelle, and the polar anionic heads are on the surface of the micelle, pointing outwards to interact with water molecules.

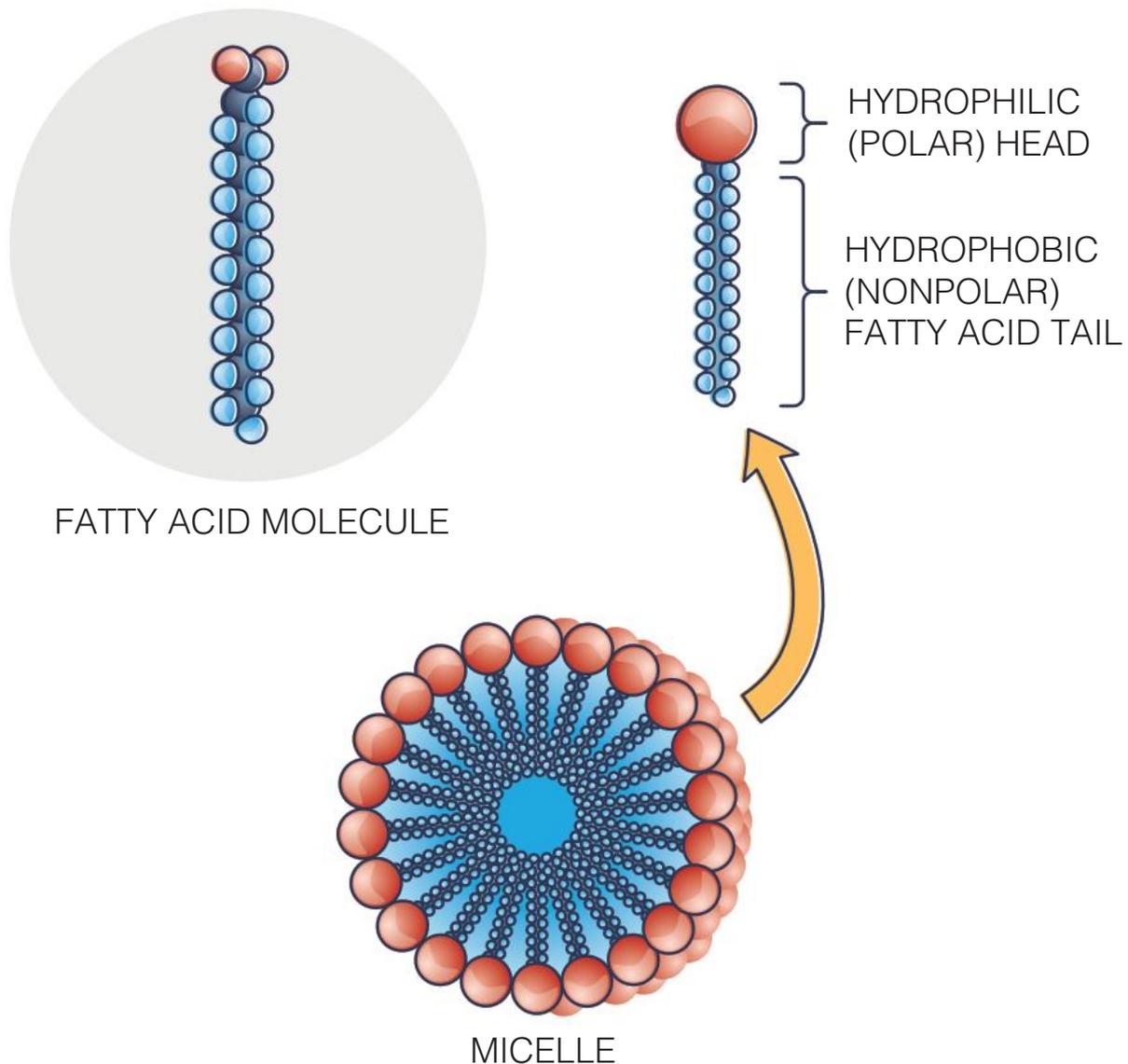


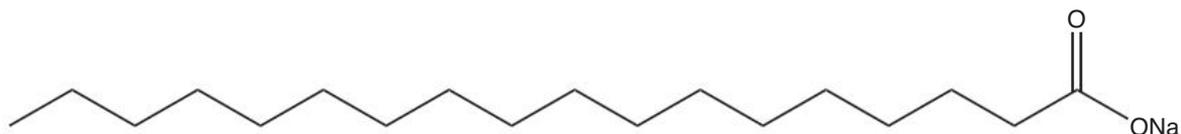
Figure 3.13 - Carboxylate anions form micelles in aqueous solution

Micelles are nanoscopic (1–100 nanometres in size). They allow non-polar substances to mix with polar substances such as water.

Applications of micelles

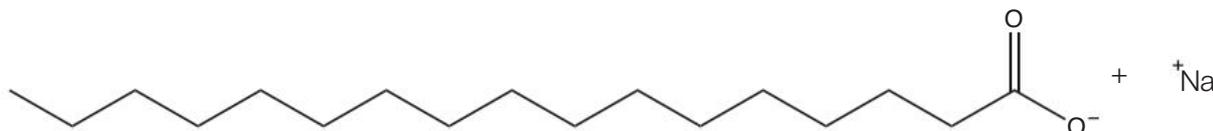
Soap micelles

In pure form, carboxylate salts of sodium are waxy white solids with the common name **soap**. Non-polar substances such as grease, oil, and fat stains are removed from fabric or surfaces by the action of soap micelles, which allow these substances to mix more readily with water and thus be washed away. The most common soap is sodium stearate.



sodium stearate
(sodium octadecanoate)

When soap dissolves in water, the ions dissociate.



When soap is mixed with grease and water, like in a washing machine or dishwasher, the anions cluster into micelles with the non-polar grease molecules in the centre. The non-polar hydrocarbon tails “dissolve” the non-polar grease molecules.

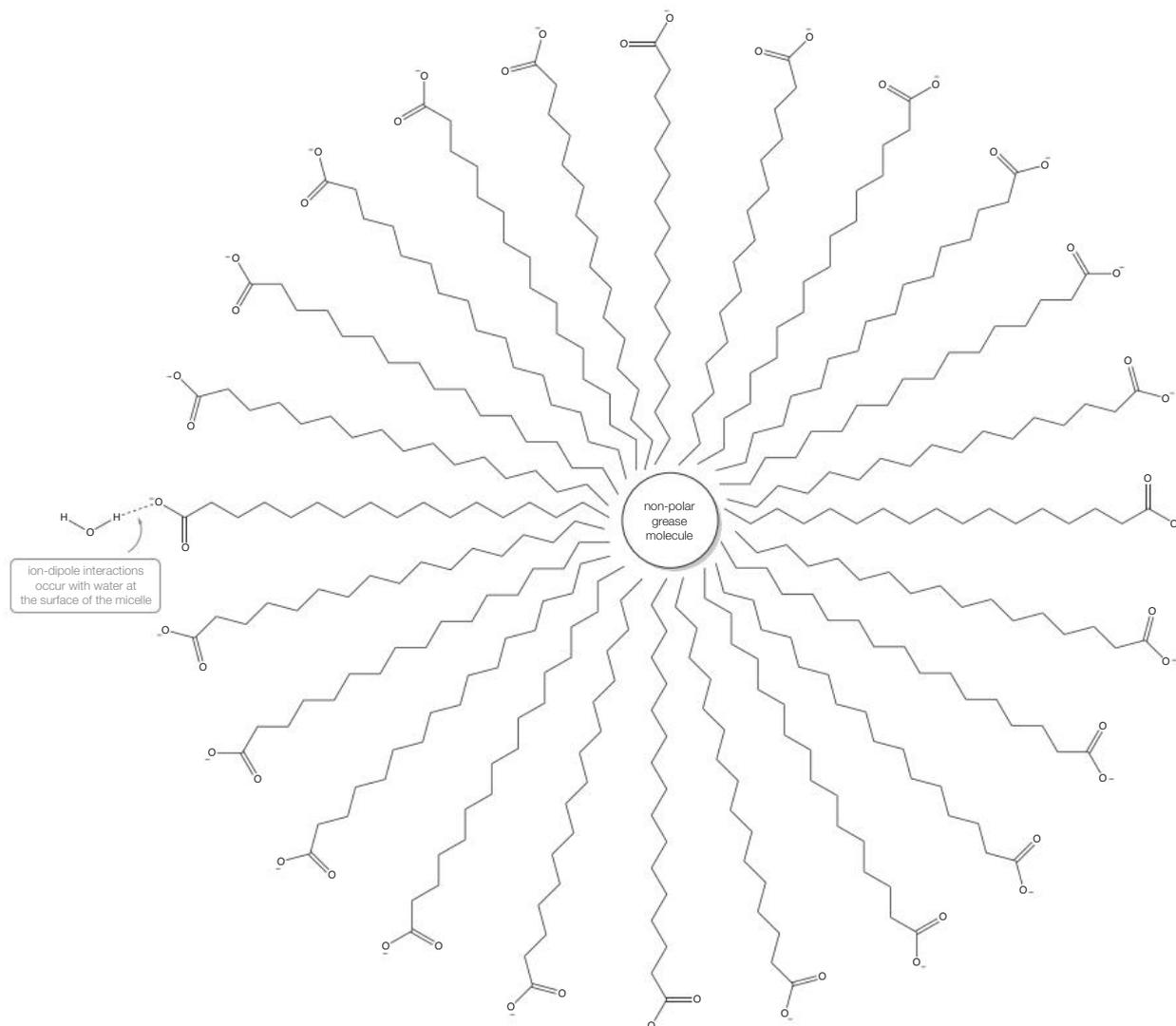


Figure 3.14- A soap micelle with “dissolved” grease in the centre

With agitation, grease lifts off the surface. The micelles repel each other, and they are washed away in the polar water.

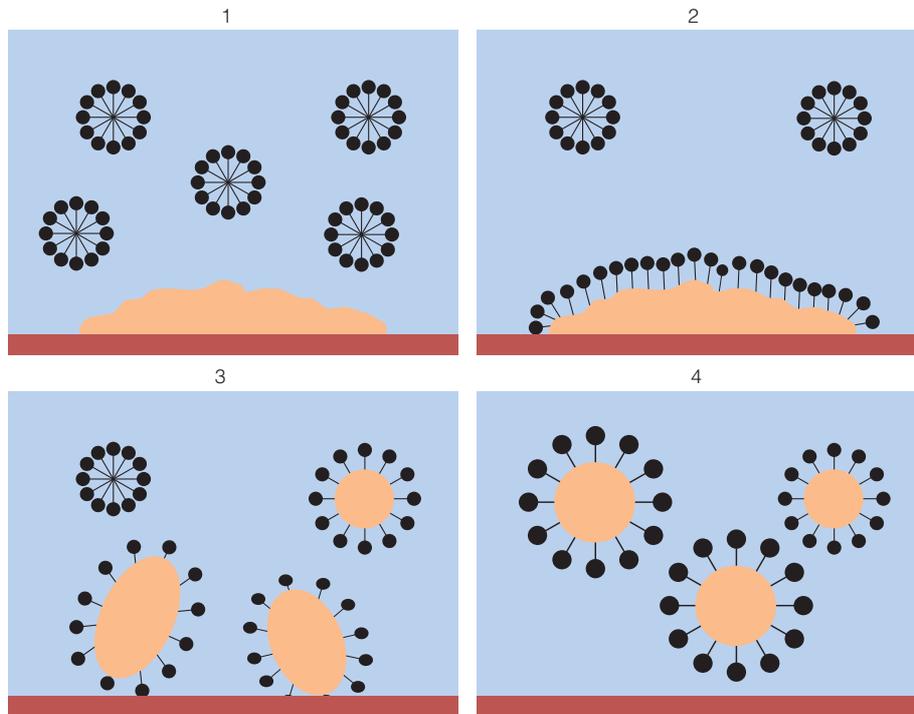


Figure 3.15: Soap molecules removing grease/dirt from a surface

3



Science as a human endeavour

Biocompatible Polymers

Non-polar, hydrophobic drugs, such as those used in cancer treatment, can be delivered around the body with nanoscopic **polymeric micelles**, also called **biocompatible polymers**.

The monomers that make up the polymer in the polymeric micelle have hydrophobic and hydrophilic parts:

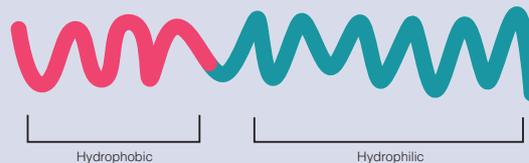


Figure 3.16 - Hydrophobic and hydrophilic parts of a polymeric micelle monomer

These monomers assemble themselves so that the hydrophobic parts face towards the centre, forming a spherical core, while the hydrophilic parts form the shell.

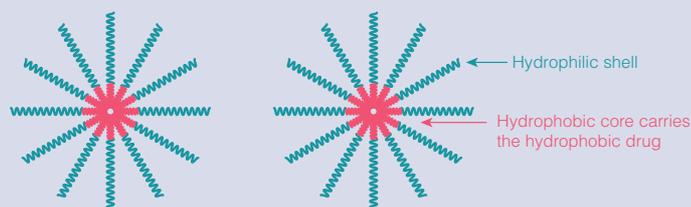


Figure 3.17: Polymer micelles

The hydrophobic core carries and protects the drug. The hydrophilic shell supports and stabilises the core in the aqueous medium, enabling it to be soluble in water.

Drugs that were originally insoluble now become soluble in water and bodily fluids, and therefore they are more readily available for the sites that require targeting. These polymeric micelles are biodegradable, so they can be excreted from the body without causing harmful side effects.

Polymeric micelles are being used in a variety of medicinal fields, including cancer treatments, oestrogen therapy, and flu prevention.

3.10 Proteins

Science understanding

Proteins are polymers of amino acids.

Amino acids contain a carboxyl group and an amino group.

Write the general formula of amino acids and recognise their structural formulae.

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Proteins are natural polymers that make up about 15% of the human body and carry out many important functions, including:

- transporting and storing oxygen and nutrients
- acting as catalysts for biological reactions
- fighting off foreign objects that invade the body
- serving as hormones to regulate body processes
- providing structural integrity and strength for tissue
- forming skin, hair, nails, and cartilage

The monomers of all proteins are compounds called **amino acids**. Although there are many types of amino acids, α -amino acids are the most significant in the biological world as they are the backbone of all proteins. The α -amino acids will be the focus of this chapter in terms of their structure, function, properties, and reactions.

Amino acids

Amino acids contain:

- A carboxyl group ($-\text{COOH}$)
- An amino group ($-\text{NH}_2$)
- An "R" group, called a side chain
- A hydrogen atom

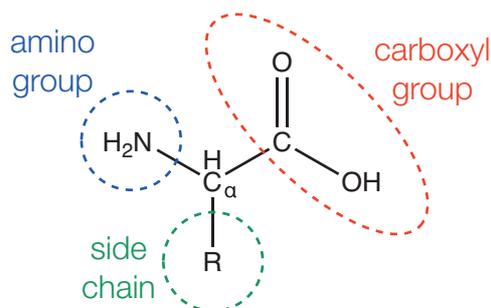
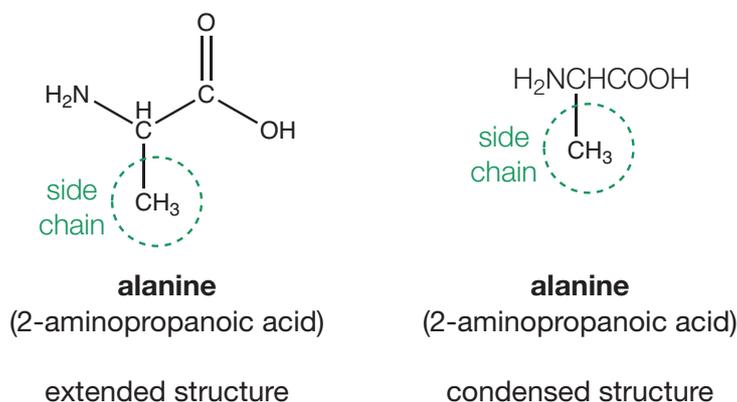


Figure 3.17 - General structural formula for an amino acid

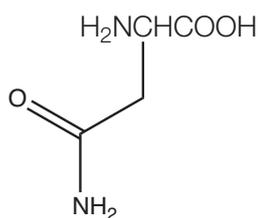
These are called ' α -amino acids' because the side chain is attached to the α -carbon. (Larger amino acids have more carbons which are labelled β , γ , and so on). Different α -amino acids vary only by what is attached at the position marked 'side chain'.

Alanine is one of the simplest amino acids. It has a methyl group ($-\text{CH}_3$) side chain. Because only the side chain varies between different amino acids, they are often drawn in a condensed format.



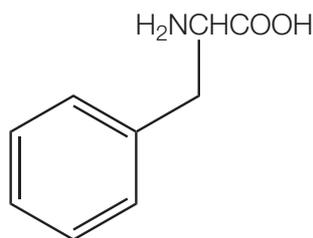
Polarity of amino acids

There are 20 different amino acids present in most proteins, each having a unique side chain. These unique side chains determine the overall polarity of the amino acids. Polar side chains contain nitrogen and oxygen atoms and are hydrophilic (water loving). Non-polar side chains contain mostly carbon and hydrogen atoms and are hydrophobic (water hating).



glutamine
(2,5-diamino-5-oxopentanoic acid)

polar side chain



phenylalanine
(2-amino-3-phenylpropanoic acid)

non-polar side chain

The polarity of the side chains affects the secondary interactions that can form between the chains, and thus impacts the three-dimensional structure and shape of the protein polymer.

Essential amino acids

Of the 20 unique amino acids, only 10 can be synthesised by the human body. The other 10 cannot be made by the body and must be ingested; these are called *essential amino acids*. Essential amino acids are a necessary part of the human diet.

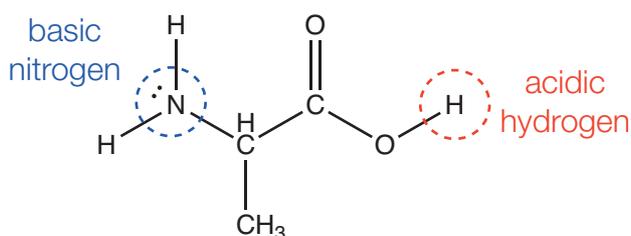
Science understanding

Amino acids have both acidic and basic properties.

Draw the structural formula of the product formed when an amino acid self-ionises, given its structural formula.

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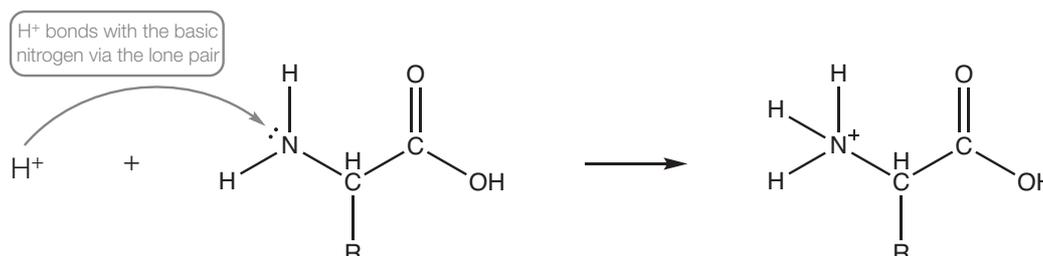
Amino acids have a carboxyl group with an acidic hydrogen that can be donated. They also contain an amino group, which has a basic nitrogen that can accept a proton due to its lone pair of electrons. These groups exist within the same molecule.



Amino acids are **amphiprotic**. Because amino acids contain both an acidic group and a basic group, amino acids can act as proton donors or proton acceptors depending on the pH of the solution.

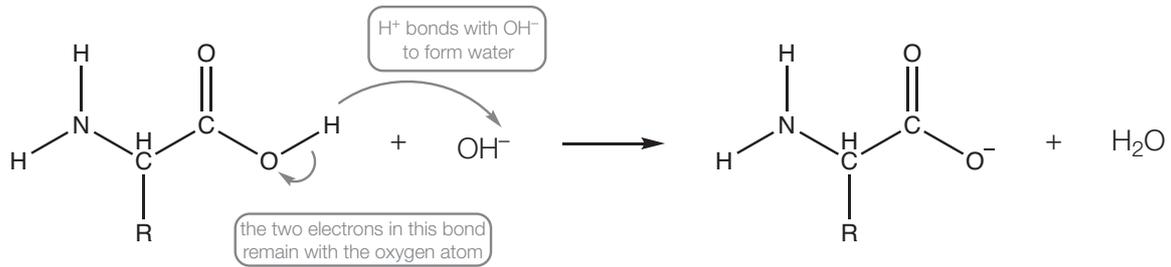
Acidic solution, pH < 7

An acidic solution contains free protons (H^+ ions). In an acidic solution, the amino group accepts an H^+ and forms a protonated amine.



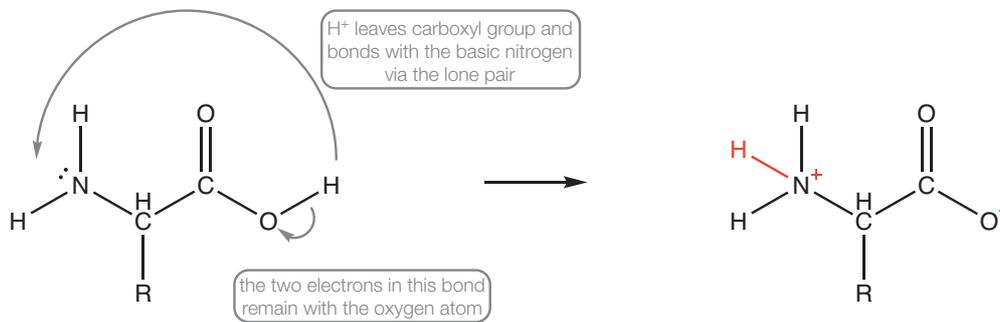
Alkaline solution, pH >7

An alkaline solution contains hydroxide ions (OH^-). In an alkaline solution, the carboxyl group donates its acidic hydrogen and forms a deprotonated amine.



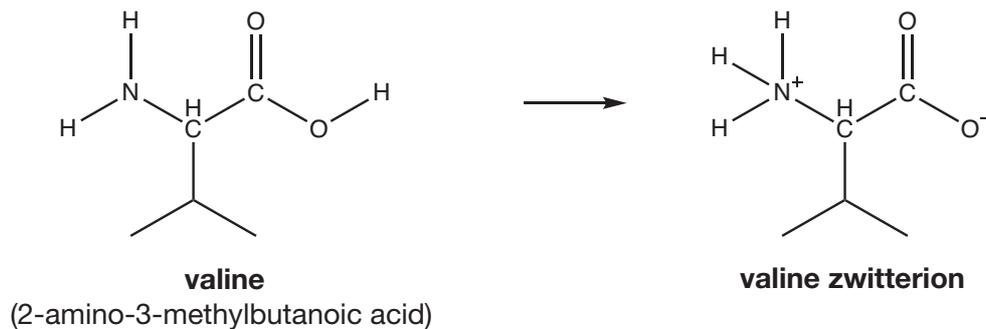
Neutral solution, pH \approx 7

In water, or any near-neutral aqueous solution, these acidic and basic groups react with each other; the carboxyl group donates a proton to the amino group. This forms a **zwitterion**: a molecule with positively and negatively charged functional groups, but no overall charge.



zwitterion

The following diagrams show the structure of valine, an essential amino acid, and its zwitterion form.



Properties of zwitterions

Amino acids exist as zwitterions, even in their solid state. Due to their ionic dipole, zwitterions are also called "internal salts" of amino acids. They have many of the same properties as salts, including high melting points, forming crystalline solids, and being generally soluble in water (depending on the polarity of the side chain).

Science understanding

Amino acids can undergo condensation to form protein chains.

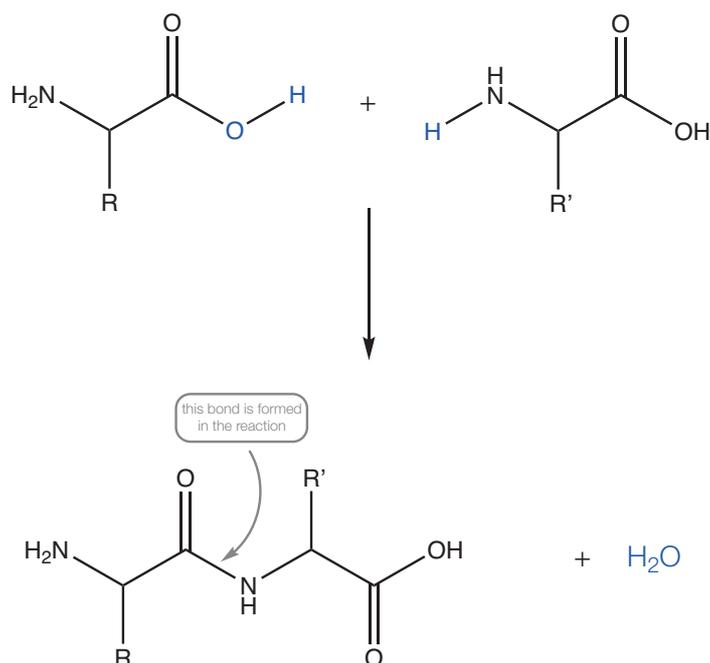
The amide groups within proteins are also known as 'peptide links'.

Draw the structural formula of a section of a protein chain that could be formed from amino acids, given their structural formulae or vice versa.

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Amino acids undergo condensation reactions to form a protein polymer chain. The amino group from one amino acid reacts with the carboxyl group from another amino acid. The side chains do not react.

Example



Amino acids are joined together by the **amide functional group**.

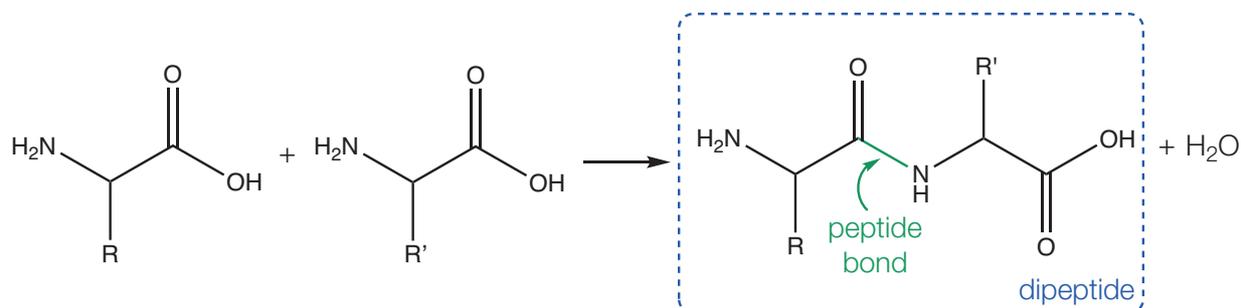
Biologists and biochemists also call this a **peptide bond** or **peptide linkage** when it appears in the context of amino acids and proteins.



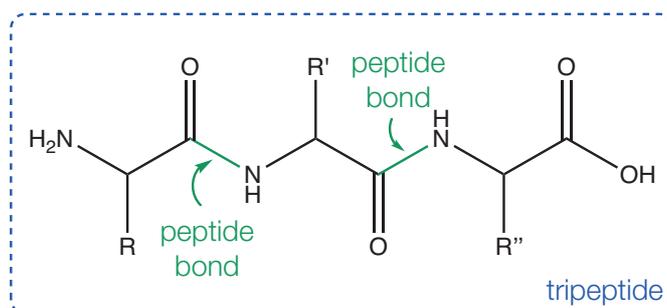
amide functional group

Dipeptides, tripeptides, and polypeptides

When **two amino acids** join via a condensation reaction, they produce a **dipeptide**. There is one peptide link.



When **three amino acids** join together they produce a **tripeptide**. There are two peptide links.

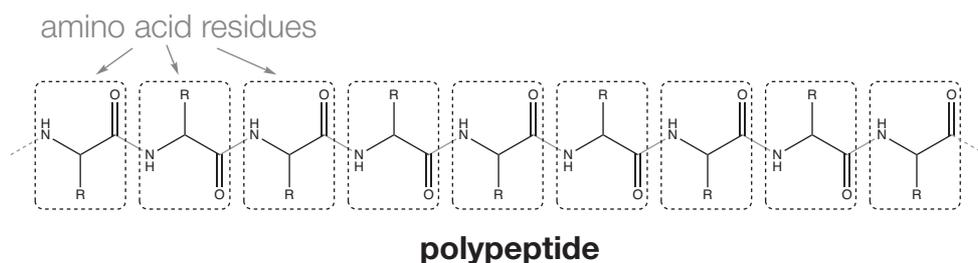


Hence, the prefix for a peptide depends on the number of amino acids that form it.

The part of the amino acid that remains after water is removed and which is incorporated into the polymer is called an **amino acid residue**.

Amino acids can join together in condensation reactions to produce chains of almost any length. Peptides made from fewer than 20 amino acid monomers are called **oligopeptides** ('oligo' meaning few), while peptides with greater than 20 amino acid monomers are called **polypeptides** ('poly' meaning many).

Proteins are polypeptides.

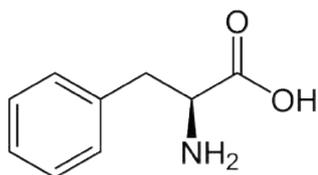


When drawing a **polypeptide** (or, equivalently, a section of a **protein chain**), appropriate notation (i.e., a squiggly or dotted line) is used to show that the chain continues at either end.

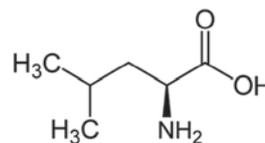
Questions

32. Peptide synthesis is characterized as the formation of a peptide bond between two or more amino acids via a condensation reaction.

(a) Draw the dipeptide that is formed from the following amino acids.



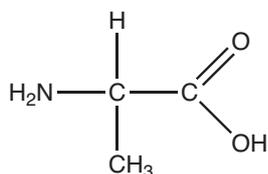
Phenylalanine



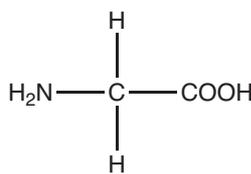
Leucine

(2 marks) KA4

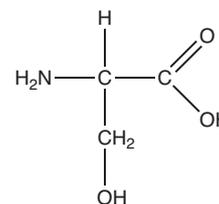
(b) Draw the polypeptide that is formed from the following amino acids.



Alanine



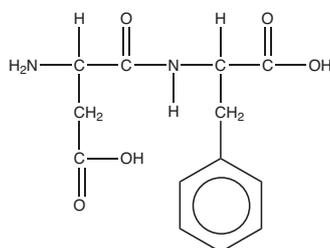
Glycine



Serine

(2 marks) KA4

(c) Aspartame is an artificial sweetener that contains the dipeptide of aspartic acid and phenylalanine. Given the structure of the dipeptide below, draw the two amino acids that form it.



Aspartame

(4 marks) KA4

Science understanding

The unique spatial arrangement of a protein depends on secondary interactions between sections of the chain and, in aqueous environments, between the chain and water.

Identify where secondary interactions can occur, given the structural formula of a section of a protein chain.

The biological function of a protein is a consequence of its spatial arrangement.

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Primary structure of proteins

Proteins are composed of 20 unique amino acids that can be arranged in any order, which means there are many, many possible protein structures. This versatility has allowed organisms to evolve specific proteins for various functions.

The order in which the amino acid residues are connected along a protein chain is called the protein's **primary structure**. The residues are joined together by **peptide bonds**, which are covalent bonds.

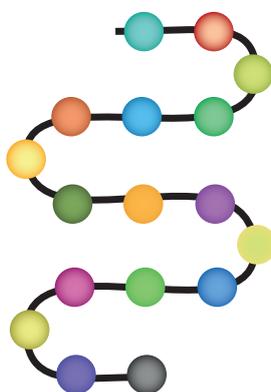


Figure 3.18 - The "primary" structure of a protein refers to the order in which the amino acids are joined

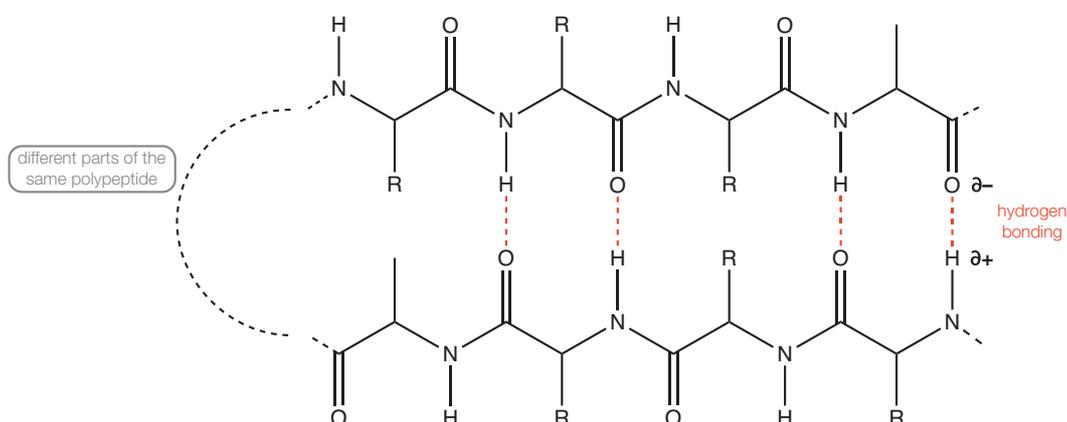


Science as a human endeavour

The primary structure is responsible for the protein's unique identity. A change in one amino acid can completely alter the biochemistry of the protein. For example, sickle-cell anaemia is a genetic disorder caused by one amino acid with a hydrocarbon side chain being replaced by an amino acid with an acidic side chain. Another example is oxytocin and vasopressin. Oxytocin is a hormone that triggers milk secretion, while vasopressin regulates the flow of urine from the kidneys. Their polypeptide primary structure only differs by two amino acids, yet these proteins have vastly different functions.

Secondary structure of proteins

In aqueous solution, protein chains fold and coil in specific ways; this is referred to as the protein's **secondary structure**. The secondary structure is determined by the hydrogen bonding between non-adjacent amide functional groups. The hydrogen in the amino group of one residue forms a hydrogen bond with the oxygen in the carbonyl group of another residue.



When hydrogen bonding can occur regularly between the N-H of each amino acid residue and the C=O located four residues earlier in the sequence, a coiled structure called an **alpha helix** (or α -helix) forms. This structure is the most common type of secondary protein structure and can be predicted from the sequence of amino acid residues.

In diagrams showing the structure of a whole protein, α -helices are represented using a curled ribbon.

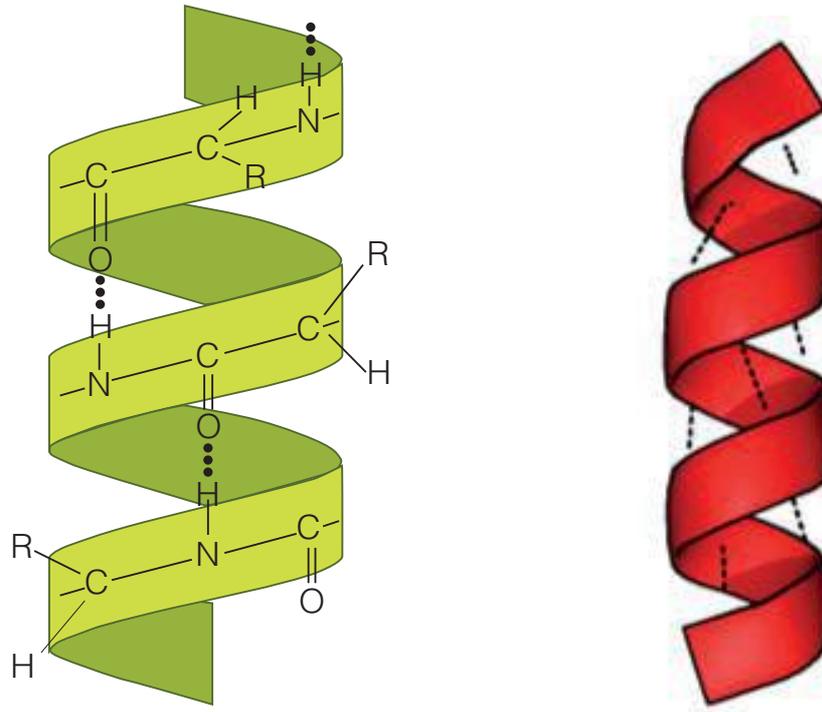


Figure 3.19 - a short section of α -helix secondary structure

When hydrogen bonding occurs between different parts of the protein chain, they form a pleated plane called a **beta sheet** (or β -sheet). This arrangement is also an extremely common motif of protein secondary structure.

In diagrams showing the structure of a whole protein, β -sheets are represented using wide flat arrows.

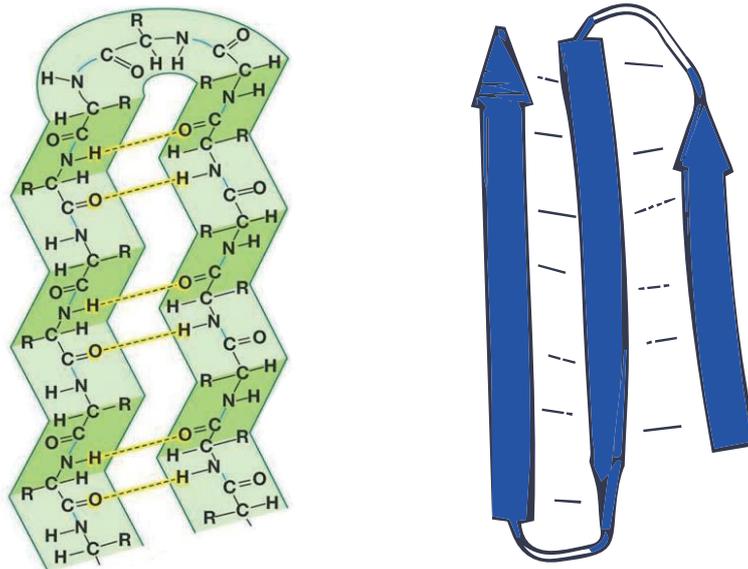
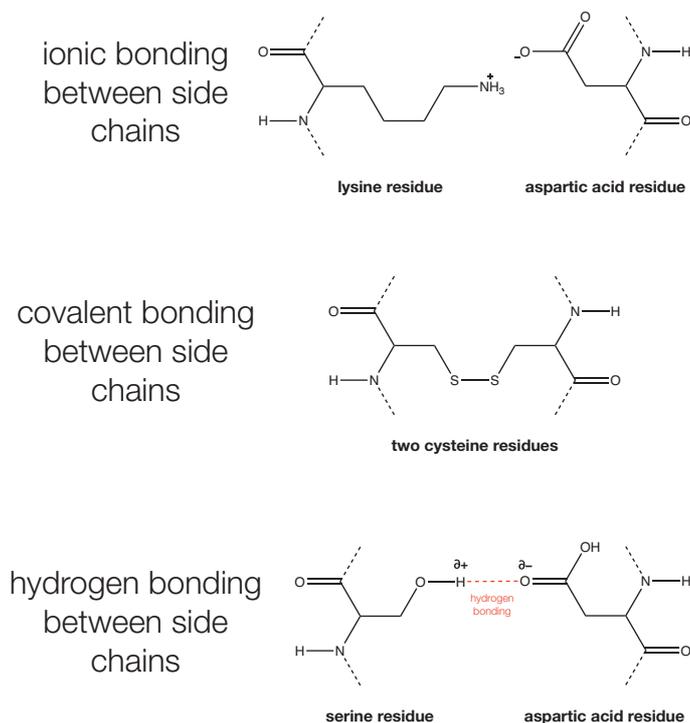


Figure 3.20 - a short section of β -sheet secondary structure

Some proteins are soluble in water because hydrogen bonding secondary interactions can form between the polar groups in the amide link and polar water.

Tertiary structure of proteins

The overall shape of a protein is called the **tertiary structure**. It refers to the way all atoms of the polypeptide chain arrange themselves in a three-dimensional shape. The tertiary structure of a protein depends largely on the particular side chains of the amino acid residues and how they interact with one another. Various side chains can form primary bonds (ionic or covalent) as well as secondary bonds, including ion-dipole, dipole-dipole, hydrogen bonding, and dispersion forces.



Interactions can occur between side chains of residues that are far apart in the sequence, but which happen to be near one another when the protein is folded.

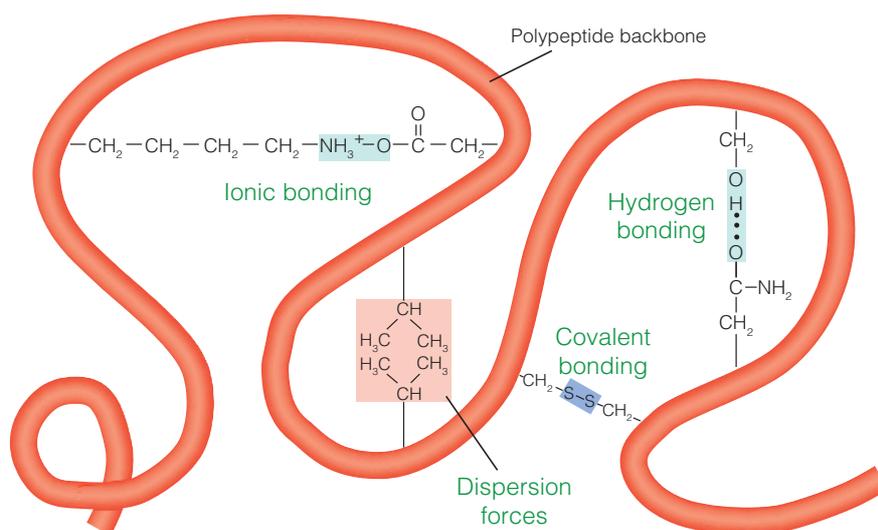


Figure 3.21 - Tertiary structure results from complex interactions between many parts of the protein

Quaternary structure of proteins

Some proteins do not function as single units; they combine with copies of themselves to create a symmetrical **protein complex**. This is called the **quaternary structure**. Each **subunit** is a large, but distinct, polypeptide molecule.

Example

Haemoglobin, the protein which transports oxygen in blood, is made up of four subunits arranged in a roughly tetrahedral structure.

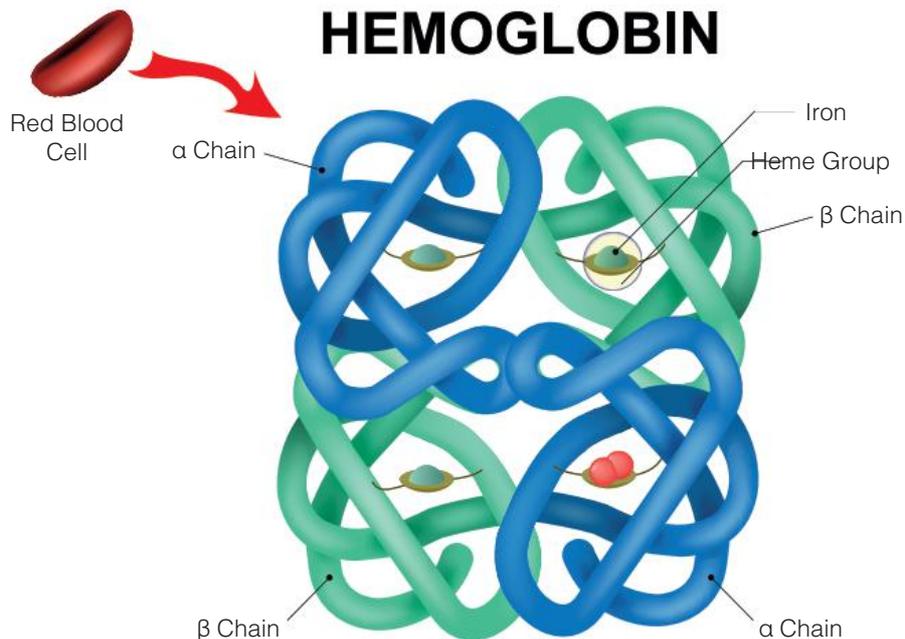


Figure 3.22 - Haemoglobin protein complex forms from four haemoglobin subunits

Protein Structure Summary

Proteins have at least three, and often four, levels of structure. The **primary structure** of a protein is its amino acid sequence. The **secondary structure** is the initial folding of the sequence into alpha helices and beta sheets. The **tertiary structure** is a more complex folding of the protein upon itself. **Quaternary structure** is the combination of two or more of the same protein.

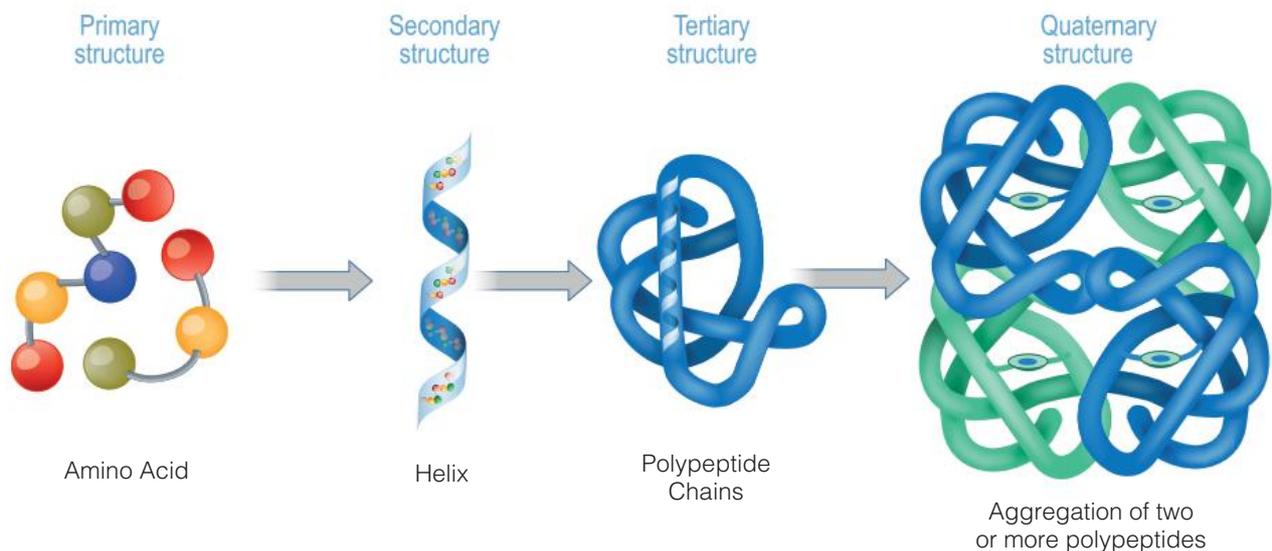


Figure 3.23 - Proteins have multiple levels of structure

Science understanding

Explain why the biological function of a protein (e.g. an enzyme) may be affected by changes in pH and temperature.

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The three-dimensional structure of a protein is crucial to its function. If a protein's structure is changed such that the protein no longer functions, the protein is **denatured**. Even small changes can result in a protein losing all functionality. Two major factors that affect protein structure, and hence function, are **heat** and **pH**.

Effect of heat on protein structure

When proteins are heated to high temperatures, there is sufficient thermal energy to break secondary or even primary bonds. This disrupts the tertiary structure of the protein, and can also lead to a change in the macroscopic properties of the substance.

Example

Albumen is the main protein found in egg white. Albumen is water soluble but becomes insoluble when cooked. This is because the heat allows individual protein chains to change shape and form new primary bonds with other protein chains, creating a tangled web of cross-linked polypeptides.



Figure 3.23 - Proteins can change drastically when heated

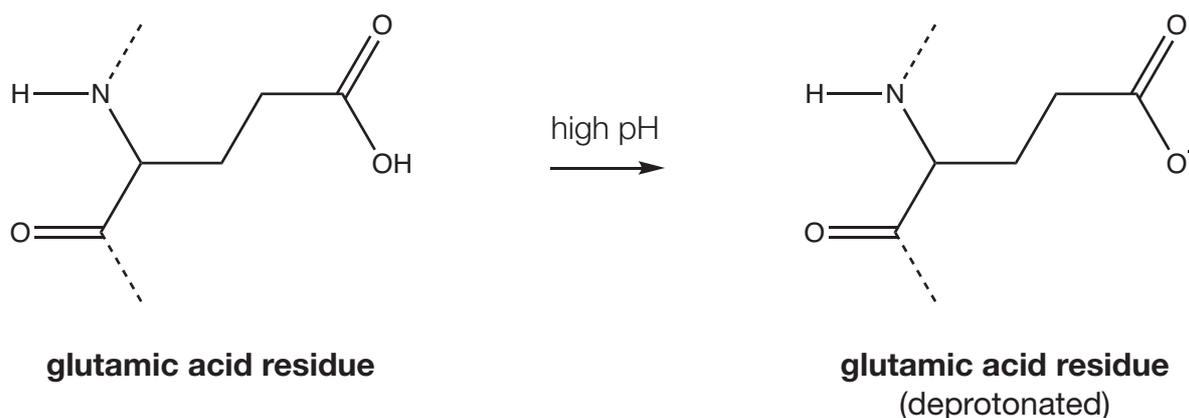
Effect of pH on protein structure

Many amino acid side chains are either acidic or basic; they can donate or accept protons. The pH of the solution will affect how these side chains are able to form bonds.

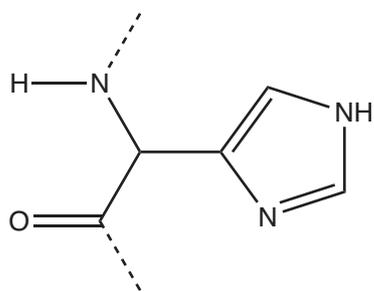
Acidic side chains will donate a proton when the pH increases.

Example

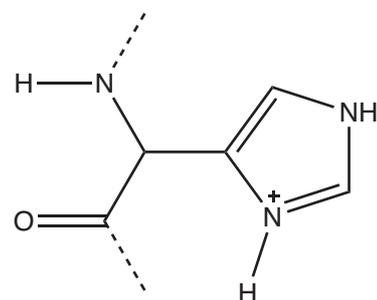
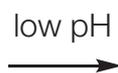
Basic side chains will accept a proton when the pH decreases.



Example



glutamic acid residue



glutamic acid residue
(protonated)

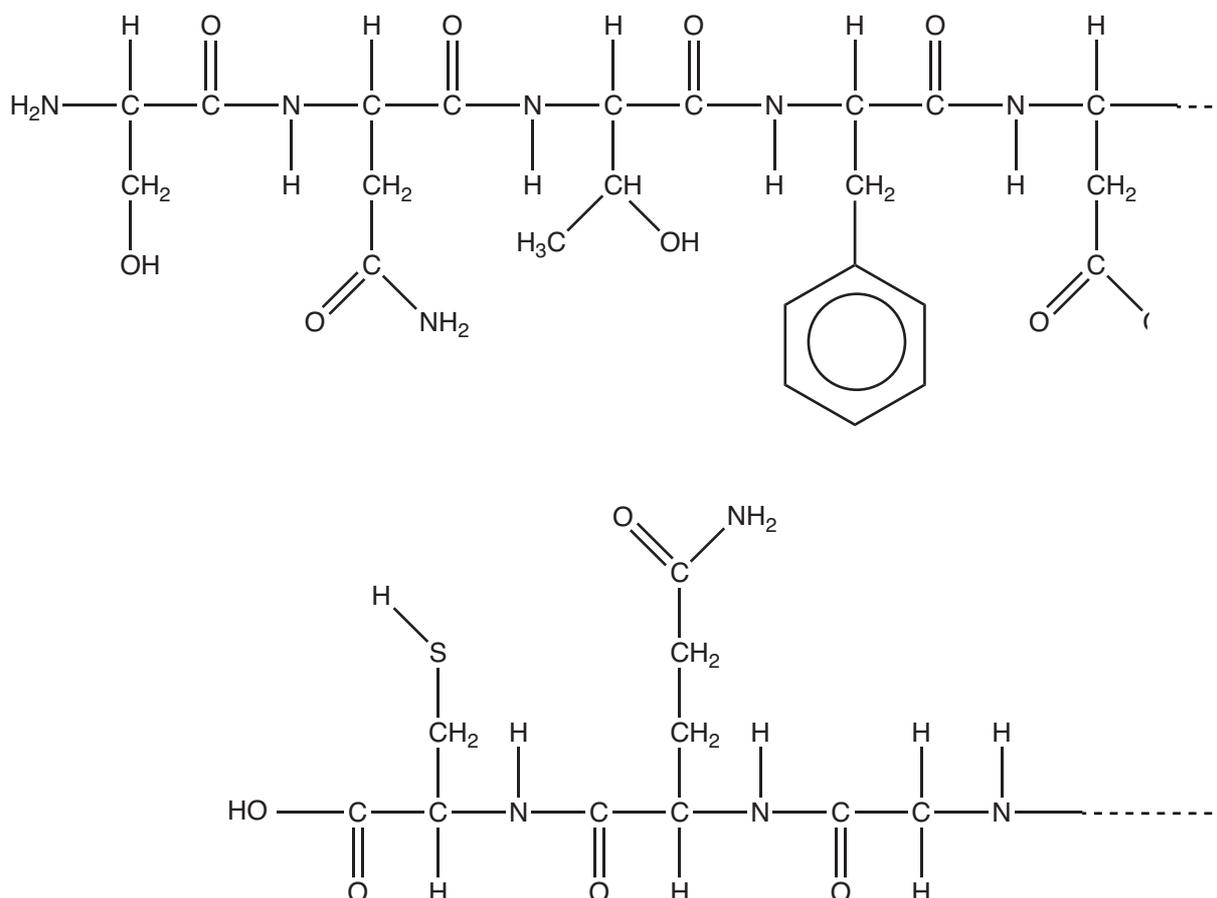
If the secondary interactions change, the protein molecule unfolds and denatures. Because the structure has changed, the protein is no longer able to function.

Enzymes

Enzymes are an important class of proteins. They are large molecules that act as natural catalysts for very specific reactions. Without enzymes, life would not be sustainable. As with all proteins, enzymes require specific temperature and pH ranges to function correctly. This is the primary reason that organisms die when they are too cold or too warm.

Questions

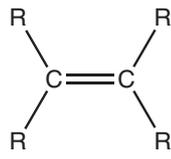
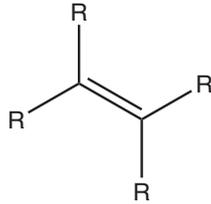
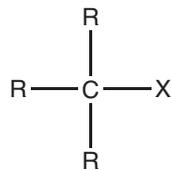
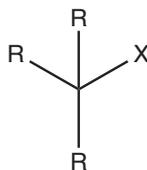
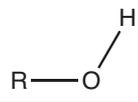
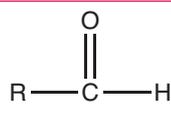
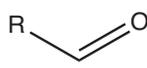
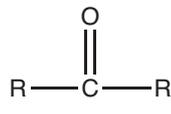
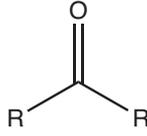
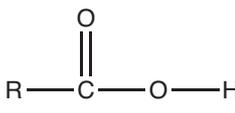
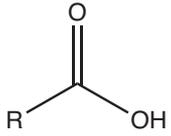
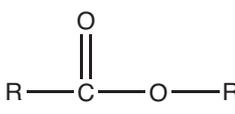
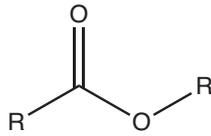
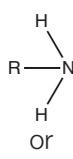
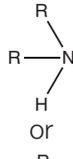
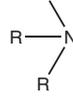
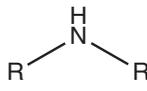
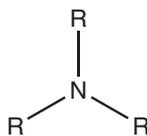
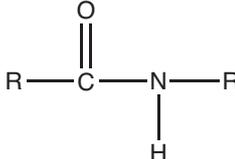
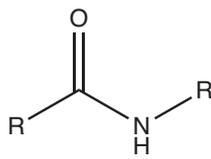
33. A part of a protein chain is shown below.



(a) Circle one peptide link in the chain above.

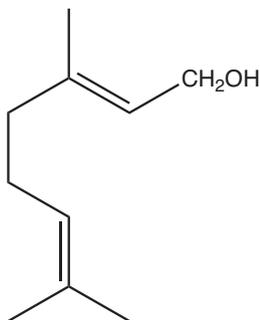
(1 mark) KA1

Chapter 3 functional groups summary

Homologous series	Functional group	Extended Structure	Skeletal Structure	Suffix or prefix
Alkene	Alkene			-ene
Alkyne	Alkyne	$R-C\equiv C-R$		-yne
Haloalkane (or halogenalkane or alkyl halide)	Halogen	 <p>$X = \text{halogen}$</p>		"Halo" e.g., fluoro-, chloro-
Alcohol	Hydroxyl			-ol
Aldehyde	Aldehyde (terminal carbonyl)			-al
Ketone	Ketone (non-terminal carbonyl)			-one
Carboxylic acid	Carboxyl			-oic acid
Ester	Ester			-yl -oate
Amine	Amino	 <p>or</p>  <p>or</p> 	$R-NH_2$ or  or 	-amine
Amide	Amide			-amide

Summary test 3: Organic and biological chemistry

1. Geraniol is a chemical compound found within many essential oils of fruits. It has a pleasant odour and can also be used as a natural insect repellent. Its structure is below.



- (a) Write the molecular formula of geraniol.

..... (1 mark) KA1

- (b) Geraniol can be partially oxidised with an oxidising agent. Draw the product.

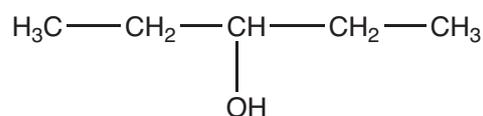
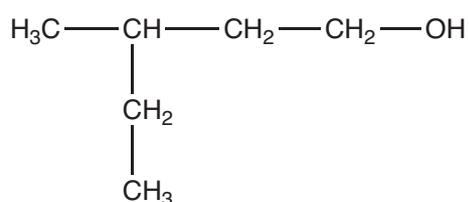
(2 marks) KA4

- (c) Many alcohols can also be used as fuels to provide energy.

- (i) Write an equation for the complete combustion of ethanol.

(2 marks) KA4

- (ii) Classify the following alcohols as primary, secondary or tertiary.



- (i)..... (ii).....

(2 marks) KA1

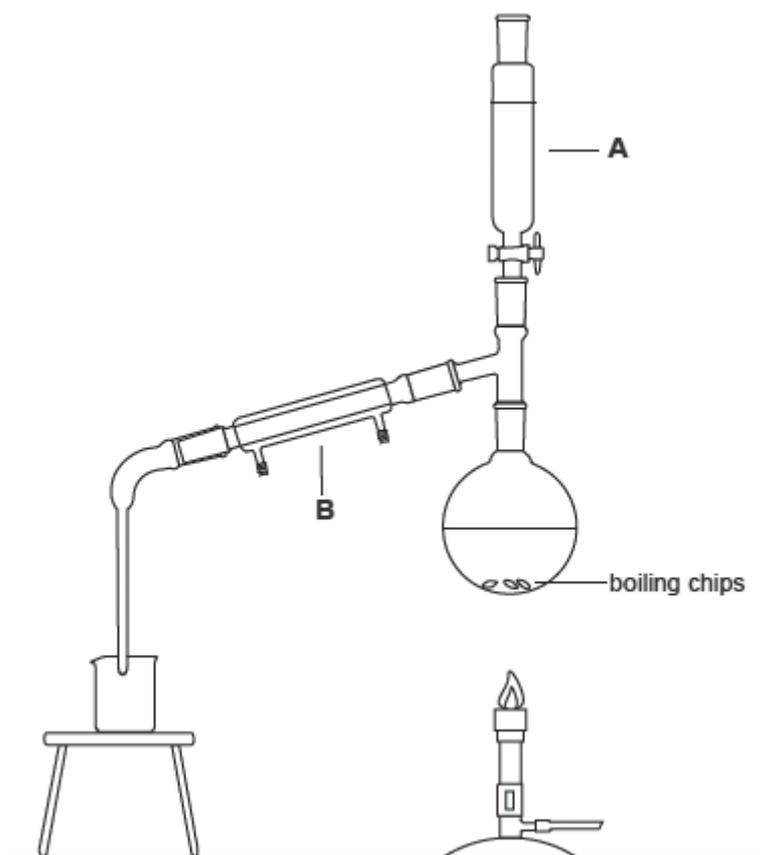
- (iii) Determine the organic product formed when each of the compounds is heated under reflux with excess acidified dichromate added dropwise. If no reaction occurs, write NR.

Compound	Organic product
$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	
$\text{CH}_3\text{CH}_2\text{COCH}_3$	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	

(4 marks) KA1

Aldehydes are used in many ways. Some aldehydes are found in natural materials, while others are made synthetically.

An aldehyde can be prepared from an alcohol, using the apparatus shown below:



- (iv) Name the pieces of glassware labelled **A** and **B**.

A is

..... (1 mark) KA1

B is

..... (1 mark) KA1

- (v) On the diagram above, show the direction of the water flow on the glassware labelled **B**.

(1 mark) KA1

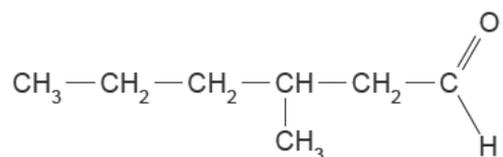
- (vi) The glassware labelled **A** contained acidified dichromate ($\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$). When it reacted with the alcohol, the $\text{Cr}_2\text{O}_7^{2-}$ ions converted to Cr^{3+} ions. Write the half-equation for this conversion.

(2 marks) KA1

- (vii) Name the functional group that would be formed if the alcohol, acidified dichromate ($\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$) and H_2SO_4 were refluxed together rather than reacted in the apparatus shown.

..... (1 mark) KA1

- (d) The structural formula of one aldehyde is shown below:



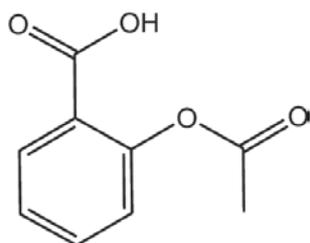
- (i) Give the systematic name of the aldehyde shown above.

..... (2 marks) KA1

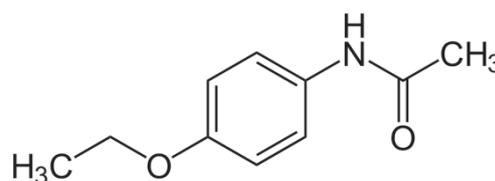
- (ii) Draw the structural formula of the ketone that is a functional group isomer of the aldehyde shown in (d).

(2 marks) KA4

2. The following compounds are the active ingredients in over-the-counter drugs used as analgesics.



Compound A



Compound B

- (a) Name two functional groups in Compound A.

.. .. .
 (2 marks) KA1

- (b) Describe and explain a chemical test that could be undertaken in a laboratory to distinguish between Compound A and Compound B.

.. .. .

 (3 marks) KA1

- (c) Explain why Compound B is slightly soluble in water.

.. .. .

 (3 marks) KA1

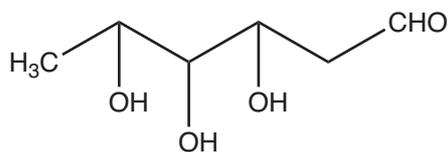
- (d) Draw the products formed when Compound B undergoes hydrolysis at pH 3.4.

(2 marks) KA4

- (e) Draw the products formed when Compound B undergoes hydrolysis at pH 11.8.

(2 marks) KA4

3. Carbohydrates are often found in nature. The purple foxglove plant produces important cardiac medication that reduces pulse rate, regulates heart rhythm, and strengthens heartbeat. When hydrolysed, it produces the monosaccharide shown below, labelled Monosaccharide A:



Monosaccharide A

- (a) Write the molecular formula of Monosaccharide A.

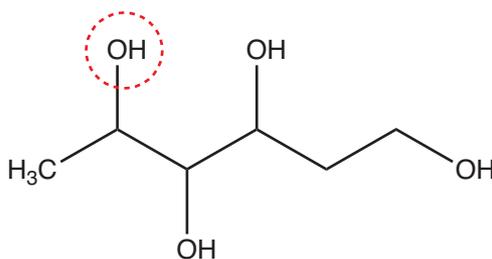
..... (1 mark) KA1

- (b) Explain why Monosaccharide A is classified as a carbohydrate.

.....

 (2 marks) KA1

- (c) An isomer of Monosaccharide A is shown below, labelled Monosaccharide B.



Monosaccharide B

- (i) Name monosaccharide systemically.

..... (2 marks) KA1

- (ii) Explain what is meant by the term "isomer".

..... (1 mark) KA1

- (iii) Classify the hydroxyl group that is circled as primary, secondary, or tertiary.

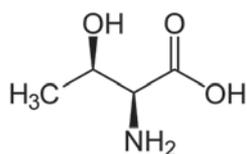
..... (1 mark) KA1

- (iv) Describe and explain a chemical test that could be performed in a laboratory to distinguish between Monosaccharide A and Monosaccharide B.

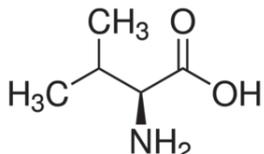
.....

 (4 marks) KA1

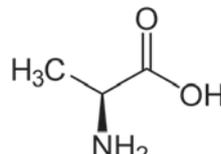
4. Questions (a) to (c) relate to the amino acids shown below.



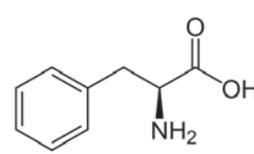
Threonine



Valine



Alanine



Phenylalanine

(a) Name the functional groups present in each of the amino acids.

..

.. (2 marks) KA1

(b) For which of the amino acids can the side chains form hydrogen bonds with water?

..

.. (2 marks) KA1

(c) Draw a section of a protein chain formed from the amino acids valine, phenylalanine, and threonine.

(2 marks) KA4

(d) Draw the structure of alanine when placed in a solution of the following pH:

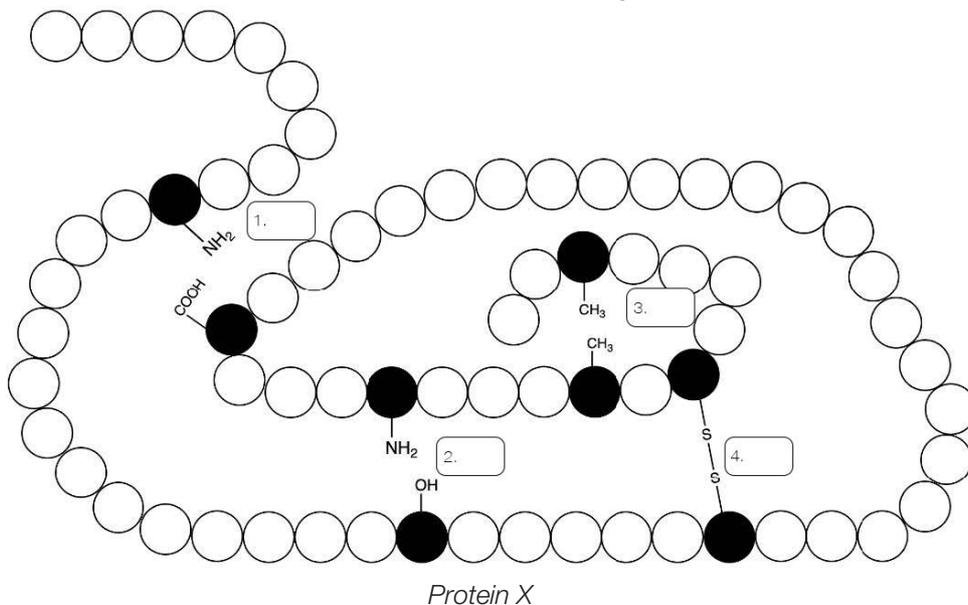
(i) pH 2.5

(ii) pH 7.1

(iii) pH 10.6

(6 marks) KA4

(e) Protein X is shown below with various interactions occurring between parts of the chain.



(i) Identify the types of interactions occurring between parts of the protein chain.

1.	
2.	
3.	
4.	

(4 marks) KA1

(ii) The optimal pH for Protein X is 6.8. State and explain what would happen to this protein if it were placed in an alkaline environment.

.. .. .

.. .. .

.. .. .

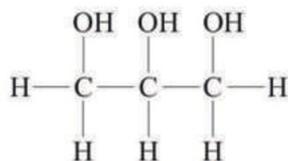
.. .. .

.. .. .

.. .. .

..... (4 marks) KA1

5. The structural formula of compound **B** is shown below:



Compound **B**

(a) Write the systematic name of compound **B**.

..

.. (2 marks) KA1

(b) The structural formula of compound **C** is shown below.



When compound **B** reacts with compound **C**, a triglyceride, **D**, is formed.

(i) Draw the structural formula of triglyceride **D**.

(2 marks) KA4

(ii) Identify the other product of this reaction.

.

.. (1 mark) KA1

(iii) Triglyceride **D** is a liquid at room temperature.

State whether **D** is more likely to come from a plant or a land animal.

.

.. (1 mark) KA1

(iv) When heated, liquid oils may be converted into solid fats, as shown below:



Identify the required reagent A, the substance B, and the condition C necessary for the conversion to occur.

A: ..

.

....

.

B: ..

.

....

.

C: ..

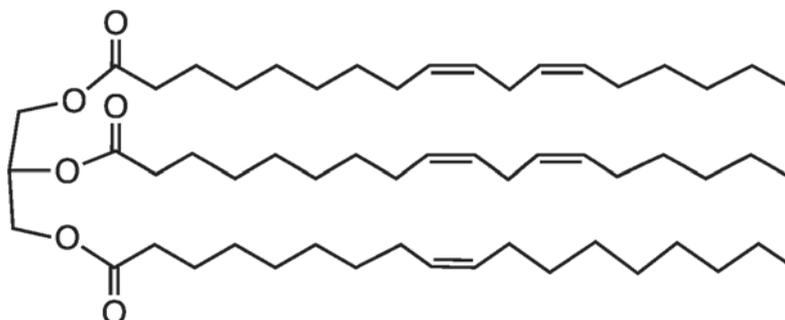
.

....

.

(3 marks) KA1

(c) The structural formula of another triglyceride is shown below:



0.1 g of this triglyceride was shaken in a non-polar solvent and reacted completely with iodine solution.

(i) Calculate the number of moles of triglyceride in the 0.1 g, given that its molar mass is $876.16 \text{ g mol}^{-1}$.

(2 marks) KA3

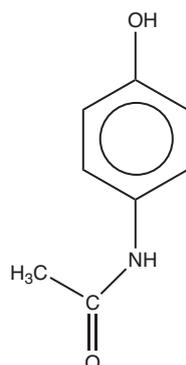
(ii) Calculate the moles of iodine solution required to react completely with the triglyceride.

(1 mark) KA3

(iii) Given the concentration of the iodine solution is 0.01 mol L^{-1} , calculate the volume of iodine solution required to react completely with the triglyceride.

(2 marks) KA3

6. The compound acetaminophen is used in over-the-counter medication such as paracetamol to relieve pain and fever. Its structure is below.



Acetaminophen (paracetamol)

(a) State the functional groups present in acetaminophen.

..... (1 mark) KA1

Topic 4: Managing resources

4.1 Energy

Science understanding

Photosynthesis and respiration are important processes in the cycling of carbon and oxygen on Earth.

In photosynthesis the light energy absorbed by chlorophyll is stored as chemical energy in carbohydrates such as glucose.

Describe and write the equation for photosynthesis.

The chemical energy present in carbohydrates can be accessed by respiration and combustion.

Describe and write the equation for the aerobic respiration of glucose.

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The carbon cycle

The **carbon cycle** describes the movement of carbon, in its various forms, between the atmosphere, oceans, biosphere (parts of Earth where life exists), and geosphere (geology of the Earth's crust) as shown in Figure 4.1.1.

The carbon cycle identifies **carbon reservoirs** (the ocean, atmosphere, living things, rocks) and the processes by which carbon moves between these reservoirs. If more carbon enters a carbon reservoir than leaves it, it is referred to as a **net carbon sink** (oceans). Conversely, if more carbon leaves a reservoir than enters it, it is referred to as a **net carbon source** (combustion of fossil fuels).

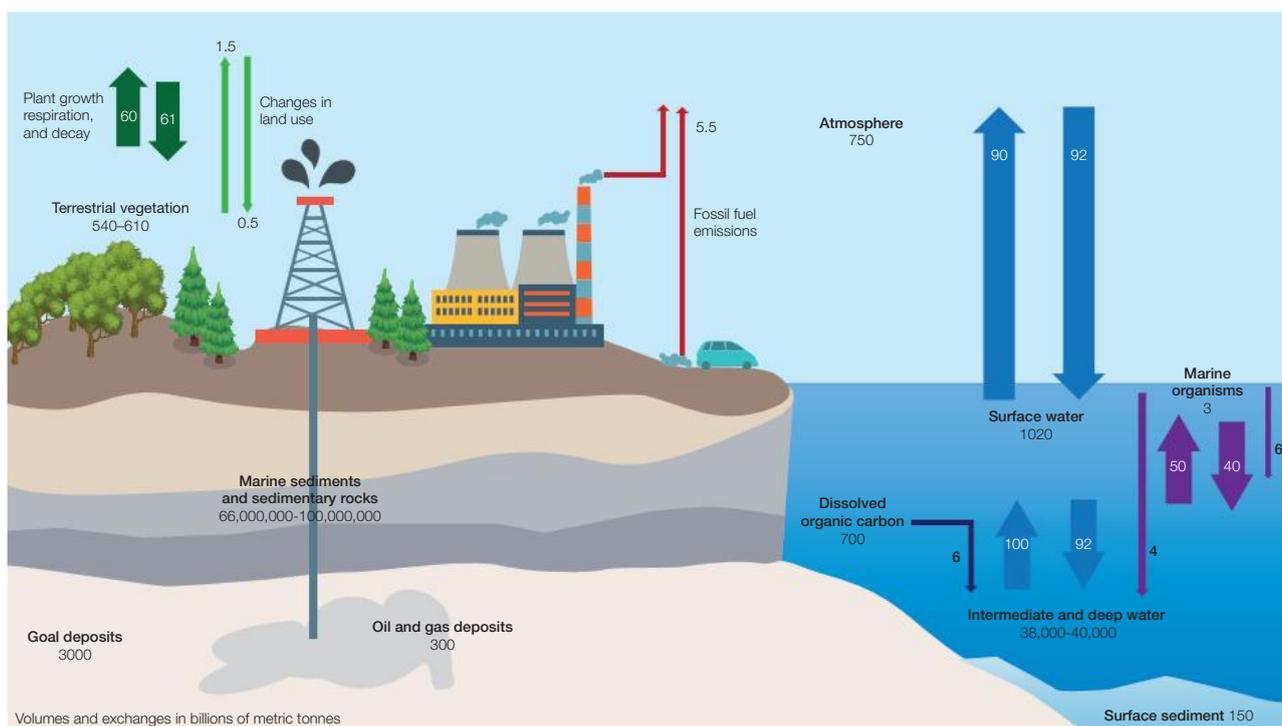
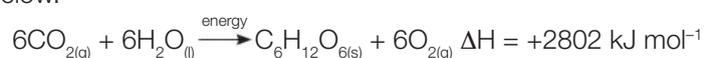


Figure 4.1.1: The carbon cycle.

Photosynthesis

Photosynthesis is the chemical process by which plants and some microorganisms (algae, phytoplankton and cyanobacteria) use carbon dioxide, water and energy absorbed from sunlight to produce oxygen and glucose. Glucose (monomer) is stored as starch (polymer) in plants and glycogen (polymer) in animals for future use. The reaction is summarised below.



Photosynthesis is an **endothermic** process, as there is a net absorption of energy. The conversion of energy from sunlight into stored chemical energy, in the form of glucose, is associated with the green pigment **chlorophyll**.

Aerobic respiration

Respiration is the chemical process by which organic compounds release energy in the cells of living things. Aerobic respiration is a series of reactions that release the energy stored in carbohydrates (and in some cases lipids) formed during photosynthesis. Respiration is an **exothermic** process, as there is a net release of energy. Respiration occurs in the cells of living organisms, making this energy available for **metabolic activity** (processes such as the synthesis of larger molecules, contraction of muscles, and maintenance of body temperature). The reaction is summarised simply through the rearrangement of the photosynthesis reaction.



Science understanding

Fossil fuels (coal, petroleum, and natural gas) have been formed over geological timescales by anaerobic decomposition of dead organisms. They are considered to be non-renewable because reserves are depleted more quickly than they are formed.

Carbon-based fuels provide energy and are feedstock for the chemical industry.

Biofuels are produced by present-day biological processes.

Identify bioethanol and biodiesel as biofuels.

Discuss the advantages and disadvantages of using carbon-based fuels as sources of heat energy, compared with their use as feedstock.

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Carbon-based fuels

Carbon-based fuels include **fossil fuels** and **biofuels**. Fuels undergo combustion with an oxidiser (oxygen) to release chemical energy stored in the covalent bonds. This energy is primarily used in electricity production and transport applications. Fuels are also used as a **feedstock** (raw material) in the manufacture of a range of consumer products or as an energy source in their production. Carbon-based fuels provide the raw materials required for the production of a vast range of products, including paints, textiles and pharmaceuticals.

Fossil fuels

Fossil fuels have been formed over hundreds of thousands of years through the decay of organic (plant and animal) matter under **metamorphic** (heat and pressure) geological conditions. Fossil fuels include coal, petroleum and natural gas. Combustible fossil fuels have been used extensively as a source of energy since the industrial revolution. Fossil fuels are a finite and **non-renewable** resource. The rate at which fuels are consumed greatly exceeds the rate of their geological formation.

Biofuels

Biomass fuels (biofuels) are derived from biomass (organic material) from plants and the waste matter from animals. Biofuels include bioethanol, biodiesel and biogas. Biofuels provide a **renewable** alternative to many fossil fuels. Bioethanol and biodiesel are being blended with petrol and diesel respectively.

In applications as an energy source and as feedstock, fossil fuels and biofuels offer a range of advantages and disadvantages.

Fossil fuel		Advantages
Reserves	Energy and feedstock	Coal, crude oil and natural gas are relatively abundant.
Extraction, processing & distribution	Energy and feedstock	Fossil fuels are easily extracted and distributed. Coal is mined and transported via train or truck. Drilling is used to extract oil, which is then transported via pipelines or oil tankers. Drilling is also used to extract natural gas, which is associated with deposits of petroleum. The gas is then processed and distributed via pipelines.
Infrastructure	Energy and feedstock	Proven technologies have been employed to generate electricity from the combustion of fossil fuels and run internal combustion engines in motor vehicles. Well-established industries exist for a multitude of products derived from crude oil and associated petrochemicals. A great deal of infrastructure has been developed and maintained worldwide for the distribution and continued use of fossil fuels.
Energy density	Energy	Combustion of fossil fuels releases large amounts of energy per gram or litre, making them highly effective fuels for energy production and transportation.

Fossil fuel		Disadvantages
Reserves	Energy and feedstock	Fossil fuel reserves are being depleted at a growing rate. Their rate of consumption is much faster than their rate of geological formation.
Production	Energy and feedstock	Fossil fuels are non-renewable.
Combustion products	Energy	<p>Combustion of fossil fuels releases large quantities of carbon dioxide, contributing to global warming (refer to Page 1).</p> <p>Other products of combustion include carbon monoxide and soot (carbon). Both contribute to global air pollution, which is a leading cause of respiratory and cardiovascular illness.</p> <p>The high temperatures experienced during the combustion of fossil fuels leads to the formation of oxides of nitrogen, which may contribute to the formation of photochemical smog and acid rain (refer to Page 19).</p> <p>The composition of coal and petroleum products are variable, but both contain sulfur impurities. On combustion, oxides of sulfur are formed, which may contribute to the formation of acid rain.</p>

Biofuels		Advantages
Reserves	Energy and feedstock	Biofuels are plentiful as they can be grown in relatively short periods of time to meet demands.
Production	Energy and feedstock	<p>Biofuels are renewable. Biofuels can be derived from traditional crops such as corn, sugar cane and oil seeds.</p> <p>Second-generation biofuels utilise non-food biomass produced as waste products from cropping or grasses not grown for food.</p> <p>Third-generation biofuels include algae, which are highly efficient at undergoing photosynthesis and produce a range of biofuel products.</p>
Energy density	Energy	Many biofuels provide energy densities comparable with traditional fossil fuels.
Products of combustion	Energy	Biofuels are often described as being carbon-neutral, as the emissions of carbon dioxide from combustion are offset by the absorption of carbon dioxide by biofuel crops and microbes during photosynthesis (plant growth).

Biofuels		Disadvantages
Production	Energy and feedstock	First-generation biofuel production competes directly with land used for agriculture, designated for food production. First and second-generation biofuels require vast areas of land.
Product of combustion	Energy	<p>Production and combustion of biofuels produce carbon dioxide, which contributes to global warming.</p> <p>Some forms of biodiesel produce higher concentrations of the oxides of nitrogen compared to traditional diesel fuel, contributing further to photochemical smog and acid rain.</p>
Infrastructure	Energy and feedstock	<p>There is currently limited production, distribution and use of biofuels.</p> <p>Very few manufacturers have motor vehicles in production, designed to run on high-concentration blends of biofuels.</p> <p>Infrastructure is not widespread for the production, distribution and use of biofuels.</p>

Science understanding

Renewable energy is generated over time scales of years to decades, from sources that are replenished much more quickly than fossil fuels.

Identify bioethanol, biodiesel, sunlight, and wind as renewable energy sources.

Compare the contributions of fossil fuels to global warming with those from renewable energy sources.

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Renewable energy sources

Renewable energy is energy that has been generated from natural renewable sources. **Renewable sources** include hydropower (including tidal), wind power, solar energy, geothermal energy and biomass fuels.

The raw materials required for energy production from renewable energy sources are generated in timescales (ranging from minutes to years) that are considerably shorter than those required for the formation of fossil fuels (millions of years). Therefore, renewable energy sources can be naturally replenished. When renewable sources are used, the demand for fossil fuels is also reduced.

Direct emissions from the use of renewable sources (apart from biofuels) do not significantly contribute to the production of greenhouse gases. However, the establishment, production, distribution and ongoing maintenance of technologies related to these energy sources generate a significant contribution to the release of greenhouse gases, which affects global warming.

Energy source	Renewable / non-renewable	Contribution to global warming
Fossil fuels	Non-renewable	Significant quantities of greenhouse gases are produced during the extraction, processing and burning of fossil fuels. Large quantities of carbon dioxide are emitted during the combustion of fossil fuels in electricity production and in the internal combustion engines of motor vehicles.
Biofuels	Renewable	Intensive farming practices rely on burning fossil fuels during the production, processing and transportation of crops and livestock. Biofuel production uses electricity derived from the combustion of fossil fuels. Greenhouse gases are emitted in the production, processing and combustion of biofuels. Some production of carbon dioxide is offset by the carbon dioxide absorbed during photosynthesis.
Hydropower (including tidal)	Renewable	Hydropower does not directly generate greenhouse emissions. However, construction of the plant and the distribution and maintenance of equipment and associated power networks uses energy derived from fossil fuels, thus contributing to atmospheric emissions of greenhouse gases and pollutants.
Wind	Renewable	Wind power does not directly generate greenhouse emissions. However, the production and maintenance of wind turbines and infrastructure require the input of energy derived from fossil fuels, thus contributing to atmospheric emissions of greenhouse gases and pollutants.
Solar	Renewable	Photovoltaic cells do not directly generate greenhouse emissions. However, the production, distribution and maintenance of solar arrays and associated power networks uses energy derived from fossil fuels, thus contributing to atmospheric emissions of greenhouse gases and pollutants.
Geothermal	Renewable	Greenhouse gases – methane and carbon dioxide (released from steam in groundwater) – are emitted directly into the troposphere when energy is harnessed from the Earth's crust. Drilling, the construction of the plant and the distribution and maintenance of equipment and associated power networks uses energy derived from fossil fuels, thus further contributing to greenhouse emissions.

Science understanding

Describe the production, from biological materials, of ethanol and biodiesel, including the writing of chemical equations for the reactions involved.

Explain how fossil fuels contribute more than biofuels to global warming.

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Bioethanol

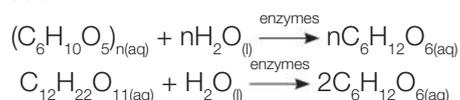
Bioethanol has been pursued as an alternative fuel source to reduce demands on dwindling supplies of petroleum, which is the raw material used to produce petroleum-based fuels. Ethanol is blended with petrol in varying ratios, or is used as a pure liquid in motor vehicles that have been designed to accommodate the fuel.

Bioethanol is produced from the action of microorganisms during **fermentation** of simple carbohydrates derived from natural vegetation. Ethanol is the product of enzyme-catalysed reactions occurring inside **yeast** (single-celled microorganism). Fermentation of the carbohydrate glucose is an anaerobic process and is represented by the equation below.



The production of carbon dioxide is observed as effervescence. Heat is generated as fermentation is an exothermic process.

Ethanol can be produced directly from plant sources containing simple carbohydrates (monosaccharides such as glucose or fructose) or indirectly from the hydrolysis of complex carbohydrates (polysaccharides such as starch and cellulose, or disaccharides such as sucrose). Polysaccharides and disaccharides undergo hydrolysis reactions to form monosaccharides prior to fermentation. This can be achieved through the action of enzymes (proteins) such as amylase and cellulase.



The ethanol content is limited by the types of yeast and enzymes present during fermentation. Higher concentrations of ethanol are obtained through fractional distillation (Figure 4.1.2).

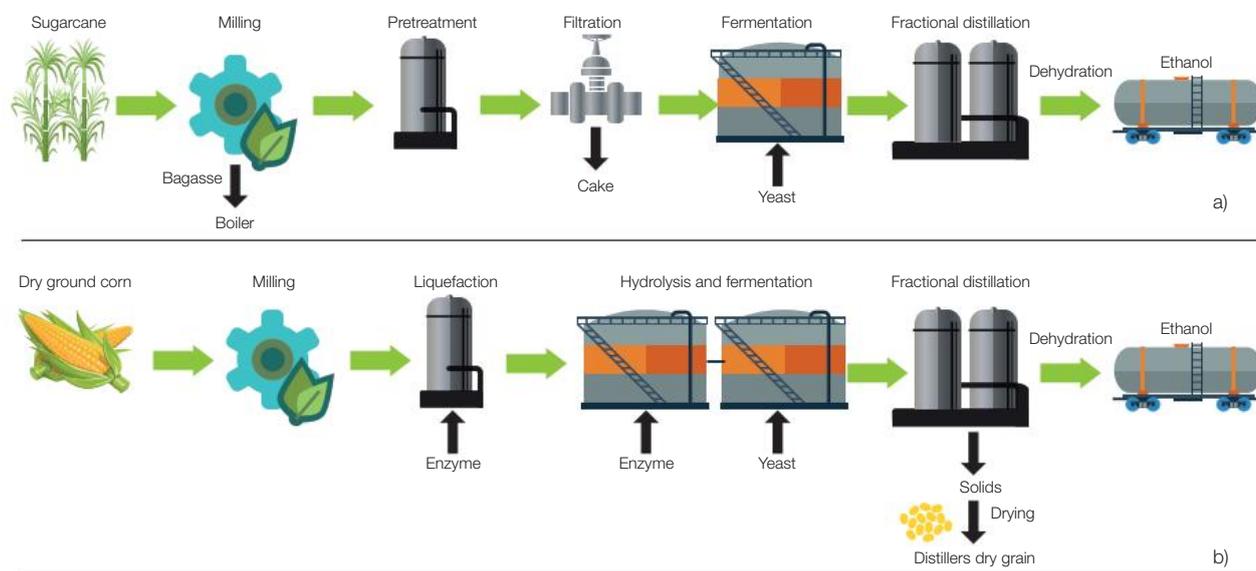


Figure 4.1.2: Stages in the production of bioethanol.

Biodiesel

Biodiesel has been pursued as an alternative to petroleum diesel derived from crude oil. As a renewable fuel source, biodiesel has the potential to reduce demands on traditional fossil fuels and is easily incorporated into diesel blends.

Biodiesel is a liquid biofuel derived from triglycerides including animal fats and oils from both plants and algae. Biodiesel is produced through the **transesterification** (conversion of the carboxylic acid present in one ester into another) of triglycerides (Figure 4.1.3). In the first stage of the process, methanol (CH_3OH) is mixed with a catalyst, typically a strong base such as sodium or potassium hydroxide (NaOH , KOH).

The resulting mixture is then reacted with a triglyceride. An esterification reaction occurs with the fatty acids (long-chain carboxylic acids) present in the triglyceride. The resulting products are the esters (fatty acid methyl esters) and glycerol (propane-1,2,3-triol).

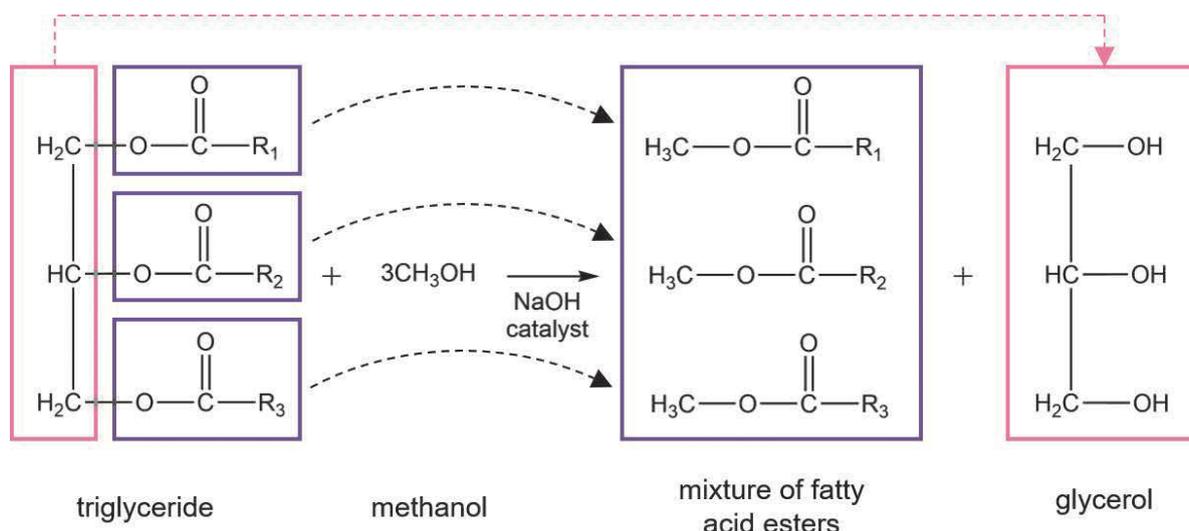
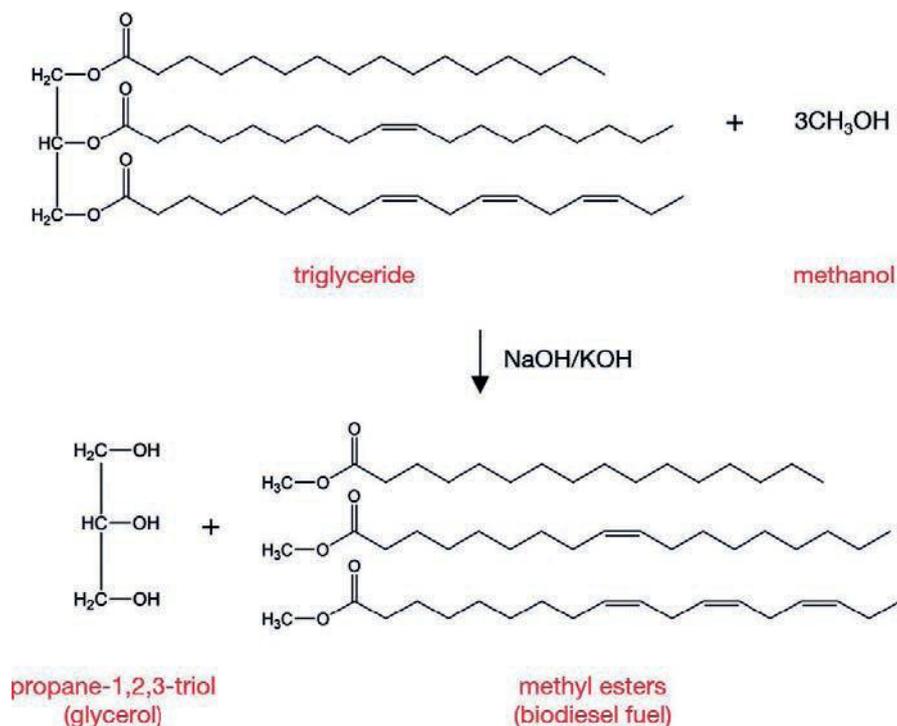


Figure 4.1.3: Production of biodiesel.

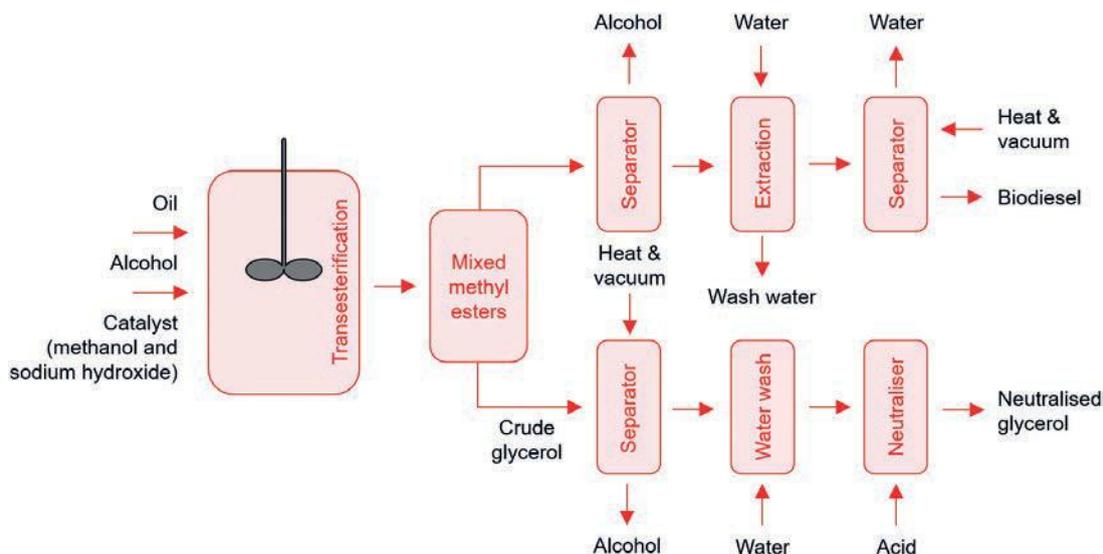
Example

The following triglyceride, found in canola oil as a waste vegetable oil, can be converted into biodiesel.



Question

2. Biodiesel can be produced according to the following industrial flowchart.



(a) A number of stages are undertaken during the production of biodiesel.

(i) **Identify** two raw materials used in the formation of biodiesel.

.....
 .. (2 marks) **IAE3**

(ii) Heat required for multiple stages may be supplied via the combustion of fossil fuels.

State one disadvantage of the addition of heat released from the combustion of fossil fuels.

.....
 .. (1 mark) **KA2**

(iii) Methanol is combined with a sodium hydroxide catalyst.

State and **explain** the effect of the addition of a catalyst on the rate of reaction.

.....

 (3 marks) **KA1**



- (b) The alcohols methanol and glycerol are by-products of the process. The structural formula and boiling point of methanol are given below.

Molecule	Structure	Boiling point (°C)
methanol	$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H} \end{array} $	64.7
glycerol	$ \begin{array}{ccccc} & \text{H} & \text{H} & \text{H} & \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{H} \\ & & & & \\ & \text{OH} & \text{OH} & \text{OH} & \end{array} $	290

- (i) **State** the systematic name of glycerol.

..... (2 marks) **KA4**

- (ii) During the washing phase, glycerol demonstrates a high degree of solubility.

Explain, with reference to the structure above, why glycerol is soluble in water.

.....

 (3 marks) **KA2**

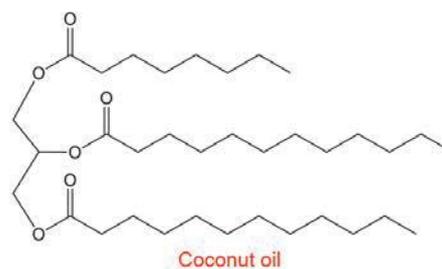
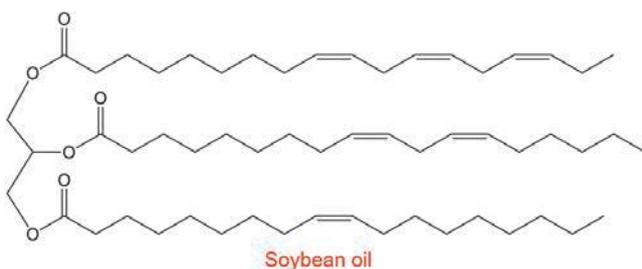
- (iii) Methanol and glycerol are able to be effectively separated using fractional distillation.

Explain how methanol and glycerol are able to be separated using fractional distillation.

.....

 (2 marks) **KA2**

- (c) Biodiesel produced from soybean oil and coconut oil can both be used as liquid fuels. The triglycerides present in both are shown in the diagram below.



- (i) **Circle** one ester functional group on the structure of soybean oil above. (1 mark) **KA1**

- (ii) **State** and **explain**, with reference to the structures above, which oil would be expected to have the higher melting point.

.....

 (3 marks) **KA2**

(iii) **Draw** two of the methyl esters formed between the fatty acids in soybean oil and methanol.

(4 marks) **KA4**

(iv) **State** one advantage of the production of biodiesel derived from soy beans.

.....
 (1 mark) **KA3**

(v) Raw coconut oil is used directly as a diesel substitute in some developing countries.

Suggest one reason why it is used in this raw form and not processed into biodiesel.

.....
 (1 mark) **KA3**

Science understanding

The complete combustion of fuels containing carbon and hydrogen produces carbon dioxide and water and energy. Write thermochemical equations for the complete combustion of fuels in which the only products are carbon dioxide and water.

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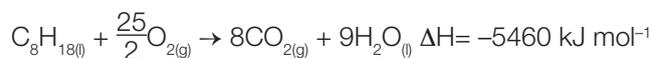
4

Complete combustion

Combustion is a reaction between a fuel and an oxidant (oxygen) that occurs at higher temperatures. Combustion is an exothermic process. The heat generated from combustion is harnessed in electricity production, industry, and transport applications.

Complete combustion occurs when there are enough moles of oxygen available to completely oxidise all carbon atoms (in the fuel) into carbon dioxide (CO₂).

For example, when fuels undergo combustion in an internal combustion engine, air and fuel are provided in a stoichiometric ratio that theoretically promotes complete combustion. 2,2,4-trimethylpentane (C₈H_{18(l)}) is one of the components of petrol that undergoes combustion. The complete combustion of the molecule is shown below.



Thermochemical equations

A thermochemical equation represents chemical change as well as the associated energy change for a chemical reaction. The four components of a thermochemical equation are identified below.

Component	Explanation
Correct species	The correct formulae for all reactants and products for the reaction must be included.
Fully balanced	A fully balanced chemical equation is required. (This may include non-integer values for balancing oxygen in combustion equations to represent the molar enthalpy for the combustion of one mole of the fuel.)
States of matter	Standard states of matter, (s) (l) (g) and (aq), are required for each species in the reaction.
Enthalpy change	The molar enthalpy change, ΔH, is included with a corresponding sign to express the energy change associated with the chemical reaction.

Example

1371 kJ of heat is released when one mole of bioethanol undergoes complete combustion.

Write a thermochemical equation for the complete combustion of ethanol.

Explanation	Step
Correct species	$\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
Fully balanced	$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
States of matter	$\text{C}_2\text{H}_5\text{OH}_{(l)} + 3\text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)}$
Enthalpy change	$\text{C}_2\text{H}_5\text{OH}_{(l)} + 3\text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)} \quad \Delta H = -1371 \text{ kJ mol}^{-1}$

Science understanding

Incomplete combustion, producing carbon (soot) and carbon monoxide, is more likely with longer-chain carbon-based fuels.

Explain why incomplete combustion is more likely with longer-chain carbon-based fuels than with shorter chains.

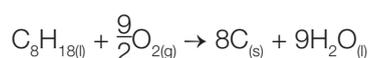
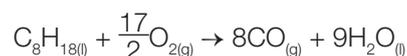
Discuss the undesirable consequences of incomplete combustion.

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Incomplete combustion

Incomplete combustion occurs when there are insufficient moles of oxygen available to completely oxidise all carbon atoms in the fuel. This results in products in partial oxidation states, such as carbon (C) and carbon monoxide (CO). Carbon dioxide, represents the maximum oxidation state for carbon (+4). Carbon and carbon monoxide represent partial oxidation states (0 and +2 respectively).

Incomplete combustion occurs during the combustion of fuels in industrial furnaces and internal combustion engines. For example, under varying load on an internal combustion engine, it is difficult to maintain the required stoichiometric ratio of fuel and oxidant to ensure complete combustion. In reality, the products of combustion include those of both complete and incomplete combustion.



Fuels that contain larger hydrocarbon molecules are more likely to form products of incomplete combustion in air. Air contains approximately 21% oxygen by weight. As the length of the hydrocarbon chain increases or the degree of unsaturation increases, the ratio of carbon to oxygen increases, limiting the oxygen available to form carbon dioxide. Larger molecules also experience stronger dispersion forces, resulting in a less volatile fuel with limited ability to mix effectively with gaseous molecules during combustion.



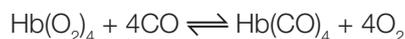
Figure 4.1.4: Bunsen flames produced during complete and incomplete combustion.

Products of incomplete combustion

The products of incomplete combustion are undesirable due to their impact on the built and natural environment.

Carbon monoxide

Carbon monoxide binds to haemoglobin (the molecule used to transport oxygen in the blood) and forms carboxyhaemoglobin. There is an equilibrium established in the body between oxygenated haemoglobin (HbO_2) and deoxygenated haemoglobin (Hb) as shown in the equation below. Carbon monoxide binds much more strongly than oxygen to haemoglobin, shifting the position of equilibrium to the right in favour of the formation of carboxyhaemoglobin.



The presence of carboxyhaemoglobin decreases the oxygen-carrying capacity of the blood, which limits the delivery and utilisation of oxygen in the body. Exposure to carbon monoxide at high concentrations can lead to significant toxicity in the human body. Exposure in low concentrations (100–200 ppm) can lead to fatigue and dizziness; exposure at high concentrations (2000–4000 ppm) can lead to loss of consciousness.

Soot

Soot is a complex aggregate of carbon nanoparticles and the bound products of incomplete combustion of fuels (Figure 4.1.5). Nanoparticles of soot (15–20 nanometres) released from these sources aggregate to form larger particles (80–100 nanometres). Soot primarily comes from the combustion of coal and biomass in power stations, coke in furnaces, and fossil fuels in internal combustion engines. Burning diesel fuel in motor vehicles is a major source of soot emissions.

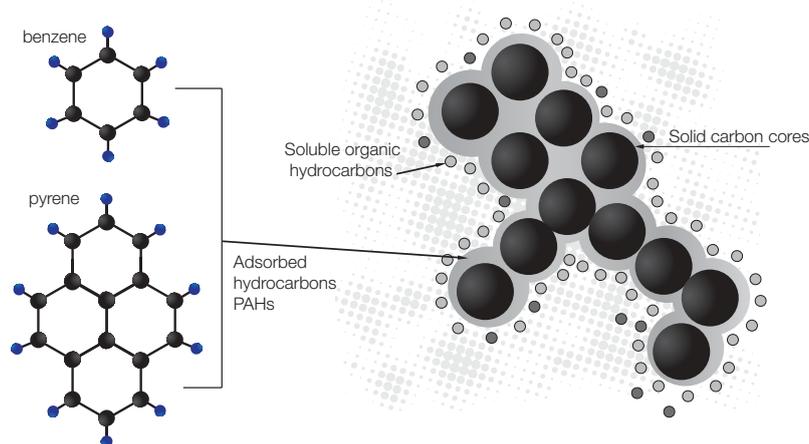


Figure 4.1.5: Soot aggregate.

Soot can limit visibility in urban areas and blackens surfaces causing **visual pollution**. Soot deposits on the surface of buildings and natural vegetation. When soot covers the leaves of plants it limits photosynthesis, leading to poor growth.

When inhaled as a fine airborne particulate, soot can lead to decreased respiratory function in humans and animals. Nanoparticles of soot can penetrate deep into the alveoli of the lungs (the lungs can only remove particles greater than approximately 200 nanometres in size), causing respiratory issues such as acute bronchitis and aggravated asthma. Long-term exposure to soot increases the risk of cardiovascular disease.

Concerns have also been expressed about the absorption of **carcinogens** (cancer-causing compounds) present on the surface of carbon such as **polycyclic aromatic hydrocarbons** (PAHs) and the toxicity of metal oxides containing arsenic, cadmium and chromium. Chemical pollutants accumulate on the surface of soot particles, which transport them to the lungs and eventually the bloodstream.

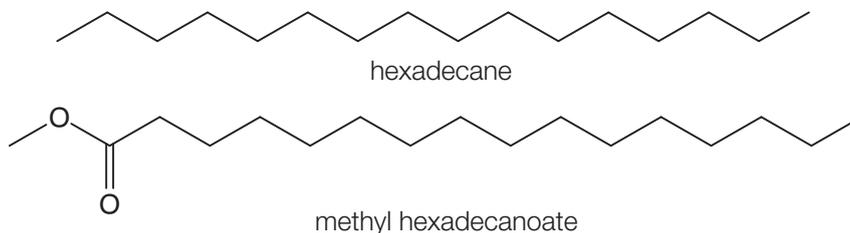
Soot particles are known to have considerable impact upon climate. Black carbon in soot is a major contributor to climate change through global warming (second only to carbon dioxide). Black carbon absorbs solar radiation at all wavelengths causing localised warming in the troposphere and on the surface of the Earth. This is of particular concern in the Arctic region where soot deposits increase the rate of melting and loss of Arctic ice and snow and the associated albedo (refer to Page 1).

Soot is also associated with the formation of high-altitude cirrus clouds in the troposphere. Soot particles provide sites for the formation of ice crystals. Increased cloud cover leads to greater reflectivity of solar radiation, cooling the Earth.

Question

3. Many modern motor vehicles use direct injection diesel engines (fuel is injected into the combustion chamber). Direct injection engines offer greater efficiency and power, and produce fewer pollutants in exhaust emissions.

- (a) Petroleum diesel contains hydrocarbons in the range of 8–21 carbon atoms. Hexadecane ($C_{16}H_{34}$), a component of petroleum diesel, and methyl hexadecanoate, a component of biodiesel, are shown below.



- (i) Hexadecane exists as a liquid at room temperature (25°C).

Explain, in terms of intermolecular forces, why hexadecane is a liquid at this temperature.

.....

 (2 marks) **KA1**

- (ii) **Determine** the molecular formula of methyl hexadecanoate.

..... (2 marks) **IAE3**

- (iii) The enthalpy of combustion of hexadecane is $-10701 \text{ kJ mol}^{-1}$.

Write a thermochemical equation for the complete combustion of hexadecane.

(4 marks) **KA4**

- (iv) **State** and **explain** whether each molecule of hexadecane would require more or fewer molecules of oxygen than methyl hexadecanoate to achieve complete combustion.

.....

 (2 marks) **IAE3**

- (v) Diesel is commonly recognised as containing hydrocarbons in the range of 8–21 carbons, while petrol is commonly recognised as containing 4–12 carbons.

Suggest why products of incomplete combustion are more common during the use of diesel as a fuel in motor vehicles when compared to the use of petrol.

.....

 (2 marks) **KA3**

Science understanding

The energy released in combustion of fuels can be determined experimentally.

Use experimental data to determine the enthalpy of combustion of a fuel.

Undertake thermochemical calculations involving enthalpy changes and temperature changes of a specified mass of water given the necessary data.

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Enthalpy of combustion

The combustion of fuels results in a net release of energy (exothermic reaction). The energy released by a quantity of fuel can be determined experimentally.

Molar enthalpy of combustion

The **molar enthalpy of combustion** (ΔH_{comb}) represents the quantity of heat released per mole of fuel that undergoes complete combustion. The temperature change can be measured and recorded for the heat released from the combustion of a measured mass of fuel to a known volume of water.

Quantity	Description	Units
Q	Quantity of heat transferred	J
ΔH	Molar enthalpy of combustion	kJ mol^{-1}
m	Mass of water (or liquid) heated (1g = 1mL)	g
c	Specific heat capacity of the liquid	$\text{J g}^{-1} \text{ } ^\circ\text{C}^{-1}$
ΔT	Temperature change of the liquid	$^\circ\text{C}$
n	Moles of fuel that have undergone combustion	mol

The quantity of **heat** released in a combustion reaction is calculated using the expression:

$$Q = m \times c \times \Delta T \text{ (J)}$$

Example

Coal-fired power stations transform chemical energy (from combustion of coal) into electrical energy. 0.127 g of black coal was burnt and used to heat 100 mL of water. The temperature of the water increased from 18.3°C to 24.9°C. It is assumed that all heat from the reaction is transferred to the 100 mL volume of water. Calculate the heat released, in kJ, for the total mass of coal burnt and the heat energy released, per gram. (Specific heat capacity of water $c = 4.18 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$.)

Explanation	Step
Calculate the change in temperature (ΔT).	$\Delta T = 24.9 - 18.3 = 6.6^\circ\text{C}$
Substitute the quantities into the equation, where (m) is the mass of water equal to the volume and (c) is the heat capacity provided for the liquid heated.	$Q = m \times c \times \Delta T$ $Q = 100 \times 4.18 \times 6.6$
Apply units to the answer.	$= 2758.8 \text{ J}$ $= 2.76 \text{ kJ}$
Calculate per g by dividing by the mass of coal burnt.	$= \frac{2758.8}{0.127}$ $= 21.7 \text{ kJ g}^{-1}$

The **molar enthalpy of combustion** can be determined using:

$$\Delta H = \frac{m \times c \times \Delta T}{1000 \times n} \text{ (kJ mol}^{-1}\text{)}$$

Example

Brazil is a world leader in the production and use of biofuel, having generated a sustainable industry of bioethanol production from sugarcane for many years. Some cars in Brazil have been designed to run on E100, a fuel consisting of pure ethanol.

The molar enthalpy of combustion of ethanol was investigated through the use of a spirit burner containing ethanol. The burner was ignited under a 100 mL volume of water contained in an aluminium can and allowed to burn until the temperature increased by 20.0°C. The mass of the spirit burner decreased by 120.73 g to 120.21 g. (Specific heat capacity of water $c = 4.18 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$.)

Calculate the experimental enthalpy of combustion for ethanol.

Explanation	Step
Calculate the change in mass for the fuel.	$\begin{aligned} \Delta m &= m_{\text{initial}} - m_{\text{final}} \\ &= 120.73 - 120.21 \\ &= 0.520 \text{ g} \end{aligned}$
Calculate the moles of fuel combusted from the change in mass recorded.	$\begin{aligned} M(\text{C}_2\text{H}_5\text{OH}) &= (2 \times 12.01) + (6 \times 1.008) + 16.00 \\ M(\text{C}_2\text{H}_5\text{OH}) &= 46.068 \\ n &= \frac{m}{M} \\ &= \frac{0.52}{46.068} = 0.0113 \text{ mol} \end{aligned}$
Substitute the quantities, mass of water heated, change in temperature and constant into the equation for molar enthalpy of combustion. Apply units for the molar enthalpy, including the sign of the enthalpy change.	$\begin{aligned} \Delta H &= \frac{m \times c \times \Delta T}{1000 \times n} \\ \Delta H &= \frac{100 \times 4.18 \times 20.0}{1000 \times 0.0113} \\ &= -740 \text{ kJ mol}^{-1} \text{ (3 sig. fig)} \end{aligned}$

Molar enthalpy and heat energy are associated through the following equations:

$$\Delta H = \frac{Q \text{ (kJ mol}^{-1}\text{)}}{n \text{ (mol)}}$$

$$\therefore Q = n \times \Delta H \text{ (kJ)}$$

A rearrangement of the equation for molar enthalpy may also be used to determine the temperature change:

$$\Delta T = \frac{\Delta H \times 1000 \times n}{m \times c} \text{ (}^{\circ}\text{C)}$$

Questions

4. Coke is a fuel with a high carbon content, often derived from coal or crude oil. It is widely used in the production of iron from the mineral haematite, in a blast furnace.

(a) Coke, predominantly carbon, is used as a fuel and to generate the reducing agent carbon monoxide. A range of reactions occur with carbon in the blast furnace, two of which are considered below.

The **complete** combustion of coke can be represented by the equation below.



Incomplete combustion also occurs during the combustion of coke.



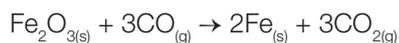
(i) **Calculate** the energy, in kJ, released when 5.00 tonne (1 tonne = 10^6 g) of coke is reacted with oxygen if 100% of the coke is oxidised to carbon dioxide.

(4 marks) **KA4**

(ii) **Calculate** the energy, in kJ, released when 5.00 tonne of coke is reacted with oxygen if 80% of the coke is oxidised to carbon dioxide and the remaining 20% is oxidised to carbon monoxide.

(5 marks) **KA4**

(b) Haematite (Fe₂O₃) is reduced to molten iron in the blast furnace.



(i) **Assign** oxidation numbers to carbon in the equation and hence **state** why carbon monoxide is the reducing agent.

.....
 (3 marks) **KA1**

(ii) The annual production of iron is 959 Mt (megatonne) globally.

Calculate the mass, in kg, of carbon dioxide released during production.

(5 marks) **KA4**

(c) Exposure to coke furnace emissions occurs for workers in the steel industry. Emissions from coke furnaces include soot and compounds containing benzene (polycyclic aromatic hydrocarbons, PAHs).

(i) **Describe** the dangers associated with the inhalation of PAHs contained in soot.

.....

 (2 marks) **KA2**

(ii) Regulations have been set by the EPA to limit the exposure to PAHs in the work environment to 0.150 ppm over an 8-hour shift. The average adult inhales and exhales 8 L of air per minute.

Calculate the mass, in mg, of PAHs inhaled into the lungs at this upper limit over an 8-hour period.

(2 marks) **KA4**



5. Bushwalkers used liquid fuel to heat a Trangia stove for cooking. The liquid fuel contained 95% ethanol and 5% methanol. A pot of water of 500 mL volume was heated from 21.0 °C using the liquid fuel. Molar enthalpy of combustion for the fuels is shown below.

Fuel	%	Molar mass (g mol ⁻¹)	Molar enthalpy (kJ mol ⁻¹)
methanol	5%	32.04	-715.0
ethanol	95%	46.07	-1371

- (a) Only 5.00 g of fuel remained in the Trangia.
 (i) **Calculate** the total number of moles of liquid fuel combusted according to the ratio indicated.

(6 marks) **KA2**

- (ii) **Calculate** the maximum temperature that can be obtained from the combustion of 5.00 grams of the liquid fuel. (Specific heat capacity of water $c = 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.)

(6 marks) **KA2**

- (b) **Suggest** two reasons why the temperature of the water was much lower than the calculated value.

.

 (2 marks) **IAE4**

Experimental determination of the enthalpy of combustion

Energy changes associated with combustion reactions can be measured experimentally. **Calorimetry** is the measurement of the energy changes associated with a chemical reaction. It is a measure of the heat transfer during a chemical reaction or change of state.

Simple calorimeter

A simple calorimeter is typically an insulated reaction vessel with a thermometer used to measure associated energy changes. However, during the combustion of a fuel, a thermometer (or temperature probe) is used to measure the temperature change associated with the heat energy imparted to a volume of water. Due to the nature of combustion, limited thermal insulation can be applied to the apparatus (Figure 4.1.6).

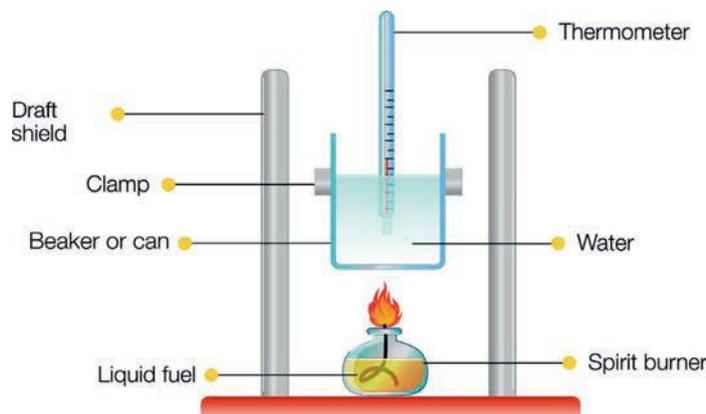


Figure 4.1.6: Simple calorimeter for measuring the enthalpy of combustion.

Determination of the enthalpy of combustion using a simple calorimeter

- A spirit burner containing a liquid fuel is weighed initially and the mass (m_{initial}) recorded.
- A known mass (hence volume) of distilled water is transferred to a metal can (or beaker). (The density of pure water is 1 g mL^{-1} therefore, 1 mL of water has a mass of 1 g .)
- A thermometer is introduced to the can and the initial temperature (T_{initial}) of the water is recorded.
- The spirit burner is placed under the mass of water. The wick of the burner is ignited. Heat flows from the burner to the mass of water, thus increasing the water temperature. The final temperature obtained is recorded (T_{final}) and the flame extinguished.
- The spirit burner is reweighed and the final mass (m_{final}) recorded. The associated loss in mass represents the change in mass (Δm) and is used to calculate the number of moles (n) of fuel combusted.
- Using the specific heat capacity of water (c) as a given constant, the heat energy or molar enthalpy is calculated.

? Science inquiry skills

Skills in context

Limitations in the experimental design

There are several limitations in the experimental design (many linked directly to assumptions that have been applied) that lead to obtaining values which are considerably lower than literature values.

Random errors

Slight variation occurs in human measurements of volume, mass and temperature. Small quantities of the volatile liquid fuel evaporate from the wick prior to lighting or after extinguishing the flame, when initial and final measurements of mass are taken. Slight variations in the positioning of the wick and burner may lead to inconsistent heat transfer.

Systematic errors

The first assumption made is that all heat released from the fuel is transferred to the water (Conservation of energy), with no external transfer of heat.

The can or beaker offers very little thermal insulation; therefore a great deal of heat is lost from the system to the external surroundings or absorbed by the apparatus, lowering the maximum temperature achieved.

The second assumption is that combustion is complete. (The molar enthalpy of combustion obtained through experiment is compared with an accepted literature value for the complete combustion of fuel.)

The liquid fuel is burnt in air and, depending on the size of the hydrocarbon molecules, combustion is unlikely to be complete, with insufficient oxygen leading to incomplete combustion and lower energy values being obtained. Less energy is released during incomplete combustion and energy is absorbed by the large component of nitrogen molecules present in the air.

The third assumption is that the thermometer and water have had sufficient time to reach thermal equilibrium before a measurement is taken and before the system begins to return to its original temperature.

To obtain a suitable temperature rise, the fuel typically undergoes combustion for a period of minutes. During this time, heat energy is lost to the surroundings outside of the calorimeter, allowing the water to begin to return to its original temperature. A lower final temperature results.

Bomb calorimeter

A bomb calorimeter (Figure 4.1.7) is a carefully engineered closed system that is used to efficiently and accurately obtain enthalpy values for the combustion of liquid and solid fuels. The values obtained from a bomb calorimeter offer high levels of accuracy when compared to literature values for the enthalpy of combustion. Bomb calorimetry is used to determine the enthalpy of combustion of fuels. Bomb calorimetry is also commonly used to determine the energy values quoted for many foods.

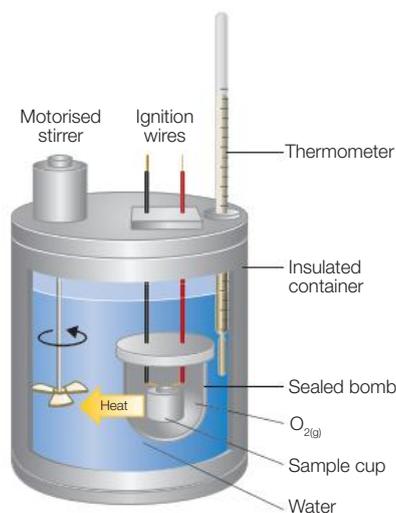


Figure 4.1.7: Bomb calorimeter.

Determination of the enthalpy of combustion using a bomb calorimeter

- A liquid or solid (crushed in a mortar and pestle) sample of the fuel of a predetermined mass is weighed and added to the sample cup that sits in the hanger.
- A fuse is set and the apparatus is lowered into the steel body and sealed.
- Air is displaced from the bomb through the introduction of pure oxygen.
- The bomb is lowered into a volume of water in an insulated vessel, with a stirrer and temperature probe.
- The bomb is ignited, and combustion of the fuel occurs instantly.
- Heat energy from the bomb slowly enters the surrounding water and the maximum temperature achieved is recorded.
- The molar enthalpy can be calculated using the calibration from a compound with a known molar enthalpy of combustion.

? Science inquiry skills

Skills in context

Improvements

The bomb calorimeter offers several improvements over a simple calorimeter.

The fuel undergoes combustion in pure oxygen, which generates complete combustion of all the available fuel.

As water surrounds the bomb, heat exiting the bomb moves directly into the water, with very little being retained by the stainless-steel bomb. The sealed container is close to achieving a closed system. The energy from the ignition wire is even accounted for.

The stirrer and adequate insulation ensure that a reliable measurement of the increase in water temperature can be obtained with a calibrated temperature probe.

4

Question

6. Octane ratings, often expressed as RON (research octane number), are provided for common fuels sold at petrol stations as a standard measure of the performance of a fuel. High-performance engines require the use of fuels with higher octane ratings (typically 95 and above).
- (a) The octane rating is a number that is determined by comparing the combustion of the fuel against mixtures of 2,2,4-trimethylpentane and heptane in differing ratios.
- (i) **Draw** the structural formula of 2,2,4-trimethylpentane.

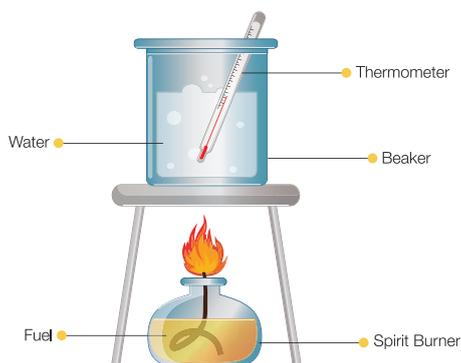
(2 marks) **KA4**

- (ii) The molar enthalpy of combustion of pure hexane is $-4163 \text{ kJ mol}^{-1}$.

Write a thermochemical equation for the complete combustion of hexane.

(4 marks) **KA4**

- (b) The molar enthalpy of combustion of 2,2,4-trimethylpentane (C_8H_{18}) and heptane (C_7H_{16}), both found in fuels, can be determined experimentally.
- (i) A simple calorimeter can be used to gain an approximation of the values. The apparatus below was used for the approximation.



The following data was collated during the investigation.

Fuel	C_8H_{18}	C_7H_{16}
Mass of water (g)	100	100
Initial mass of spirit burner (g)	136.20	134.70
Final mass of spirit burner (g)	135.76	134.27
Initial temperature ($^{\circ}C$)	21.0	21.0
Final temperature ($^{\circ}C$)	41.0	41.0
Specific heat capacity ($J\ g^{-1}\ ^{\circ}C^{-1}$)	4.18	4.18

- (1) **Calculate** the moles of each fuel that underwent combustion.

(6 marks) **KA4**

- (2) **Calculate** the molar enthalpy of combustion for each fuel using the data provided in the table.

(6 marks) **KA4**

Science understanding

Fuels, including fossil fuels and biofuels, can be compared in terms of their energy output and the nature of products of combustion.

Calculate the quantities of heat evolved per mole, per gram, and per litre (for liquids) for the complete combustion of fuels.

Compare fuels given appropriate data.

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Specific energy and energy density of fuels

When selecting and evaluating the effectiveness of fossil fuels and biofuels, many factors are considered, including viscosity, melting and boiling points, the products of combustion, specific energy and energy density.

Specific energy ($\frac{\Delta H}{M}$) represents the heat released per gram of fuel, whereas **energy density** ($\frac{\Delta H}{M}$) $\times \rho$ represents energy released per litre of fuel undergoing combustion.

Both quantities are of interest in transport applications, where liquid fuels have to be stored in the vehicle. It is more economical to generate larger quantities of energy per gram or litre of fuel stored and combusted in the internal combustion engine of a motor vehicle. A vehicle is able to travel further on each litre of fuel consumed, which leads to greater efficiency. The molar enthalpy of combustion and energy density are considered for a range of fuels below.

Fuel	Source	Molar mass (g mol ⁻¹)	Density (g L ⁻¹)	Heat energy released		
				Molar enthalpy	Specific energy	Energy density
				kJ mol ⁻¹	kJ g ⁻¹	kJ L ⁻¹
methane CH ₄	natural gas	16.04		891	55.55	
propane C ₃ H ₈	liquid petroleum gas (LPG)	44.10		2220	50.34	
ethanol C ₂ H ₅ OH	bioethanol	46.07	789	1371	29.75	23475
octane C ₈ H ₁₈	petrol	114.2	703	5530	48.42	34042
hexadecane C ₁₆ H ₃₄	diesel	226.5	775	10701	47.25	36615
methyl linoleate C ₁₇ H ₃₁ COOCH ₃	biodiesel	294.5	889	11690	36.69	35288

Energy conversions

Conversions are undertaken between molar enthalpy, specific energy and energy density to allow comparisons between fuels.

$$\frac{\text{kJ}}{\text{mol}} \div M \frac{\text{kJ}}{\text{g}} \times \rho \frac{\text{kJ}}{\text{L}}$$

$$\frac{\text{kJ}}{\text{L}} \div \rho \frac{\text{kJ}}{\text{g}} \times M \frac{\text{kJ}}{\text{mol}}$$

Where ρ = the density of the fuel in g L⁻¹.

Question

7. Methanol, ethanol, E85 (a blend of 85% ethanol), and petrol were compared in terms of energy density, specific energy and molar enthalpy. Selected data is shown below.

Fuel	Molar mass (g mol ⁻¹)	Density (g L ⁻¹)	Energy density	Specific energy	Molar enthalpy
			(kJ L ⁻¹)	(kJ g ⁻¹)	(kJ mol ⁻¹)
methanol	32.04	792			-715.0
ethanol	46.07	789	23475		
E85	mixture	770–790	25650	33.20 (determined experimentally)	
petrol	mixture	720–760	34800	47.30 (determined experimentally)	

- (a) Some forms of motorsport burn pure liquid methanol or blends of ethanol as a fuel.

(i) **Write** a thermochemical equation for the complete combustion of methanol.

(4 marks) **KA4**

(ii) **Calculate** the energy density, in kJ L⁻¹, and specific energy, in kJ g⁻¹, for methanol and input these values into the table.

(4 marks) **KA4**

(iii) One of the problems associated with fuels containing alcohols is the miscibility of water in the fuel which can lead to corrosion in the engine.

Explain, with the aid of a labelled diagram, the solubility of water and methanol.

.....

 (3 marks) **KA1**

- (b) Ethanol blends are being introduced to petrol stations and sold alongside traditional fuels.
- (i) **Calculate** the specific energy in kJ g^{-1} and molar enthalpy in kJ mol^{-1} for ethanol to complete the table for this fuel.

(4 marks) **KA4**

- (ii) Compare the energy densities of ethanol and petrol.

Discuss one implication of the energy density of these fuels for the use of blended fuels with a high concentration of ethanol in transport applications.

.....

.....

.....

..... (2 marks) **IAE3**

- (iii) **State** and **explain** one environmental advantage of using fuels blended with bioethanol.

.....

.....

.....

..... (2 marks) **KA2**

Science understanding

Although most electricity is generated using fuels to drive steam turbines, electrical energy can be also be generated using photovoltaic cells (known as solar cells) and directly from oxidation of fuels using galvanic cells.

State the advantages and disadvantages of direct electricity generation (photovoltaic and fuel cells) compared to using steam turbines.

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Electricity generation from steam turbines

Steam turbines are used to generate electricity. Over 90% of Australia's electricity production currently comes from combustion of coal and natural gas. These fossil fuels undergo combustion, heating water to produce high pressure steam to drive turbines. The turbine is linked to a generator to produce electricity (Figure 4.1.8).

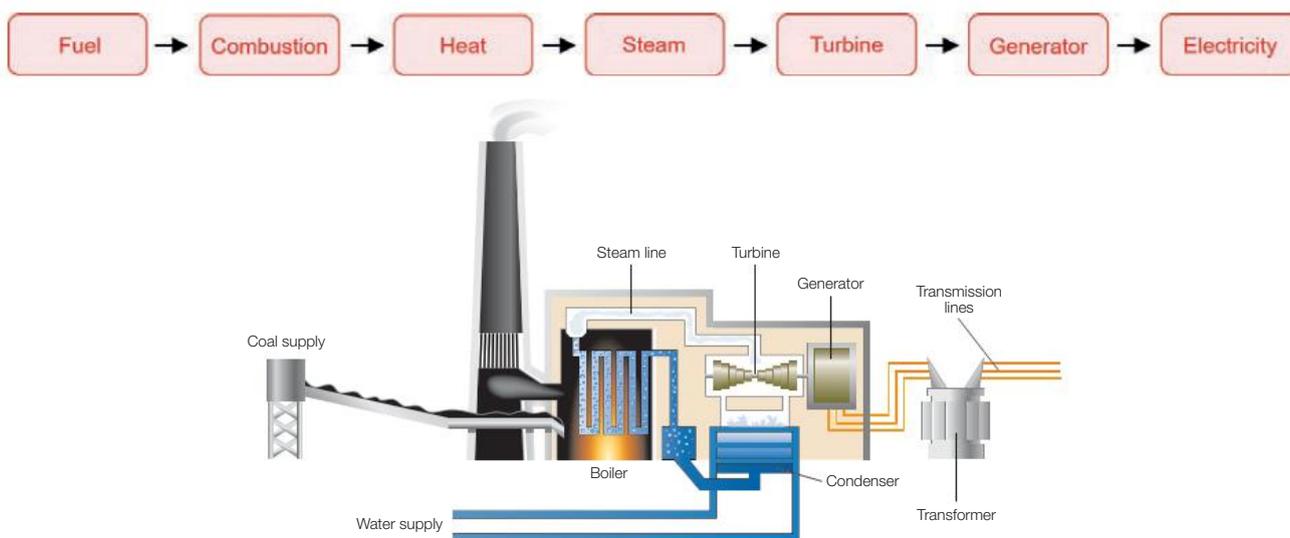


Figure 4.1.8: Conversion of coal to electricity.

Burning coal and natural gas in power stations releases vast quantities of carbon dioxide into the atmosphere and oceans. Atmospheric pollutants are also formed from the release of oxides of sulfur and nitrogen. Heated water from power stations can also be released to local marine environments, thus affecting surrounding ecosystems.

Electricity generation from photovoltaic cells

Photovoltaic cells convert sunlight directly into electricity. Photovoltaics use semiconductor materials to allow electrons to absorb photons of light and shift them from the semiconductor to generate a current (Figure 4.1.9). Photovoltaic cells produce no pollution during operation. There are, however, considerable carbon emissions associated with the production of photovoltaic cells.

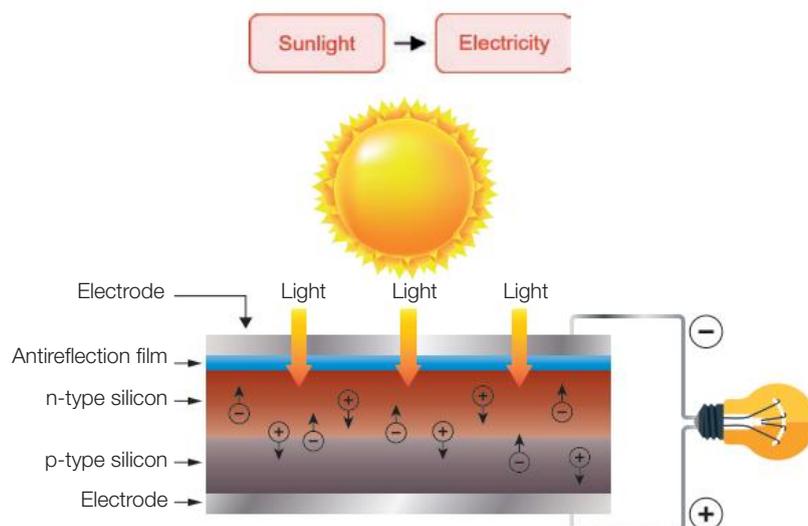


Figure 4.1.9: Conversion of sunlight to electricity.

Science understanding

Fuel cells, including flow cells, are galvanic cells in which the electrode reactants are available in continuous supply.

State the advantages and disadvantages of fuel cells compared with other galvanic cells.

Identify the anode and cathode and their charges, as well as the direction of ion and electron flow, in a fuel cell, given sufficient information.

Write electrode half-equations for a fuel cell given sufficient information.

Discuss the advantages of flow cells compared with other fuel cells.

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Electricity production and storage in electrochemical cells

Galvanic cells

Galvanic cells (also known as **voltaic cells**) are electrochemical cells that rely on spontaneous redox reactions to generate a flow of current. Chemical energy is converted into electrical energy during the redox reaction when an electrical circuit is connected (Figure 4.1.10).

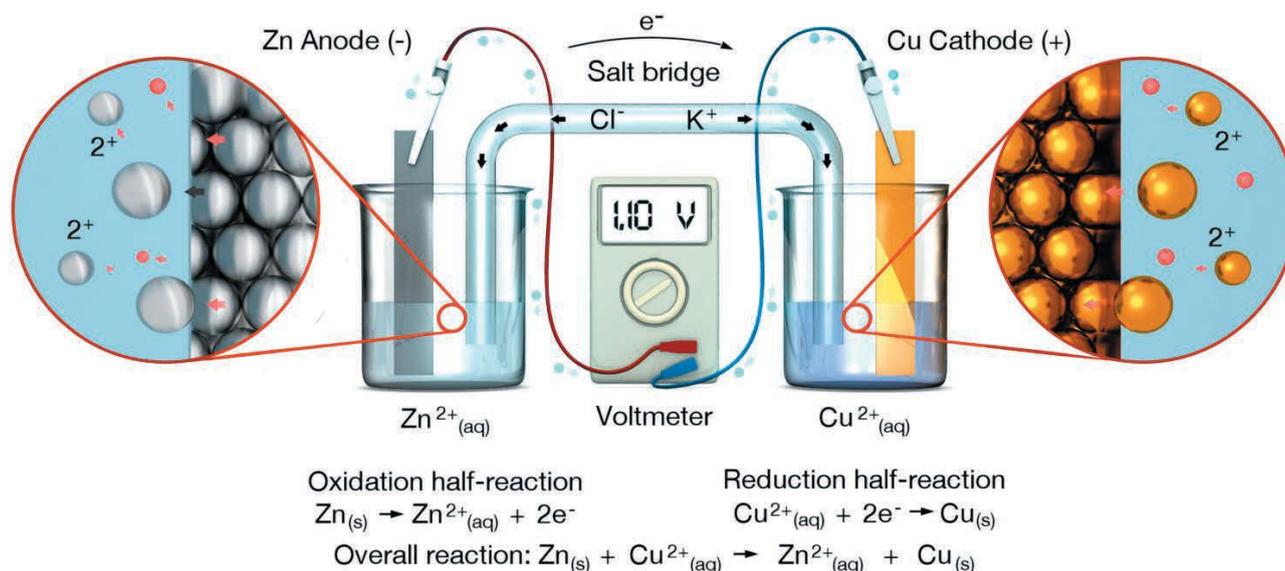


Figure 4.1.10: Simple zinc-copper galvanic cell

The operation of a galvanic cell can be summarised as follows.

Galvanic cell	
Energy conversion	Chemical energy to electrical
Anode reaction	Oxidation
Cathode reaction	Reduction
Electron flow	Anode to cathode
Sign of anode	Negative (-)
Sign of cathode	Positive (+)
Anion movement	Anode
Cation movement	Cathode

Fuel cells

A **fuel cell** is also a galvanic cell. A fuel cell differs from galvanic cells in that typically a fuel and oxidant are in continuous supply.

In a conventional galvanic cell or **battery** (group of cells), the oxidiser and reducer are stored in the cell and are consumed during operation until it is discharged. In a **primary cell**, one or more reactants become depleted and the cell or battery is disposed of. **Secondary (rechargeable) cells** and batteries have the ability for the redox reactions to be reversed, effectively reforming the reactants. Secondary cells can be recharged for many cycles; however, the regeneration of reactants is less effective over time.

A fuel cell does not require the **oxidiser** and **reducer** to be stored or regenerated. Fuels such as hydrogen and methanol are fed directly into the cell. The oxidant, often simply oxygen from the air, is also drawn into the cell. Oxidation of the fuel at the anode and reduction of the oxidant at the cathode generates a flow of electrons through an external circuit. Electrode reactions are promoted by a metal catalyst. A solid electrolyte or selective membrane separates the electrodes and associated oxidiser and reducer.

There are many types of fuel cells, often defined by the material used as the fuel or electrolyte.

Type of fuel cell	Operating temperature (°C)	Electrolyte	Fuel
Proton exchange membrane fuel cell – PEMFC	40–90	polymer	hydrogen
Alkaline fuel cell – AFC	40–200	potassium hydroxide	hydrogen
Direct methanol fuel cell – DMFC	60–130	polymer	methanol
Phosphoric acid fuel cell – PAFC	200	phosphoric acid	hydrogen
Molten carbonate fuel cell – MCFC	650	molten carbonate	methane, hydrogen, carbon monoxide
Solid oxide fuel cell – SOFC	600–950	solid oxide	methane, hydrogen, carbon monoxide

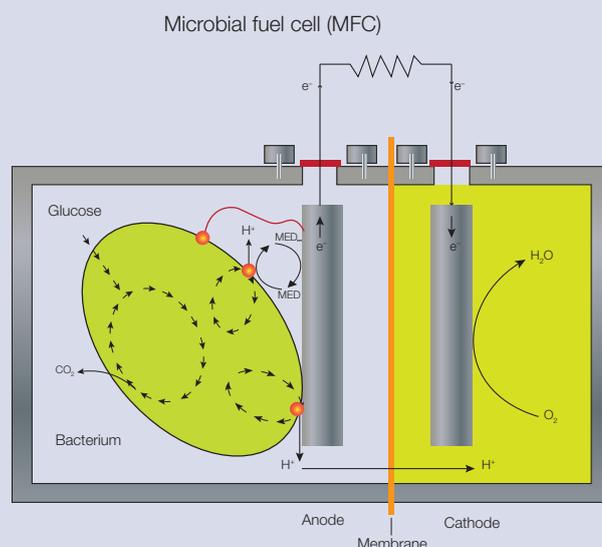
4

Science as a human endeavour

Microbial fuel cell (MFC)

Microbial or biological fuel cells generate electrical currents using bacteria and the reactions they undertake in nature. MFCs convert chemical energy to electrical energy by the action of microorganisms. A membrane separates the anode and cathode. Electrons generated during oxidation are either transferred directly through the anode material or commonly through a mediator (a chemical species that transfers electrons from the bacteria).

MFCs provide low power and current so have limitations in their current proposed applications. They do, however, offer the advantage of having components inside the cell that are completely biodegradable. For this reason, they are being considered for powering biosensors and generating electricity from wastewater disposal.



Example

A **proton exchange membrane (PEM) fuel cell** uses the supply of hydrogen gas as a fuel and oxygen from the air as an oxidiser. Each cell generates a low voltage that is dependent on the identity of both the fuel and the oxidiser. When combined in stacks as batteries, the cells are able to power devices in wide and varied applications. They have been used in electronics during space missions and have shown promising potential to drive electric motors to propel vehicles.

Hydrogen is fed into the anode half-cell as the fuel. Hydrogen undergoes oxidation on the surface of the porous anode, assisted by the presence of a metal catalyst (typically platinum). Protons (hydrogen ions) are able to migrate from the anode half-cell to the cathode half-cell through a selective proton exchange membrane. Electrons that are unable to pass through the membrane can flow through the external circuit; this generates a current. The electrons combine with hydrogen ions and oxygen molecules at the cathode, reducing the oxygen to water. As a waste product of the reduction reaction, water can be released from the cell (Figure 4.1.11).

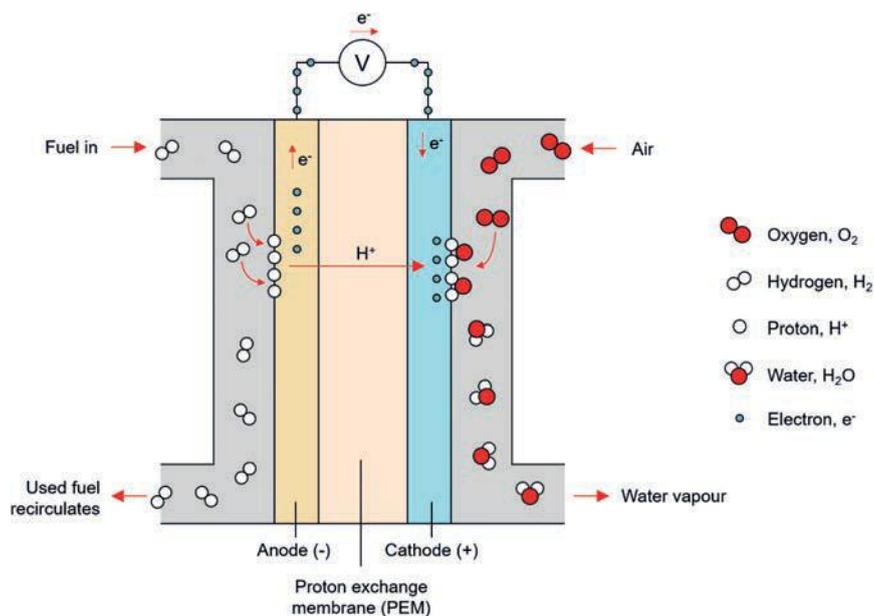


Figure 4.1.11: PEM fuel cell.

Cell reactions

Discharging (galvanic)

Anode (-)	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
Cathode (+)	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$
Overall	$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

Fuels cells, as an emerging technology, offer a range of advantages and disadvantages when competing against established technologies.

Advantages

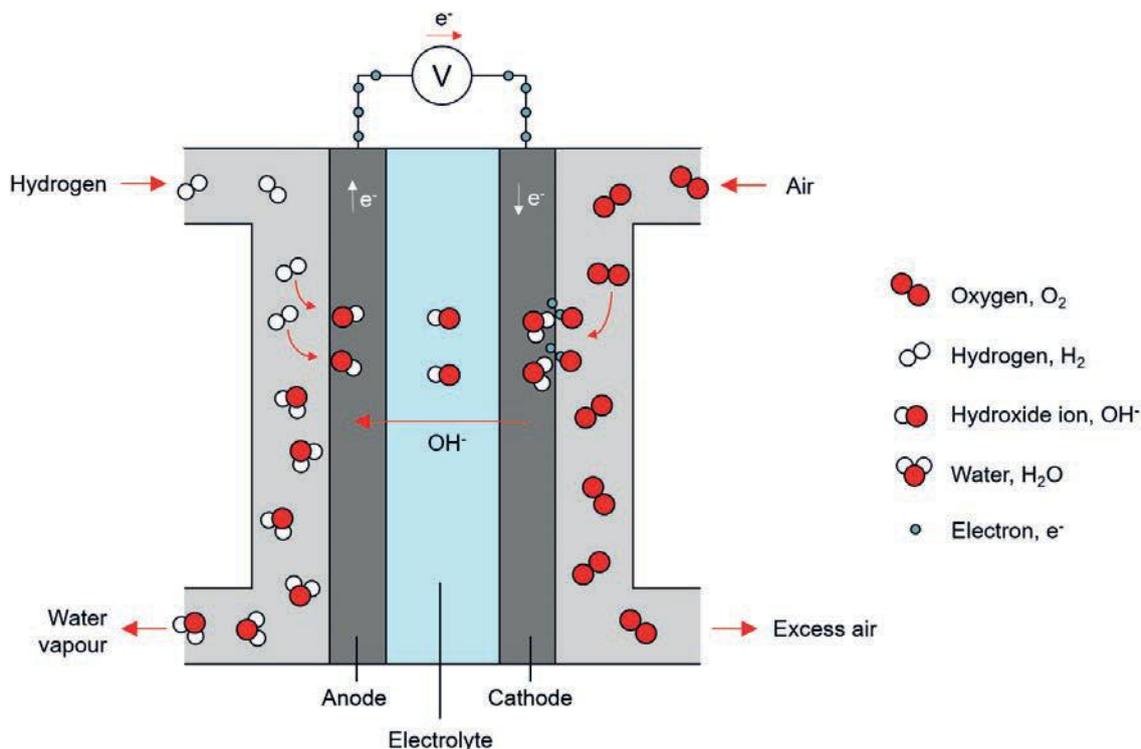
In comparison to conventional galvanic cells

- Hydrogen is abundant as a fuel source, obtained easily from water and hydrocarbons. Other fuels, such as methanol, are commonly available and renewable.
- Components in the cell do not need to be regenerated if high-quality fuels are used. The cell can operate almost indefinitely, thus offering reliability.
- Cells offer high energy density and can be used in large-scale applications.
- Waste products are removed from the cell during operation.
- Cell power output is consistent and does not decrease over the duration of use.

Advantages	
In comparison to internal combustion engines and electricity generation from fossil fuels	Cells are silent during operation, with no moving mechanical parts that wear or require lubrication.
	Very few, if any, atmospheric pollutants are formed during operation.
	Waste products from fuel cells in most applications include water and carbon dioxide. Oxides of nitrogen and sulfur are not released as atmospheric pollutants.
Disadvantages	
In comparison to traditional galvanic cells	Hydrogen may be obtained from non-renewable fossil fuels such as coal and natural gas.
	Hydrogen must be supplied in high purity, and challenges are associated with its safe storage.
	Electrodes are easily contaminated if impurities are present in the fuel.
	Metal catalysts (such as platinum) used on the surface of the electrodes are often expensive and in limited abundance.
	Limited infrastructure currently exists for hydrogen transport and refilling.
The technologies are relatively new and expensive.	

Question

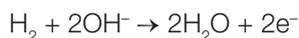
8. Electrochemical cells including fuel cells and sensors are used in space missions. Alkaline fuel cells have been used in space missions by NASA since the 1960s due to their reliability, efficiency and safety.



- (a) A diagram of an alkaline fuel cell is shown above.
- (i) **Identify** the energy change that occurs in the cell. (2 marks) KA1
- (ii) **Label** the positive and negative electrode on the diagram of the cell. (2 marks) KA1



(b) The cell is able to generate potable water. The reaction at one of the electrodes is shown below.



(i) **State** and **explain** whether this electrode equation represents oxidation or reduction.

.....

 (2 marks) **KA2**

(ii) **Hence**, state whether this reaction is occurring at the anode or cathode.

..... (1 mark) **KA1**

(iii) **Suggest** one advantage of the generation of water as a product from the cell during a mission to space.

.....
 (1 mark) **KA3**

(c) Alkaline fuel cells offer several advantages over conventional galvanic cells when used during space flight.

Discuss two of the advantages offered by fuel cells compared to traditional galvanic cells.

.....

 (4 marks) **KA2**

(d) The two electrodes are separated by potassium hydroxide as an electrolyte contained in a porous material. The electrolyte is susceptible to absorption of carbon dioxide, reducing the efficiency of the cell.

(i) Carbon dioxide reacts with potassium hydroxide to form potassium carbonate and water as products.

Write a fully balanced chemical equation for this reaction.

(2 marks) **KA4**

(ii) In the infamous Apollo 13 mission, exploding oxygen tanks on the spacecraft left astronauts with limited oxygen and rising carbon dioxide concentrations beyond the capacity of the lithium hydroxide carbon dioxide absorbers.

Suggest how an understanding of the chemistry of oxides and alkaline fuel cells could have been used to assist in these circumstances.

.....

 (2 marks) **KA2**

- (e) Carbon dioxide and carbon monoxide concentrations are monitored during missions using electrochemical cells. Carbon monoxide sensors rely on the oxidation of carbon monoxide to carbon dioxide at the negative electrode, generating an electrical current.
- (i) **State** the type of cell that produces electrical energy from redox reactions.
 (1 mark) **KA1**
- (ii) **State** whether the negative electrode represents the anode or cathode.
 (1 mark) **KA1**
- (iii) **Write** a balanced half-equation for the cell reaction in acidic conditions.

(2 marks) **KA4**

Flow cells

A **flow cell** is a rechargeable fuel cell. Two **electrolytes** (anolyte and catholyte) are separated by an ion-selective membrane (Figure 4.1.12). Both half-cells are also joined to external tanks of the electrolyte linked with pumps to circulate the electrolytes. When the cells are depleted, the electrolytes are pumped from the cell and regenerated.

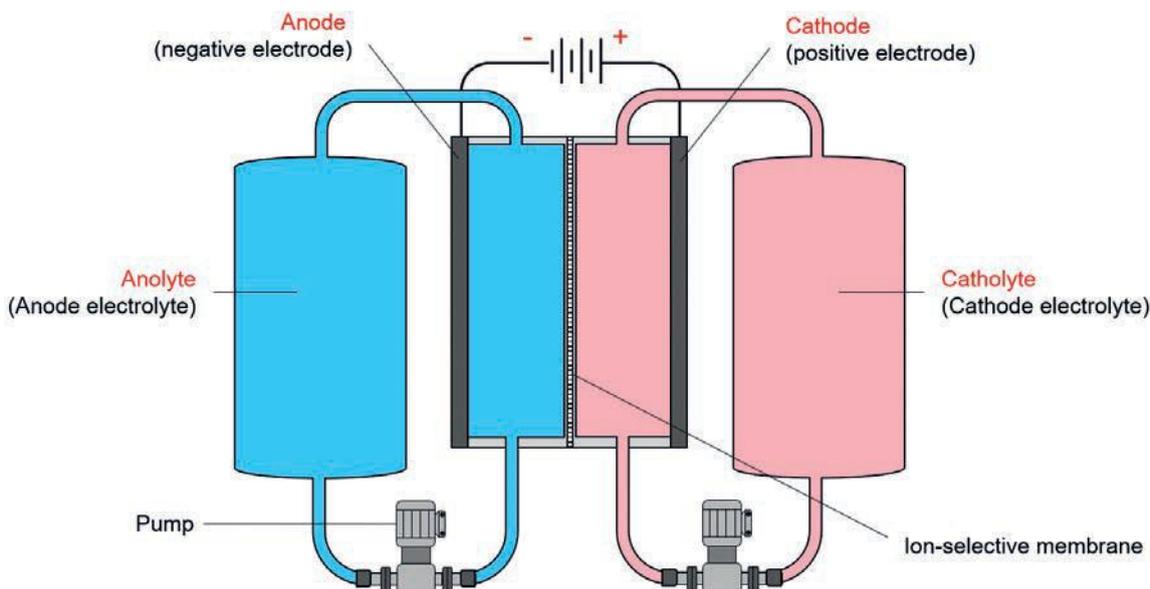


Figure 4.1.12: Flow cell.

Flow cells offer a number of significant advantages over fuel cells as another type of galvanic cell.

Advantages	
In comparison to fuel cells	Virtually unlimited capacity, as electrolytes are stored externally; therefore flow cells are effective for large stationary applications.
	Cells are rechargeable, which means that electrolytes can be used indefinitely. They are quickly charged through the addition of electrolyte.
	Can be left discharged for extended periods and recharged indefinitely without loss of output.
	No emissions of atmospheric pollutants during operation.
	Components of the cell can be laid out in varying configurations, which can include burying the electrolyte tanks underground.

Example

A **vanadium flow battery** (or vanadium redox battery, VRB) uses the many oxidation states of vanadium to generate a flow of electrons in redox reactions. Vanadium flow batteries are implemented due to their ability to be recharged and their capacity for energy storage. Vanadium flow batteries only require one electrolyte. The electrolyte can be prepared by dissolving the vanadium pentoxide V_2O_5 in sulfuric acid.

- In the **anolyte** (anode electrolyte), vanadium(II) ions are oxidised to vanadium(III) ions with the loss of an electron.
- In the **catholyte** (cathode electrolyte), vanadium(V) is reduced to vanadium(IV) through the gain of an electron.

When discharging (galvanic cell), the electrolytes are pumped into the half cells, which are separated by a proton exchange membrane. The membrane selectively allows hydrogen ions to pass to the cathode while not allowing other ions through that are present in the electrolytes. A transfer of electrons occurs in the external circuit to balance the overall cell charge, thus generating a current.

Recharging the cell (electrolytic cell) reverses the anode and cathode reactions by forcing current to flow in the opposite direction via an external power source.

Cell reactions	
Discharging (galvanic)	
Anode (-)	$V^{2+} \rightarrow V^{3+} + e^{-}$
Cathode (+)	$VO_2^{+} + 2H^{+} + e^{-} \rightarrow VO^{2+} + H_2O$
Overall	$V^{2+} + VO_2^{+} + 2H^{+} \rightarrow V^{3+} + VO^{2+} + H_2O$
Recharging (electrolytic)	
Anode (+)	$VO^{2+} + H_2O \rightarrow VO_2^{+} + 2H^{+} + e^{-}$
Cathode (-)	$V^{3+} + e^{-} \rightarrow V^{2+}$
Overall	$V^{3+} + VO^{2+} + H_2O \rightarrow V^{2+} + VO_2^{+} + 2H^{+}$

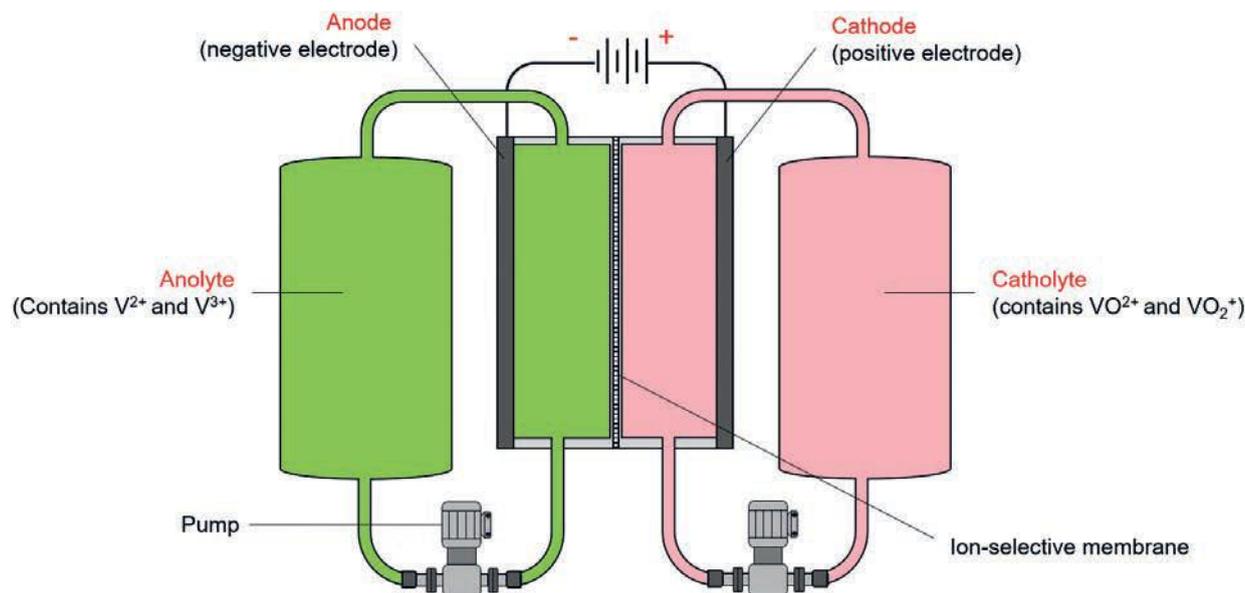


Figure 4.1.13: Vanadium flow cell.

The energy capacity of a vanadium flow cell is only limited by the size of the storage tanks for the electrolyte. The power achieved is determined by the surface area of the electrodes.

(iv) **Discuss** two advantages of the zinc-bromine cell in domestic applications for the storage and supply of electrical energy.

-
 -
 -
 -
 -
 -
 -
 -
- (4 marks) **KA2**

(v) Bromine is formed at the other electrode during charging from photovoltaic cells.

(1) **State** the energy change during charging.

-(2 marks) **KA2**

(2) Construct a half-equation for the formation of bromine from bromide ions.

(2 marks) **KA4**

(3) In domestic applications, the batteries are contained in a double-walled casing.

Suggest one reason why this level of containment is required.

-
-(1 mark) **KA3**

4.2 Water

Science understanding

Water from different sources is treated with different methods depending on its origin and intended use.

Suspended matter is commonly removed from water by flocculation, followed by sedimentation and filtration.

The surface of fine silicate and aluminosilicate particles in clays is negatively charged and can be flocculated into larger particles by the addition of salts containing highly charged cations such as aluminium ions or polymers.

Explain the use of aluminium ions and polymers in flocculating clay particles suspended in water.

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Water treatment

Techniques used for the treatment of water are dependent upon a number of factors including the source of the water and the range of organic and inorganic impurities present. Sources of freshwater are typically treated through the removal of suspended solids and disinfection to make the water **potable** (safe for human consumption). The treatment of sources of saltwater requires **desalination** (the removal of dissolved salts).

Treatment of freshwater

The following stages are typically applied in the treatment of freshwater for domestic use in Australia (Figure 4.2.1).

- **Coagulation and flocculation:** coagulation neutralises charge on suspended impurities and flocculation aggregate the impurities.
- **Sedimentation:** the floc (aggregated impurities) settle out as sediment and are removed.
- **Filtration:** remaining solid impurities are trapped and filtered out as they move through layers of sand and charcoal.
- **Disinfection:** chlorine, chloramines (derivatives of ammonia and chlorine), ozone, and ultraviolet radiation are used to kill potentially harmful microorganisms present in the water.
- **Fluoridation:** fluoride is added to the water in low concentrations to reduce tooth decay.

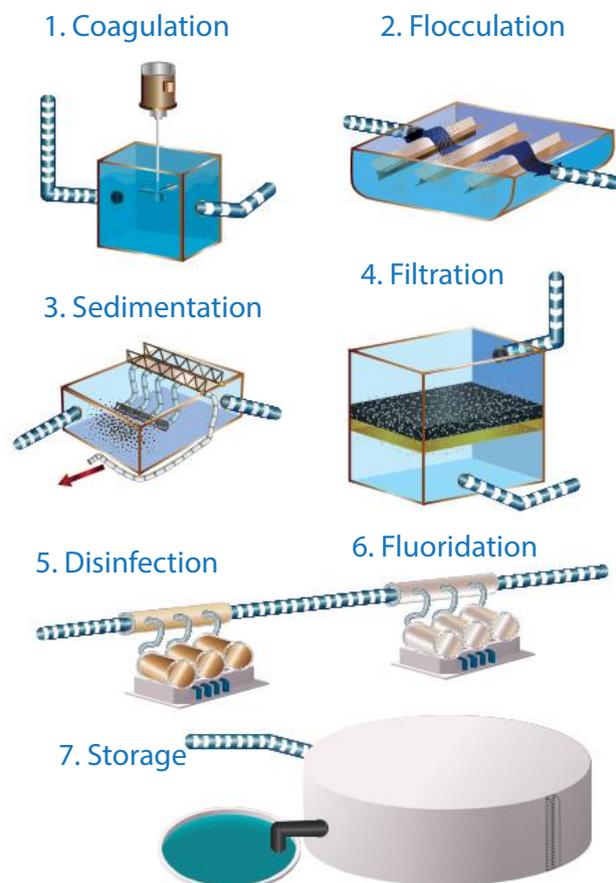


Figure 4.2.1: Stages of water treatment.

Coagulation

Dissolved and suspended particles are present in freshwater. The suspended particles originate from organic and inorganic sources. Suspended organic impurities include viruses, bacteria, algae, and decaying organic matter. Suspended inorganic impurities are formed during the weathering and erosion of rocks and include a range of aluminosilicate minerals, collectively referred to as **clays**.

After larger solid particles settle in the water, fine **colloids** (particles approximately within the nanometre (nm) to micrometre (μm) range) remain on the surface and in suspension due to the small size and the repulsion of regions of like charge. Colloidal suspensions account for the **turbidity** (cloudiness) of unprocessed water.

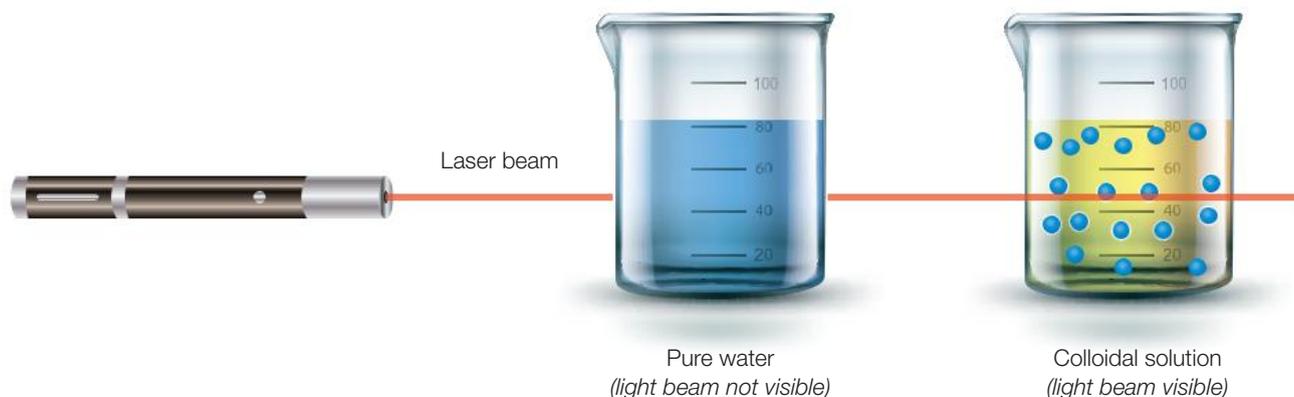


Figure 4.2.2: Colloidal suspension.

Clays are composed of minerals in the micrometre (μm) range and form colloidal suspensions in water. Clays have negatively charged regions on the surface of the **aluminosilicates** (covalently bonded networks of Si, Al and O).

Clay particles form stabilised (dispersed) colloidal suspensions due to the repulsion of negatively charged sites. During water treatment, salts and polymers are used to destabilise the suspension and aggregate clay minerals, allowing them to settle out. These stages are referred to as **coagulation** and **flocculation** respectively. Coagulation is a chemical process neutralising charge on the surface of colloids, whereas flocculation is a physical process aggregating particles.

Commonly used metal coagulants are based on salts of aluminium, such as aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3$). When added to water, the metal ions hydrolyse to form charged metal complexes (Figure 4.2.3).

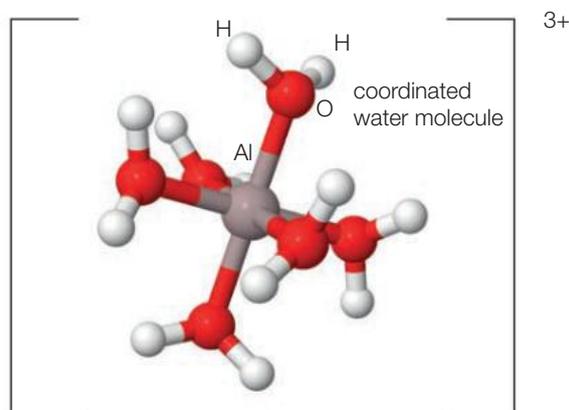


Figure 4.2.3: Hydrated complex of aluminium.

Positively charged metal complexes neutralise negative charge on the surface of clay particles. Once repulsive negative charges have been neutralised and the suspension is destabilised, dispersion forces allow the particles to aggregate to form **microfloc** (Figure 4.2.4).

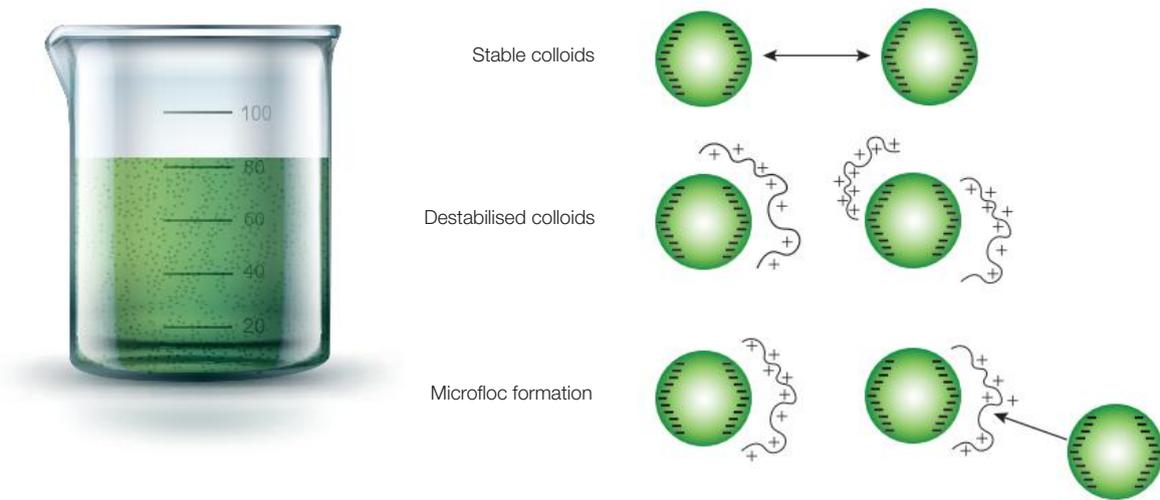


Figure 4.2.4: Coagulation of colloids.

Flocculation

Flocculation is the further aggregation of destabilised particles into larger particles. With gentle agitation, coagulated microfloc will combine to form larger **floc**. The floc settles due to their size and mass. Floc is then removed as sediment.

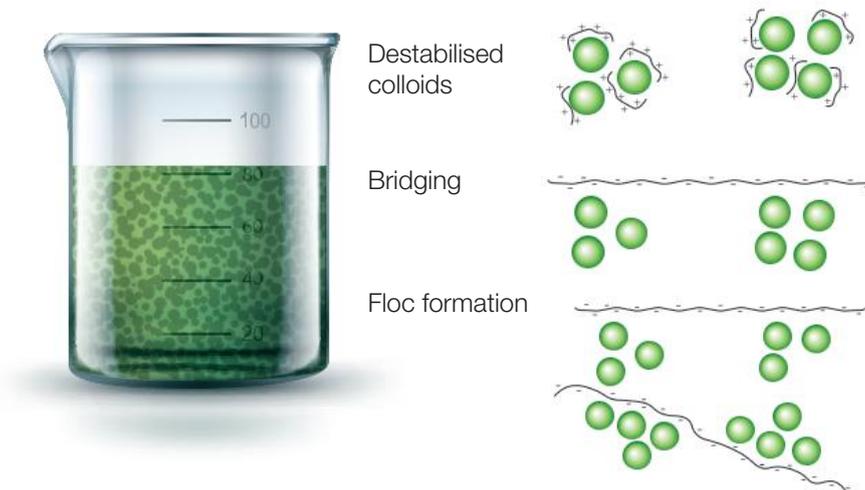


Figure 4.2.5: Flocculation of coagulated colloids.

Coagulation and flocculation can also be achieved or assisted through the addition of large molecular mass polymers (anionic and cationic) which not only neutralise the surface charge, but also physically entrap particles.

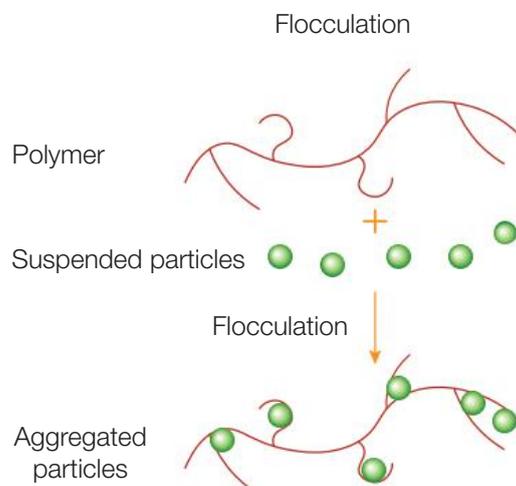
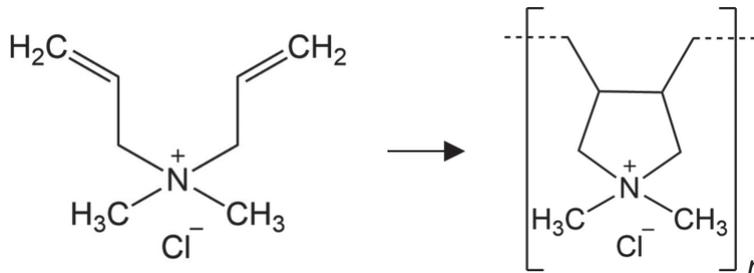


Figure 4.2.6: Coagulation and flocculation with polymers.

Question

10. Metal salts and natural and synthetic polymers are commonly used in water treatment to aid in coagulation and flocculation of colloidal particles.

(a) PolyDADMAC is an example of a synthetic polymer used as a coagulant and flocculation aid. The conversion of the monomer to the polymer, polyDADMAC, is shown below.



(i) **State** the feature of the monomer that allows for the formation of a polymer
 (1 mark) **IAE3**

(ii) **State** whether the surface of the polymer formed is anionic or cationic.
 (1 mark) **KA1**

(iii) PolyDADMAC is commonly used in conjunction with hydrated salts of aluminium such as aluminium sulfate ($Al_2(SO_4)_3$).

(1) **Write an equation** for the dissociation of aluminium sulfate in water.

(2 marks) **KA4**

(2) **State** one advantage of the use of aluminium sulfate compared to polyDADMAC during coagulation.

.....
 (1 mark) **KA2**

(3) **State** one advantage of the use of polyDADMAC compared to aluminium sulfate during flocculation.

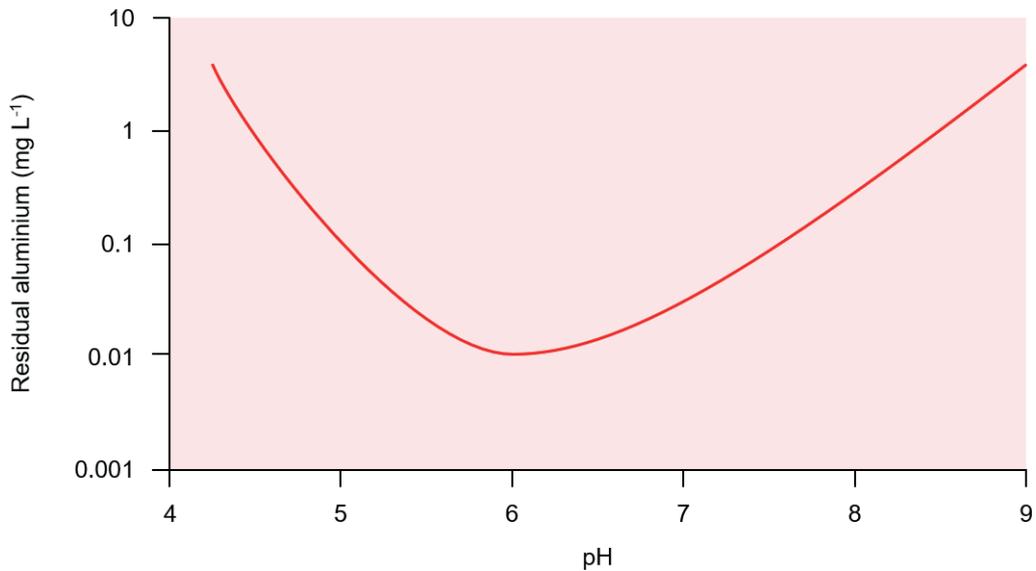
.....
 (1 mark) **KA2**

(iv) **Explain** how polyDADMAC generates coagulation and flocculation of clays during water treatment.

.....

 (3 marks) **KA1**

- (b) Aluminium residuals in drinking water from the use of aluminium during treatment are highly regulated.
- (i) The pH during treatment is controlled in terms of the effectiveness of the coagulant and flocculant but also to control the concentration of residual aluminium.



Describe the trend in the graph above.

.....

.....

.....

..... (2 marks) **IAE3**

- (ii) **Calculate** the mass, in g, of aluminium consumed in a 300 mL glass of water containing aluminium ions at a residual obtained at a pH of 6.

(3 marks) **KA2**

- (iii) Guidelines for aluminium consumption are derived from the amount of aluminium that would be absorbed by a 60 kg adult drinking 2 L of water per day at the maximum aluminium concentration of 1.5 mg L⁻¹.

Calculate the concentration, in ppm, present in a 60 kg adult consuming 2 L of water containing this aluminium concentration.

(3 marks) **KA2**

Zeolites

Zeolites can be mined naturally or formed synthetically. Zeolites are **hydrated aluminosilicate** minerals composed of linked alumina (AlO_4) and silica (SiO_4) tetrahedra. Excess negative charge on the surface of the aluminosilicate can accommodate metal cations such as sodium, magnesium and potassium. Natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$) is an example.

Tetrahedra combine to form a wide range of structures, with cavities present in the three-dimensional structure of the material. The microporous (pores in the micrometre range) nature of these extended structures provides vast surface area for interactions between the solvent and the surface of the zeolite material (Figure 4.2.8).

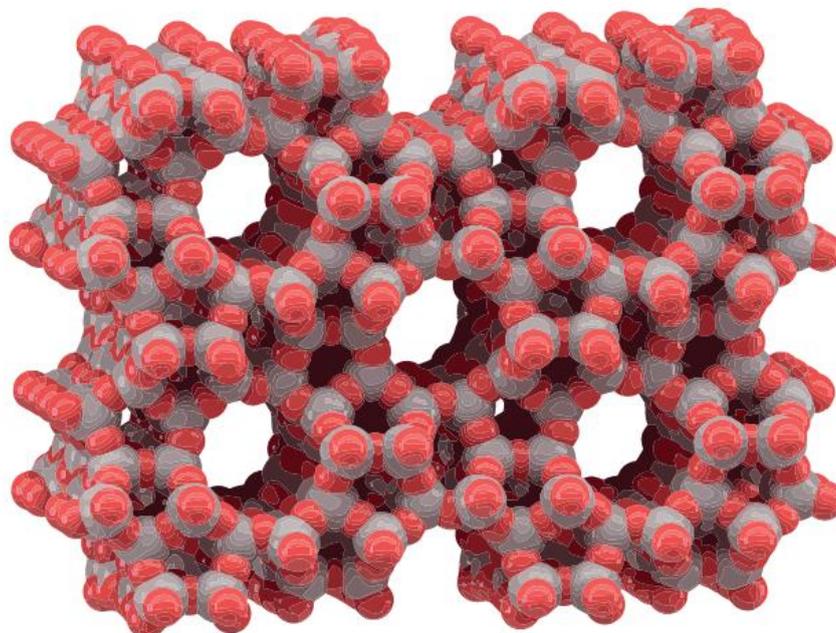
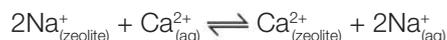


Figure 4.2.8: Porous zeolite structure.

Zeolites are used as an exchangeable adsorbent surface in analysis (refer to ion chromatography on Page 73), as a catalyst in the petrochemical industry, and to remove excess ions during water treatment and cleaning with detergent formulations.

Zeolites as water softeners

Cations held on the surface of the zeolite can readily be exchanged. Cations present in water undergo cation exchange with the cations on the surface of the zeolite. In domestic use, water softeners containing zeolites are paired with a source of sodium chloride solution. Sodium chloride solution is passed over the surface of the zeolite, which causes sodium ions to adsorb to the charged surface. As hard water passes over the zeolite, excess calcium and magnesium ions present in the water ($\text{Ca}^{2+}/\text{Mg}^{2+}_{(\text{aq})}$) exchange with sodium ions present on the negative surface of the pores ($\text{Na}^+_{(\text{zeolite})}$). The following equilibrium equation can be used to represent the process.



Eventually all the negative sites on the surface of the zeolite are occupied with cations from hard water and the zeolite loses effectiveness. At this point the zeolite can be regenerated by shifting the equilibrium to favour the backward reaction. This is achieved by the addition of concentrated sodium chloride solution.

Science understanding

Desalination is a process used to remove minerals from saline water to produce fresh potable water. Reverse osmosis and thermal distillation are two widely used methods for desalination.

Describe the disadvantages of using desalination for the production of potable water.

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Treatment of saltwater (desalination)

Desalination refers to processes that are undertaken to remove dissolved salts and minerals from water. Lowering the salinity of seawater and brackish water can make it suitable for human consumption or industrial use.

Advantage	Description
Production of potable water	Water of a quality that exceeds World Health Organization standards can be generated.
Reduction in demands on fresh water	Seawater, which is more abundant in comparison to fresh water, can be used to generate potable water. This reduces the demands on sources of fresh water and the associated ecology.
Availability is not reliant on climate	Potable water can be generated that is not reliant on rainfall or climate. For example, droughts do not affect supply. Potable water can be generated in regions of the world where fresh water is not available.
Reliable production	The processes rely on well-established, proven technologies. More efficient uses of waste heat and advanced materials have led to more effective and efficient processes.

Disadvantage	Description
Energy-intensive processes	Large amounts of energy are required to be input as electricity and heat.
Expense	Processes are expensive due to energy inputs and the requirement for specialised equipment and its ongoing maintenance.
Waste products	Disposal of the waste products, which contain high concentrations of salts (in the brine) and other chemicals used in treatment, can be problematic in some environments.
Waste heat	Waste heat, released locally in the oceans, can affect marine ecology.
Death of organisms	Inlets can drag in aquatic organisms which are subsequently killed during processing in the plant.

Two methods of desalination commonly employed are **thermal distillation** and **reverse osmosis**.

Thermal distillation

Thermal distillation is a process whereby saline water is boiled and the vapour formed is condensed and collected as pure water. This is an energy-intensive process requiring large inputs of electricity and heat. Thermal distillation is often linked to processes that generate heat as a by-product.

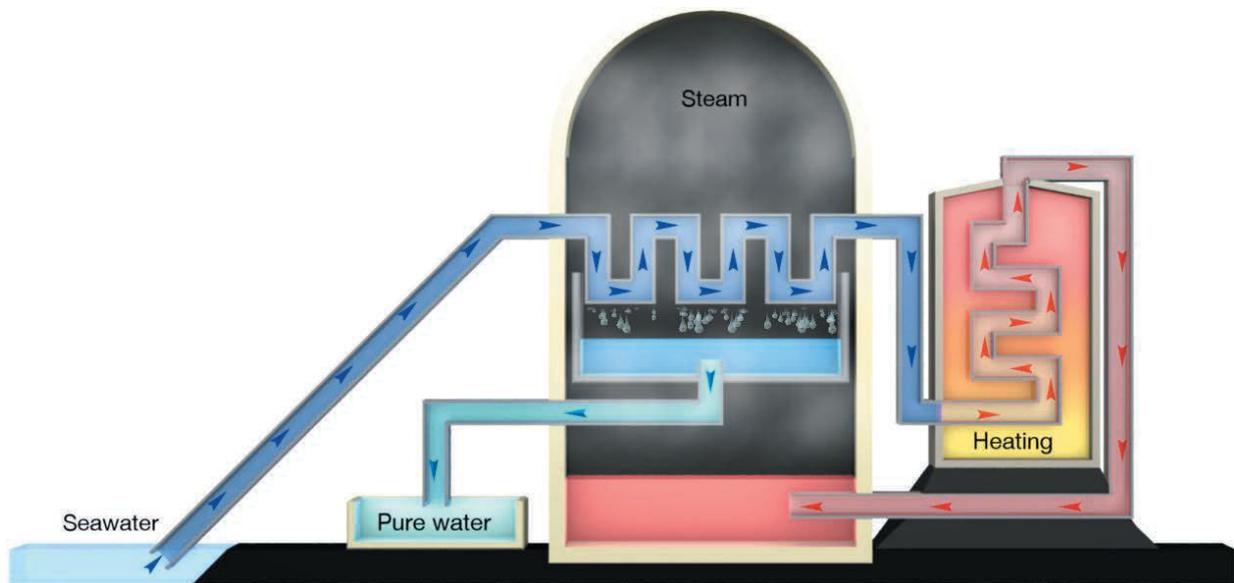


Figure 4.2.9: Thermal distillation.

Thermal distillation is used extensively in the Middle East, where rainfall is low and fuel sources from petroleum are plentiful and relatively cost-effective.

Science understanding

Reverse osmosis is a filtration technique whereby water is forced, under pressure, through a semi-permeable membrane.

Explain how reverse osmosis produces potable water from saline water.

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Reverse osmosis

Osmosis is the spontaneous movement of water molecules through a semipermeable membrane to equalise solute concentrations. The semipermeable membrane allows for the transfer of water, but not the solute.

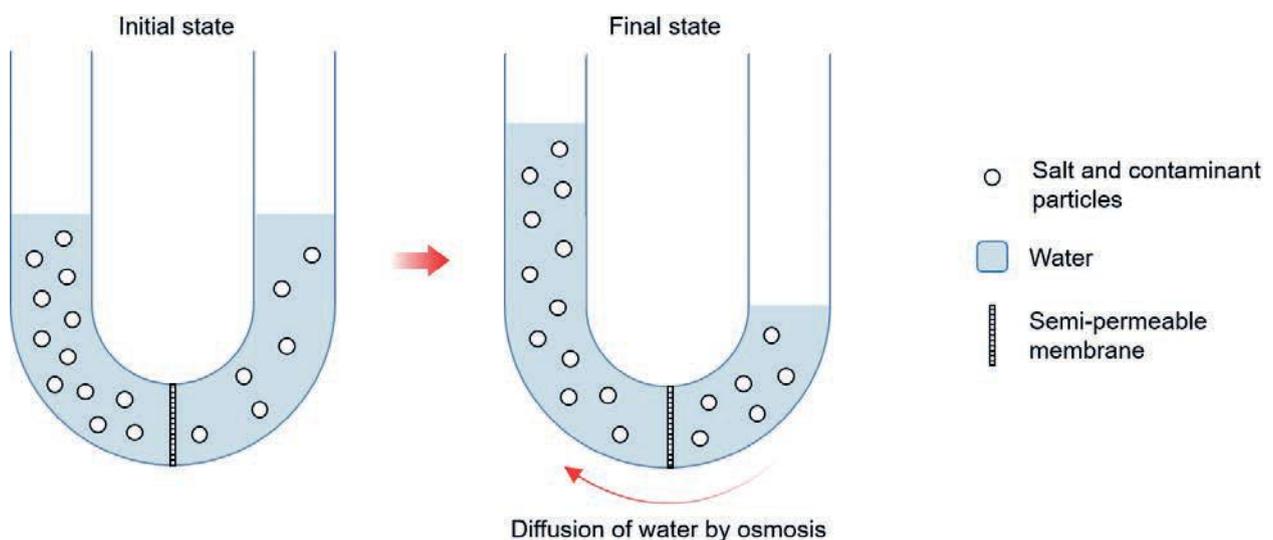


Figure 4.2.10: Osmosis.

Reverse osmosis (RO) is a process which employs a semipermeable membrane to remove dissolved ions, molecules and suspended particles (depending upon size) from water. Pressure is applied to overcome the **osmotic pressure** (the pressure required to stop the natural osmotic flow), forcing the solute to remain on the pressured side of the membrane and water to shift to the other side of the membrane (Figure 4.2.11).

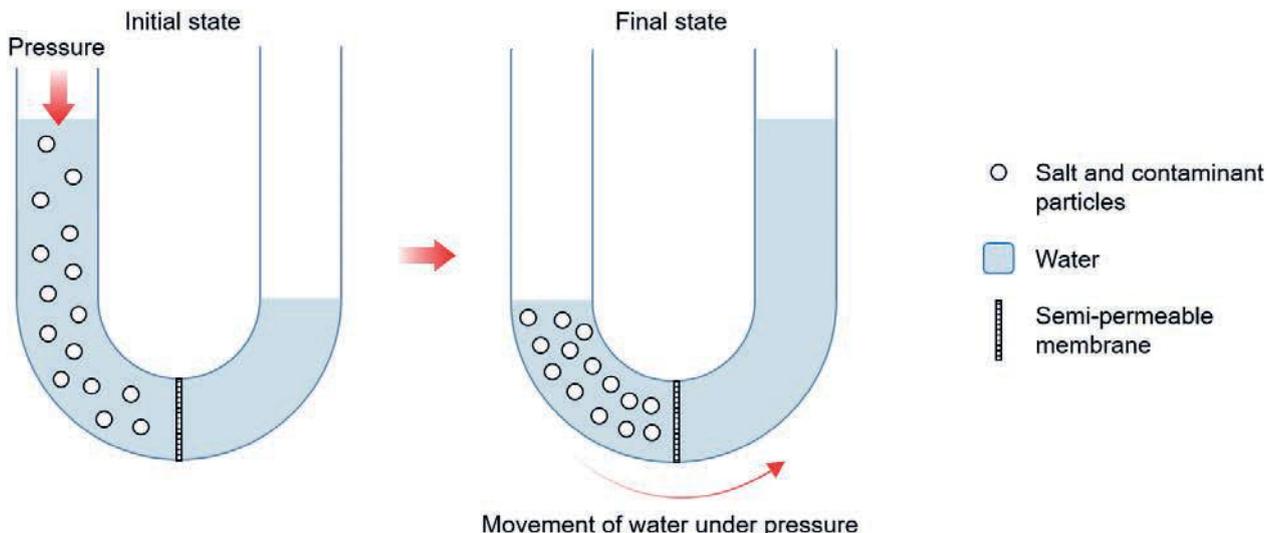


Figure 4.2.11: Reverse osmosis.

Science as a human endeavour

Adelaide Desalination Plant (ADP)

The desalination plant at Lonsdale, South Australia, has the capacity to supply up to 50% of Adelaide’s supply of household water (100 GL per year). The desalination plant utilises the reverse osmosis of seawater. The plant was funded by the government as a response to the “millennium droughts” in 2006/7 and diminishing water flow from the primary water source, the Murray River.

A saline concentrate is produced from the reverse osmosis process. The concentrate is returned to the ocean offshore through a series of diffusers. The diffusers are designed to rapidly mix the saline waste with sea water to ensure homogeneity and dilution. The marine environment is monitored with real-time data for water temperature, salinity, and currents to determine impact on the marine environment.



Question

11. Cafés often use reverse osmosis and zeolites to remove dissolved calcium and magnesium ions from water supplied to coffee machines. The ions damage boilers and affect the taste of coffee.

(a) **State** the term used to describe water containing an elevated concentration of calcium and magnesium ions.
 (1 mark) **KA1**

(b) **Explain** how reverse osmosis can remove ions present in domestic water supplies before that water is used in coffee machines.

 (2 marks) **KA1**

- (c) Calcium ions present in the water lead to the build-up and precipitation of calcium carbonate (CaCO₃) as scale in the boilers of coffee machines.

(i) As cold water is heated in the boiler of a coffee machine, carbon dioxide is lost.



Explain, with the aid of the equation above, how this leads to an increased concentration of calcium carbonate.

.....

 (4 marks) **IAE3**

(ii) Sulfamic acid, NH₂SO₃H, is used in commercial coffee machines to remove scale. It undergoes an acid–base reaction with calcium carbonate to form calcium sulfamate, Ca(NH₂SO₃)₂.

Write a balanced equation for the reaction described above.

(2 marks) **KA4**

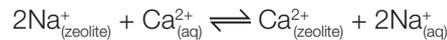
- (d) Domestic coffee machines often use zeolite resins to remove calcium and magnesium ions from water.

(i) **State** two important features of zeolites that make them effective as water softeners.

.....

 (2 marks) **KA1**

(ii) The equation below represents the equilibrium.



(1) **Explain**, using equilibrium principles, the effect on the zeolite when water with a high concentration of calcium ions is passed by the zeolite surface.

.....

 (4 marks) **IAE3**

(2) **State** how the zeolite resin can be regenerated, removing calcium ions.

.....
 (1 mark) **KA2**

- (e) Filter coffee is a mixture of dissolved and undissolved solids. Undissolved solids form a colloid suspension. Very fine paper or stainless-steel filters are used to filter the coffee.

Suggest why a colloidal suspension is still formed.

.....
 (1 mark) **KA2**



Science understanding

Hypochlorous acid, chlorine, and hypochlorites are oxidisers used for water disinfection.

Explain the effect of pH on the equilibrium between chlorine and water, and hydrochloric acid and hypochlorous acid

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Disinfection using chlorine and compounds of chlorine

Chlorine and a range of associated compounds containing chlorine are used in the large-scale and domestic **chlorination** of water for domestic use (water for households) and recreation (pools and spas).

Chlorine

Chlorine gas (Cl_2) is added to water supplies as a disinfectant. Chlorine reacts with water to establish an equilibrium with the formation of hypochlorous acid (HClO) and the products of the complete ionisation of hydrochloric acid (HCl).



The resulting equilibrium is pH dependent. The position of equilibrium is shifted by altering pH concentration of hydronium ions (H_3O^+). The equilibrium is manipulated to maintain a high concentration of hypochlorous acid and a low concentration of gaseous chlorine (Figure 4.2.12).

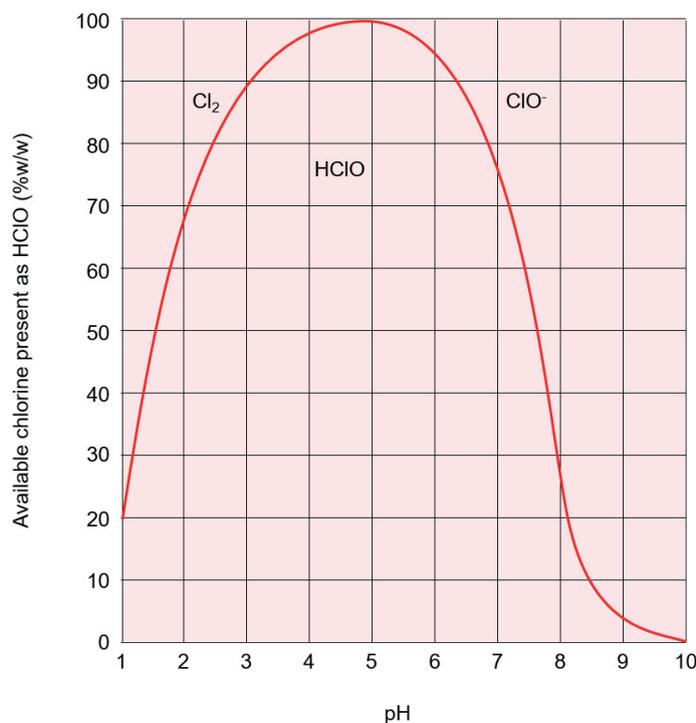
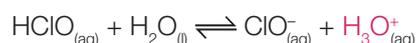


Figure 4.2.12: Effect of pH and available chlorine, hypochlorous acid and hypochlorite ions.

According to Le Châtelier's principle, the addition of a base such as sodium hydroxide (NaOH) will effectively reduce the concentration of hydronium ions through neutralisation. To counteract the change, the position of equilibrium will favour the forward reaction in response. While re-establishing the hydronium ion concentration, the concentration of hypochlorous acid will increase.

An equilibrium is also established between hypochlorous acid as a weak acid and hypochlorite ions.



Hypochlorites

Hypochlorite salts of calcium, lithium and sodium are commonly used for the disinfection of domestic water supplies and swimming pools. Hypochlorites are chlorine-containing compounds that react with water to form hypochlorous acid. They are chosen for some applications due to their ease of storage, transportation and handling as solid compounds or in alkaline solution, when compared to chlorine gas.



The equilibrium is once again sensitive to changes in pH. The pH is monitored and adjusted accordingly to maintain a high concentration of hypochlorous acid as the stronger oxidant.

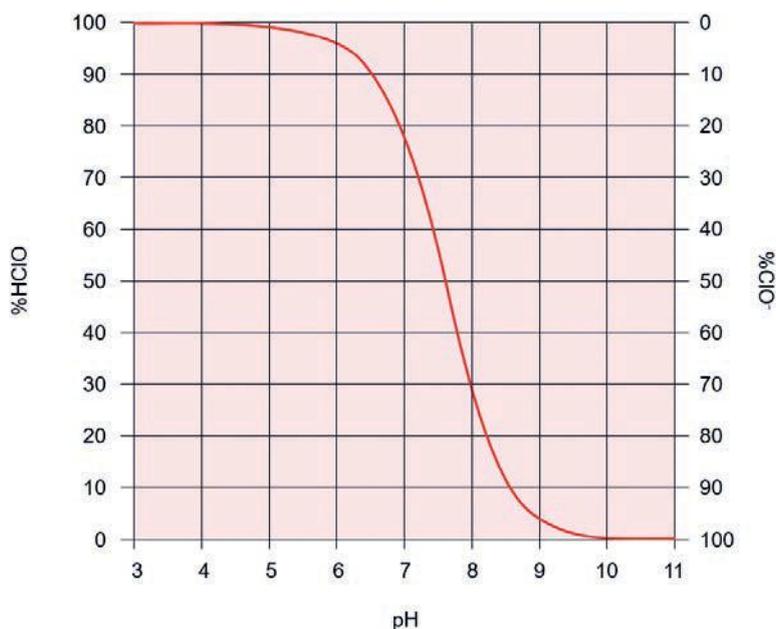
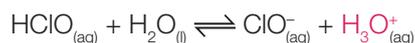


Figure 4.2.13: Effect of pH on hypochlorous acid and hypochlorite ions.

According to Le Châtelier's principle, the addition of a strong acid such as hydrochloric acid (HCl) will effectively reduce the concentration of hydroxide ions through neutralisation. To counteract the change, the position of equilibrium will favour the forward reaction in response. While re-establishing the hydroxide ion concentration, the concentration of hypochlorous acid will increase.

Once again, an equilibrium is established between hypochlorous acid and hypochlorite ions.



Chlorine, hypochlorous acid and hypochlorite ions are all oxidants. As oxidants, they have varied ability to kill **pathogens** (bacteria and other microbes) found in domestic water supplies. Hypochlorous acid and hypochlorite ions are able to enter the cell wall of bacteria and oxidise the cell contents. The oxidants break down lipids in the cell wall and oxidise enzymes and proteins inside the cell, denaturing them. This inhibits cellular reactions and the ability of the pathogen to reproduce. Hypochlorous acid is much more effective in this capacity, as, unlike hypochlorite ions, it does not carry a charge and is a stronger oxidant.

Question

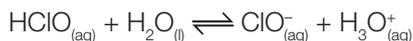
12. Chlorine and hypochlorite salts are added to outdoor swimming pools to make the water safe for use.

(a) Chlorine reacts with water to form hypochlorous acid.

(i) **Write** an equation for the reaction.

(2 marks) **KA4**

(ii) Hypochlorous acid is a weak acid, partially ionising in water according to the following equation.



The combined concentration of hypochlorous acid and hypochlorite ions is referred to as the free chlorine level.

(1) **State** the action of hypochlorous acid and hypochlorite ions during disinfection of water.

..... (1 mark) **KA1**

(2) **State** whether the concentration of hypochlorous acid would be increased at a high or low pH.

..... (1 mark) **KA1**

(iii) During disinfection, hypochlorous acid and hypochlorite ions enter the cell wall of bacteria degrading proteins.

(1) **Suggest** why hypochlorous acid is more effective than hypochlorite ions at killing pathogens.

..... (1 mark) **KA2**

(2) **State** and **explain** the effect of degrading the protein structure on the action of enzymes in the cell.

.....

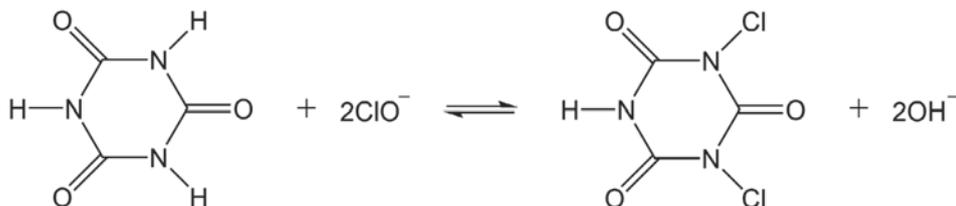
 (3 marks) **KA2**

(b) Hypochlorite ions (ClO⁻) undergo rapid decomposition by the absorption of ultraviolet light from solar radiation in photochemical reactions. In outdoor pools this poses a problem, leading to a loss of nearly 90% of the available chlorine.

(i) **State** the name given to reactions that absorb energy.

..... (1 mark) **KA1**

(ii) To stabilise levels of hypochlorite ions, cyanuric acid is added to swimming pools, thus establishing the equilibrium shown below.



4.3 Soil

Science understanding

Plants require nutrients, which they obtain from the soil.

Explain why plants need soil nutrients in soluble form.

Soil productivity is related to the availability of plant nutrients, which need to be replenished naturally or by the addition of fertilisers.

Nitrogen, phosphorus, and potassium are the major nutrients that plants require from the soil.

Explain how natural processes (including lightning, nitrogen-fixing bacteria, and decay) replenish soil nitrogen.

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Soil

Soils are complex mixtures of inorganic and organic materials. Soils vary greatly in their chemical and physical composition, depending on the region and geology. Soils are formed from the weathering of rocks, the leaching of minerals, and the decomposition of organic matter. Soil provides the structural support, water and nutrients for most plants. Soils are composed of different layers (Figure 4.3.1).

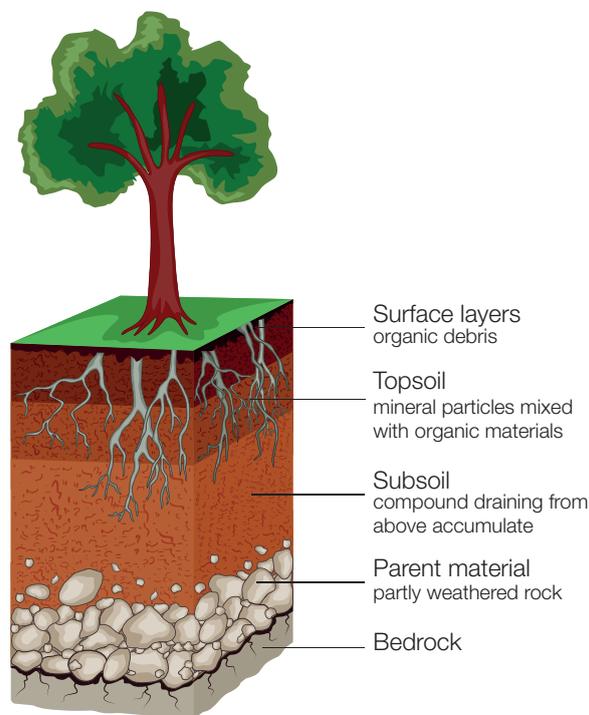


Figure 4.3.1: Layers of soil.



Science as a human endeavour

Artificial soil

Fertile topsoil is essential to plant growth, and over 90% of food production relies on plants grown in soils. Soils form over geological timescales, and therefore cannot be replenished in a human lifetime. Pollution and intensive agricultural practices using soils have led to soil degradation and lower levels of available nutrients. Increased demand on food supply from a growing population exacerbates the problem.

With the recent closure of the Hazelwood coal-fired power station in the Latrobe valley in Victoria, researchers from Monash University are looking to rehabilitate the adjoining mine site. They are investigating the artificial formation of fertile soil. They are producing mixtures of organic wastes from local sources (compost from sewage treatment, plants, and woodchips from paper mills) and inorganic mining wastes, to mimic complex soil structure. It is hoped that the rehabilitation of the mine sites across Australia will lead to the creation of thousands of jobs for displaced workers.

Nutrients in the soil

In terrestrial (on land) plants, water and nutrients (organic and inorganic ions) move from the soil to the plant via the root system. Plants take up the majority of nutrients in inorganic form as soluble ions present in **soil solution** (water in the soil). Essential ions that form nutrients for plants are shown in the table below.

Nutrients in the soil	Formula	Typical concentration in soil (mmol L ⁻¹)
nitrate	NO ₃ ⁻	100 – 50 000
ammonium	NH ₄ ⁺	100 – 2000
hydrogen phosphate and dihydrogen phosphate	HPO ₄ ²⁻ H ₂ PO ₄ ⁻	1 – 50
potassium	K ⁺	100 – 4000
calcium	Ca ²⁺	100 – 5000
magnesium	Mg ²⁺	100 – 5000
sulfate	SO ₄ ²⁻	100 – 10 000

Two important mechanisms by which nutrient ions in the soil reach the surface of the root system are **mass-flow** and **diffusion**. Soluble nutrients are transported into root cells in plants by facilitated diffusion and active transport.

The nitrogen cycle

Soluble nitrate ions are essential ions required by plants in the formation of amino acids and proteins during **nitrogen assimilation**. Animals are then able to obtain this nitrogen in the food chain. The conversion of elemental nitrogen to nitrate ions can be represented by a number of natural pathways in the nitrogen cycle (Figure 4.3.2).

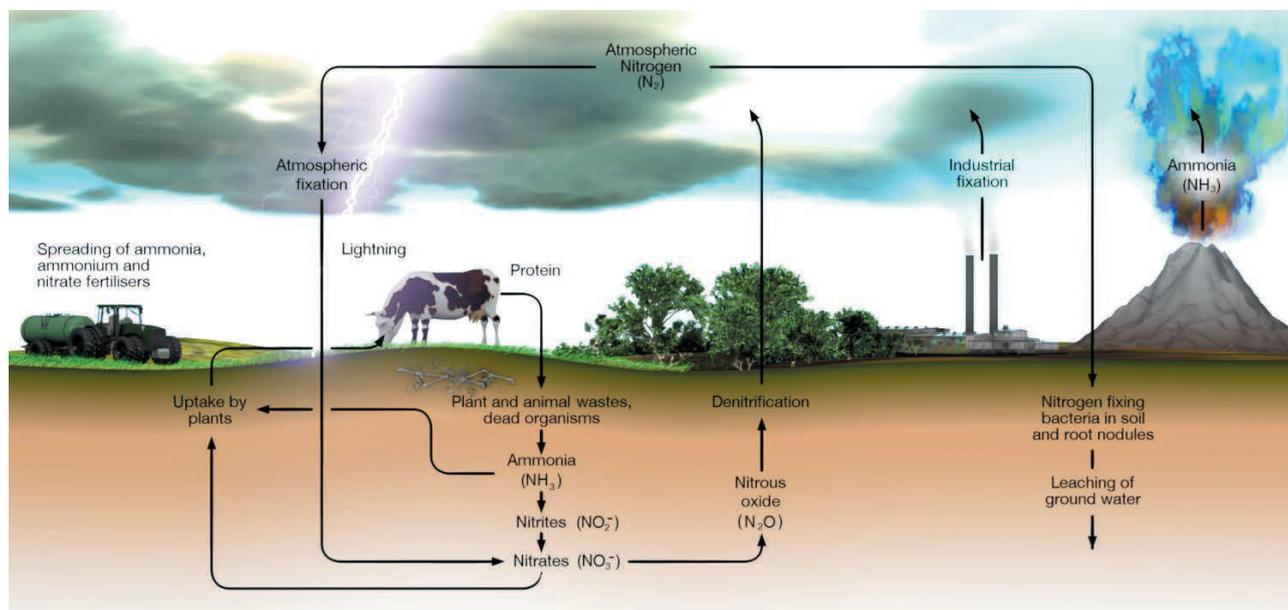
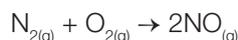


Figure 4.3.2: Nitrogen cycle

Nitrogen fixation

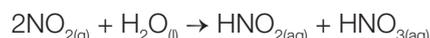
The energy required for the conversion of nitrogen to nitric oxide (NO) can be provided through natural phenomena such as lightning, volcanic activity and bushfires. Due to the high temperatures encountered during these events, sufficient energy is provided to allow nitrogen and oxygen to combine to form nitric oxide.



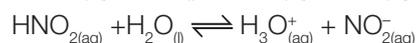
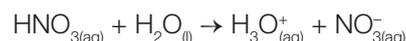
Nitric oxide is further oxidised in the atmosphere to form nitrogen dioxide (NO₂).



Nitrogen dioxide combines with water vapour present in the atmosphere to form nitrous (HNO₂) and nitric acid (HNO₃).



Nitric acid completely ionises and nitrous acid partially ionises, releasing soluble nitrate (NO₃⁻) and nitrite (NO₂⁻) ions, which enter the soil on deposition during rain.



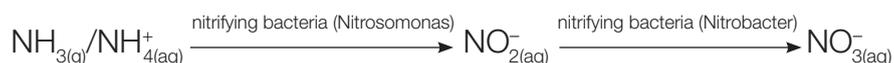
The majority of natural nitrogen fixation (over 90%), however, is due to bacteria. **Nitrogen-fixing bacteria** containing the **nitrogenase enzyme** are able to convert nitrogen and hydrogen present in the atmosphere into ammonia (NH₃) and other nitrogen-containing compounds such as ammonium ions (NH₄⁺). Nitrogen-fixing bacteria are found in the soil and on the nodules of the root systems of legumes (examples include peas and beans).

Ammonification (mineralisation)

Wastes from living humans, animals and plants result in the direct release of nitrogen-containing compounds into the soil (urea found in urine or animal faeces acting as natural fertiliser). The decay of plants and animals also results in the formation of nitrogen-containing compounds (decay of leaf litter). During anaerobic decomposition of remains, bacteria convert the nitrogen present in nitrogen-containing compounds (amino acids, proteins, nucleic acids, phospholipids) into ammonia (NH₃) and ammonium ions (NH₄⁺). (Aerobic decomposition also results in the formation of nitrate ions (NO₃⁻).

Nitrification

Classes of **nitrifying bacteria** present in the soil convert ammonia (NH₃) and ammonium ions (NH₄⁺) into nitrite ions (NO₂⁻) and further to nitrate ions (NO₃⁻).



Denitrification

In anaerobic conditions, in some soils, **denitrifying bacteria** return nitrates to atmospheric nitrogen (N₂).



Science understanding

Soil productivity is related to the availability of plant nutrients, which need to be replenished naturally or by the addition of fertilisers.

Explain why fertilisers are required to improve the productivity of some soils.

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Synthetic fertilisers

Fertilisers are primarily used to replace essential nutrients (**macronutrients**), such as nitrogen, phosphorous and potassium) that are either not present in nutrient-deficient soils or are removed from the soil during plant growth. Fertilisers have become essential to farming practices where crops are grown and harvested. Growing demands on global food production, as a result of a rapidly growing population, have necessitated the intensive cropping of **arable** land (land capable of being used for cropping). Fertilisers are also used to enhance the growing conditions in some soils that show deficiencies in certain nutrients, thus making the soil productive. Fertilisers can also be manufactured to suit the needs of crop varieties and conditions. Typically, fertilisers contain nitrogen, phosphorous, and potassium in fixed ratios; they also contain trace elements (**micronutrients**) such as boron, zinc and magnesium, that improve plant growth. Common sources of nitrogen, phosphorous and potassium used in fertilisers are shown in the table below.

Fertiliser	Production
Nitrogen Ammonia Nitric acid Ammonium nitrate	Nitrogen fertilisers are derived from ammonia. Ammonia is produced from readily available raw materials in the Haber process. Ammonia is converted into nitric acid, which can be used to produce solid ammonium nitrate fertiliser.
Phosphate Phosphoric acid Superphosphate Triple superphosphate	Rock phosphate is treated with sulfuric acid and ammonia to produce superphosphate and ammonium phosphate respectively.
Potassium Potash fertiliser	Potassium is the third macronutrient after nitrogen and phosphorous. Potash (soluble salts of potassium) fertiliser typically contains different compositions of potassium chloride, potassium sulfate and potassium nitrate. The salts are derived from mined ores or can be produced in the chemical industry.

Individual fertilisers are then granulated and commonly mixed to achieve the desired ratios for their intended use.

An Australian perspective

Food and, therefore, agriculture are fundamental to human survival. Australia's food security is linked to our local production and export. Farmers in Australia export approximately 60% of what they grow and produce. Food exports are worth \$30 billion annually. It is estimated that farming and associated industries provide 1.6 million jobs across Australia. Farming occurs on approximately 60% of Australia's land mass.

The Australian fertiliser industry has played an integral role in farming production and exports. The use of artificial fertilisers has significantly increased production. It is estimated that exports would decrease by a third without the widespread availability of fertilisers. Australian fertiliser industries have also looked to maintain production from predominantly local raw materials and reduce carbon emissions from their manufacturing and distribution methods.

Science understanding

Excess nitrogen and phosphorus can be leached from soils and can cause eutrophication in water bodies.

Explain the process and consequences of eutrophication

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Eutrophication

Eutrophication is the increased nutrient concentration in the environment due to natural processes or human activities. High nutrient concentrations stimulate growth of photosynthetic microbes such as algae, phytoplankton and cyanobacteria (these are commonly known as blue-green algae, but are actually bacteria) in bodies of water. Weathering of rocks and soils leads to natural eutrophication, as dissolved nutrients and sediments accumulate over time in bodies of water. Human activities that release nutrients into bodies of water also cause the acceleration of eutrophication. Nutrient release includes: run-off from organic and inorganic fertilisers used in farming, discharge from mining, discharge of detergents in grey water, and discharge of raw untreated sewage.

The resulting nutrient release, and increased turbidity, encourages growth of photosynthetic microbes in waterways. The resulting “bloom” (a thick mat on the surface) of microbes and increased turbidity prevent sunlight from entering the water.

Aquatic plants beneath the water are unable to maintain photosynthesis, resulting in death and subsequent decay. This results in a reduction in oxygen concentration in the waterway, as less oxygen is being produced from photosynthesis and more oxygen is consumed by aerobic bacteria during the decay of plants.

The large body of photosynthetic microbes uses up available oxygen during respiration. Some of these photosynthetic microbes also produce toxins that are harmful to certain species. Their decay by aerobic bacteria also consume available oxygen. When the supply of glucose (from dead plants and animals) increases, aerobic bacteria consume oxygen at a faster rate.

Decay of organic matter by anaerobic bacteria also produces potentially toxic products (such as hydrogen sulfide).

As the oxygen concentration is depleted in the waterway, the biological oxygen demand cannot be met for all species. Some species die and decay resulting in a decrease in the diversity of species, often changing the dominant species (such as fish).

4

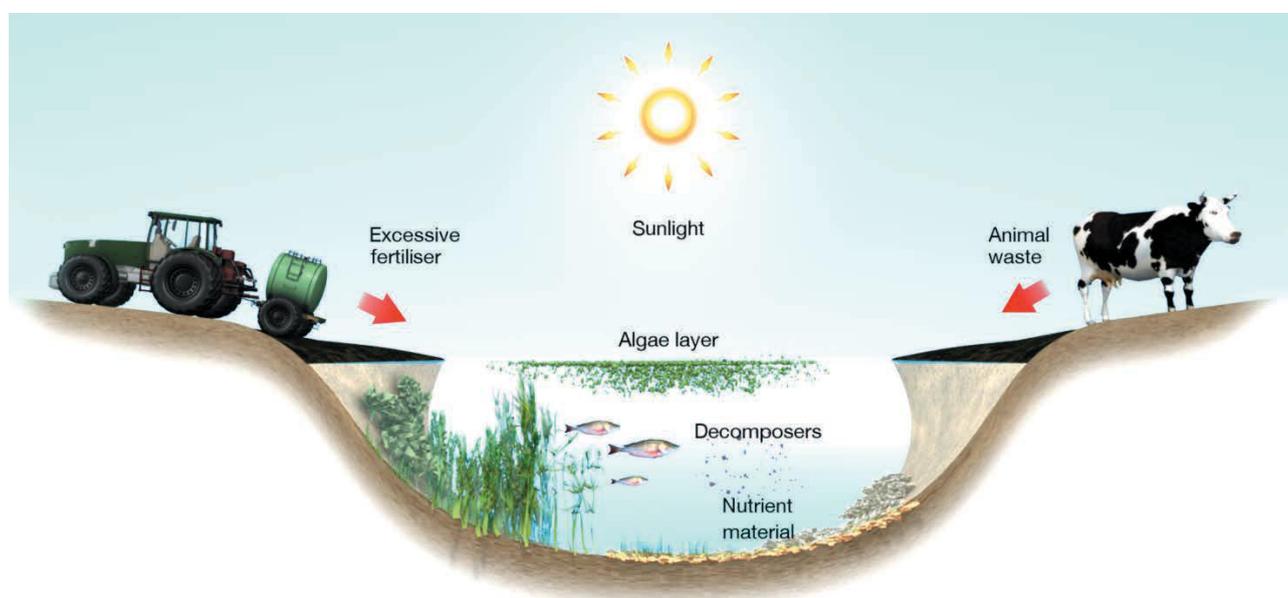


Figure 4.3.3: Eutrophication in a body of water.

Question

13. The Murray–Darling basin is an interconnected system of waterways in Australia that is heavily relied upon for farming irrigation and domestic water supply.

(a) Legume crops, such as beans, are often grown in annual rotation with cereal crops to increase the concentration of available nitrate ions in the soil.

(i) **Explain** why continual cropping and harvesting of cereals would lead to decreased concentrations of available nutrients in the soil.

.

 (2 marks) **KA1**

(ii) **Explain** how legume crops lead to an increase in the concentration of available nitrate ions in soils.

.

 (2 marks) **KA2**

(iii) Some farmers will till (dig) the green legume plants into the soil at the end of their growth period, rather than harvesting the crop.

Explain how this practice will further increase the concentration of available nitrate ions in the soil.

.

 (3 marks) **KA2**

(b) Farming practices adjacent to creeks and rivers can lead to increased nutrient levels in waterways due to fertiliser run-off.

(i) Ammonium nitrate is one commonly used fertiliser spread on the soil surface as solid granules.

(1) **Write the formula** of ammonium nitrate.

. (2 marks) **KA4**

(2) **State** why ammonium nitrate fertiliser provides an available form of nitrogen to plants, even when added to the soil as a solid.

.. . . . (1 mark) **KA1**

(ii) Fertiliser run-off can lead to increased nutrient levels in waterways resulting in blooms of blue-green algae.

(1) **State** the term used to describe increased nutrient levels in waterways.

.. . . . (1 mark) **KA1**

(2) Blue-green algae undergo photosynthesis. **Write an equation** for photosynthesis.

(2 marks) **KA4**

- (3) Blue-green algae undergo respiration while living, and decay under aerobic and anaerobic conditions.

Suggest why blooms of blue-green algae lead to lower oxygen levels, when photosynthesis is known to produce oxygen.

.....
 (1 mark) **KA2**

- (4) **Explain** how blooms of blue-green algae may lead to a reduction in aquatic species.

.....

 (4 marks) **KA1**

- (iii) At some sites along the river network, the introduction of raw sewage from livestock has been detected.

Suggest how the introduction of animal wastes could contribute to increased nutrient concentration in the waterway.

.....

 (2 marks) **KA2**

- (c) The introduction of European carp (a species of fish) to the Murray–Darling river system has seen an increase in water turbidity as colloidal clays from the riverbed are disturbed by the fish during feeding.

- (i) **Explain** how a colloidal clay suspension leads to a reduction in the concentration of available oxygen in the waterway.

.....

 (2 marks) **KA2**

- (ii) Water from the river system is used for domestic supply after treatment.

- (1) **State** why fine clay particles remain in suspension.

.....
 (1 mark) **KA3**

- (2) **State** how alum (aluminium sulfate) destabilizes clay suspensions.

.....

 (3 marks) **KA1**

- (3) **Suggest** one reason why this treatment process could not be applied to remove turbidity from the entire river system.

.....
 (1 mark) **KA3**



Science understanding

Silicon dioxide, silicates, and aluminosilicates are important components of rocks and soils.

Write the formula of the anion given the formula of a silicate or aluminosilicate.

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Silicates

Silicates are the major mineral component of the Earth's crust. Silicates constitute 92% of mineral compounds in the Earth's crust. Silicates are based on the SiO_4^{4-} tetrahedral unit (Figure 4.3.4). Each silicon is bonded to four oxygen atoms to form the corners of a tetrahedron. The variety of silicate minerals result from the sharing of one, two, three or all four corner oxygens in tetrahedrons of like units.

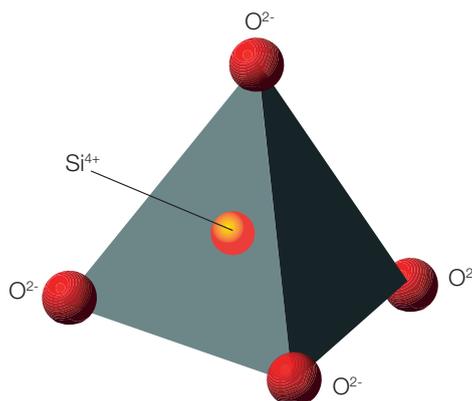


Figure 4.3.4: The silicate tetrahedron

Aluminosilicates

Aluminosilicate minerals are composed of aluminium, silicon and oxygen, where a proportion of the silicon atoms in the covalent structure have been substituted with aluminium (which can be further substituted with calcium (+2) in some cases). Aluminium (+3) is of similar size to silicon (+4) and can replace silicon atoms in silicate structures. When this substitution occurs, there is a change in the overall charge of the silicate. The negative charge increases by one for every aluminium in the formula of the structure.

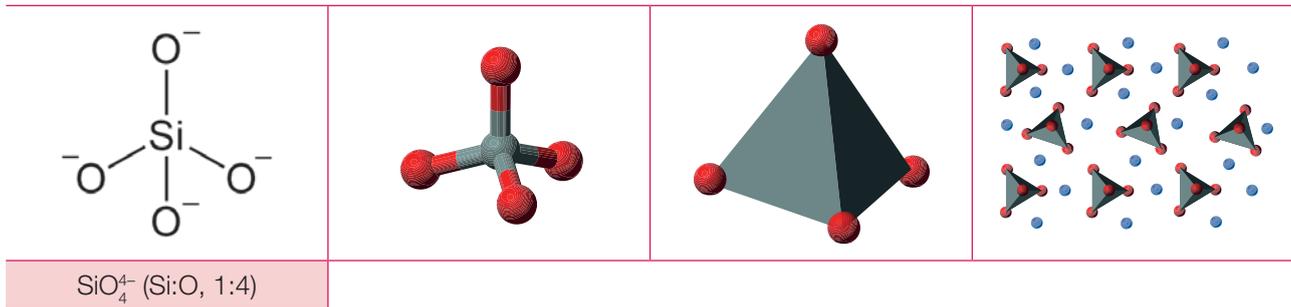
Mineral and anion formulae of silicates and aluminosilicates

The anions of silicate and aluminosilicate minerals are counterbalanced by metal cations, anions and uncharged species (such as water when hydrated).

The charge on the silicate or aluminosilicate anion can be established through two methods: either by the sum of the individual ions counterbalancing the anion, or by the sum of the oxidation numbers for the atoms present in the formula of the anion (where silicon exhibits (+4), aluminium (+3) and oxygen (-2)). The following examples for each category model these calculations.

Single tetrahedra

Silicate minerals containing single isolated tetrahedra SiO_4^{4-} are referred to as **nesosilicates** or **orthosilicates**. Tetrahedra are connected by interstitial cations (cations between units).



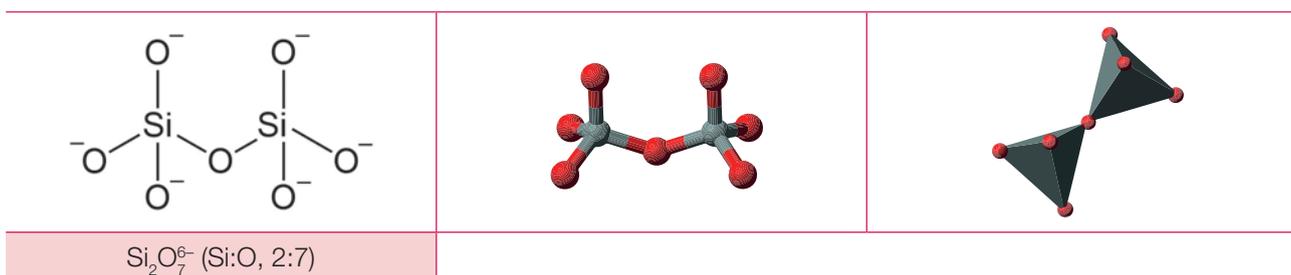
Worked examples

Silicate	Mineral	Anion	Oxidation number		Balancing charge		Charge
			Si	O	Mg	2+	
Fosterite	Mg_2SiO_4	SiO_4^{4-}	Si	O	Mg	2+	4-
			+4	-2	2+		
			Total	= +4 + 4(-2) = -4		= 2(2+) = 4+	

Silicate	Mineral	Anion	Oxidation number		Balancing charge		Charge
			Si	O	Mg	Al^{3+}	
Pyrope	$\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$	SiO_4^{4-}	Si	O	Mg	Al^{3+}	4-
			+4	-2	2+	3+	
			Total	= +4 + 4(-2) = -4		= 3(2+) + 2(3+) = 12+ = (12+) ÷ 3 = 4+	

Corner-sharing tetrahedra

Two tetrahedra can share a common oxygen atom at one common corner of the tetrahedra to form $\text{Si}_2\text{O}_7^{6-}$. Silicate minerals containing isolated double tetrahedra are referred to as **sorosilicates**.



Worked example

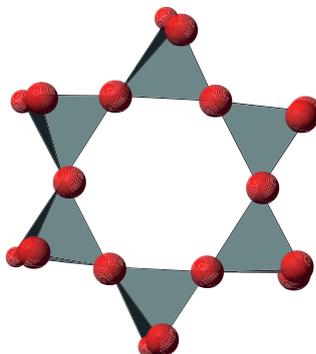
Silicate	Mineral	Anion	Oxidation number		Balancing charge				Charge
			Si	O	Ca^{2+}	Al^{3+}	OH^-	H_2O	
Lawsonite	$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$	$\text{Si}_2\text{O}_7^{6-}$	Si	O	Ca^{2+}	Al^{3+}	OH^-	H_2O	6-
			+4	-2	2+	3+	1-	0	
			Total	= 2(+4) + 7(-2) = -6		= (2+) + 2(3+) + 2(1-) = 6+			

Cyclic tetrahedra

Cyclosilicates have linked tetrahedra forming a ring structure.

Question

14. Cyclosilicates can exist as minerals that demonstrate a 1:3 silicon to oxygen ratio (such as benitoite) or a 1:6 ratio (such as beryl). The structure of the silicate present in beryl is shown below.



- (a) Beryl, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$, contains the very rare element beryllium. Beryllium and its alloys are employed in applications where their high-rigidity, lightweight materials are required.

(i) **State** the type of bonding present between silicon and oxygen atoms in beryl.
 (1 mark) **KA1**

(ii) **State** the block of the table in which beryllium belongs.
 (1 mark) **KA1**

(iii) **Calculate** the percentage, by mass, of beryllium available in the mineral beryl.
 (2 marks) **KA4**

(iv) **Calculate** the charge on the silicate anion present in Beryl.
 (2 marks) **KA4**

(v) Beryllium is non-magnetic, so tools used for maintenance of magnetic resonance imaging MRI machines and radars are often made of alloys of beryllium.
Suggest one reason why it would be important to use tools made from beryllium in these applications.
 (1 mark) **KA3**

- (b) Benitoite, containing the silicate anion $\text{Si}_3\text{O}_9^{6-}$, is a rare blue gemstone that has minor use as an ore for obtaining titanium and barium.

(i) The silicate anion found in benitoite is balanced by barium and titanium in a 1:1 ratio.
Write the formula of the benitoite mineral.
 (2 marks) **IAE3**

(ii) **Suggest** one reason why the benitoite mineral is not utilised as a major source of titanium.
 (1 mark) **KA3**

(c) Cordierite, $(\text{Fe,Mg})_2\text{Al}_3(\text{Si}_5\text{AlO}_{18})$, exists in nature as a cyclic aluminosilicate. Synthetic cordierite is used to construct the monolith inside catalytic converters.

(i) **Determine** the charge of the aluminosilicate anion present in cordierite.

..... (2 marks) **KA4**

(ii) **Calculate** the percentage of silicon that has been replaced with aluminium in the aluminosilicate.

..... (2 marks) **KA4**

(iii) **State** the effect on the charge of the silicate when substituting an aluminium atom for a silicon atom within the structure.

.....
 (1 mark) **KA1**

(iv) Aluminium ions exist on the surface of the silicate and replace silicon within the aluminosilicate structure.

Explain, in terms of bonding, which aluminium would be more easily removed, ions on the surface of the structure or those within it.

.....

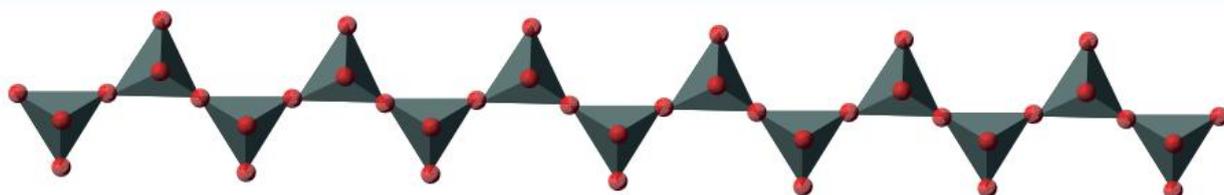
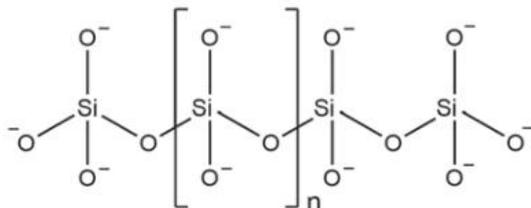
 (2 marks) **KA2**

(v) **Suggest** one reason why synthetic cordierite is a highly effective material for use as the monolith inside catalytic converters.

.....
 (1 mark) **KA2**

Single and double chain tetrahedra

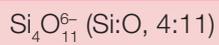
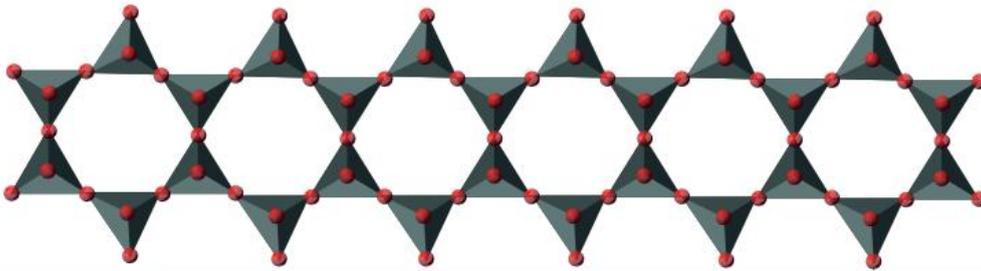
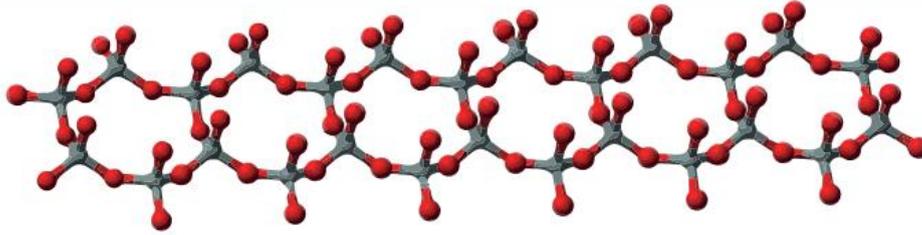
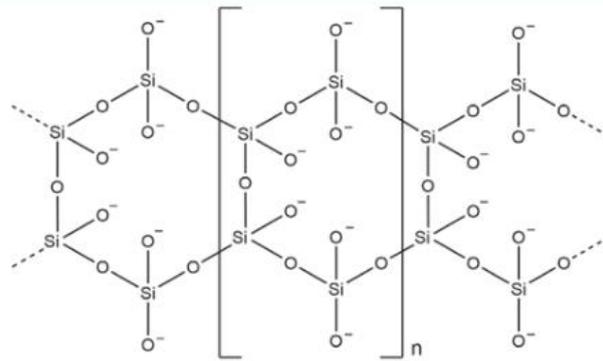
Tetrahedra can be combined in single chains $(\text{SiO}_3^{2-})_n$ and double chains $(\text{Si}_4\text{O}_{11}^{6-})_n$. Minerals containing chains are referred to as **inosilicates**. Single chains are joined by two common corner oxygens; double chains are joined by three common corner oxygens. Both single-chain and double-chain minerals demonstrate a repeating unit.



Worked examples

Silicate	Mineral	Anion	Oxidation number		Balancing charge	Charge
Ferrosilite	FeSiO_3	$(\text{SiO}_3^{2-})_n$	Si	O	Fe^{2+}	2-
			+4	-2	2+	
			Total $= (+4) + 3(-2)$ $= -2$		$= 2+$	

Silicate	Mineral	Anion	Oxidation number		Balancing charge		Charge
Diopside	$\text{MgCaSi}_2\text{O}_6$	$(\text{Si}_2\text{O}_6^{4-})_n$	Si	O	Ca^{2+}	Mg^{2+}	4-
			+4	-2	2+	2+	
			Total $= 2(+4) + 6(-2)$ $= -4$		$= (2+) + (2+)$ $= 4+$		

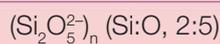
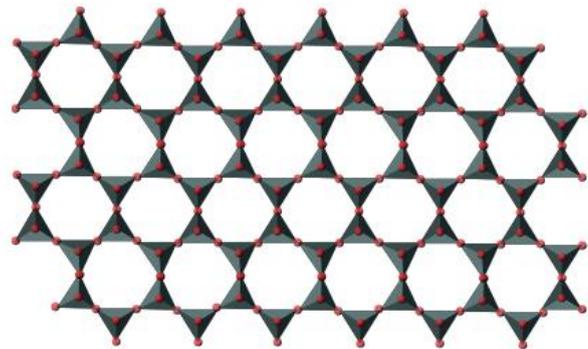
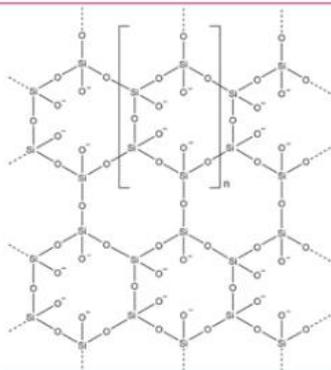


Worked example

Silicate	Mineral	Anion	Oxidation number		Balancing charge				Charge
			Si	O	Na ⁺	Fe ²⁺	Fe ³⁺	OH ⁻	
Riebeckite	$\text{Na}_2(\text{Fe(II)}_3\text{Fe(III)}_2\text{Si}_8\text{O}_{22}(\text{OH})_2)$	$(\text{Si}_8\text{O}_{22}^{12-})_n$	+4	-2	1+	2+	3+	1-	12-
			$= 8(+4) + 22(-2)$ $= -12$		$= 2(1+) + 2(3+) + 3(2+) + 2(1-)$ $= 12+$				
		Total							

Sheet tetrahedra

Tetrahedra can be combined to form sheets by sharing three corner oxygen atoms ($\text{Si}_2\text{O}_5^{2-}$). Minerals containing sheets are referred to as **phyllosilicates**.



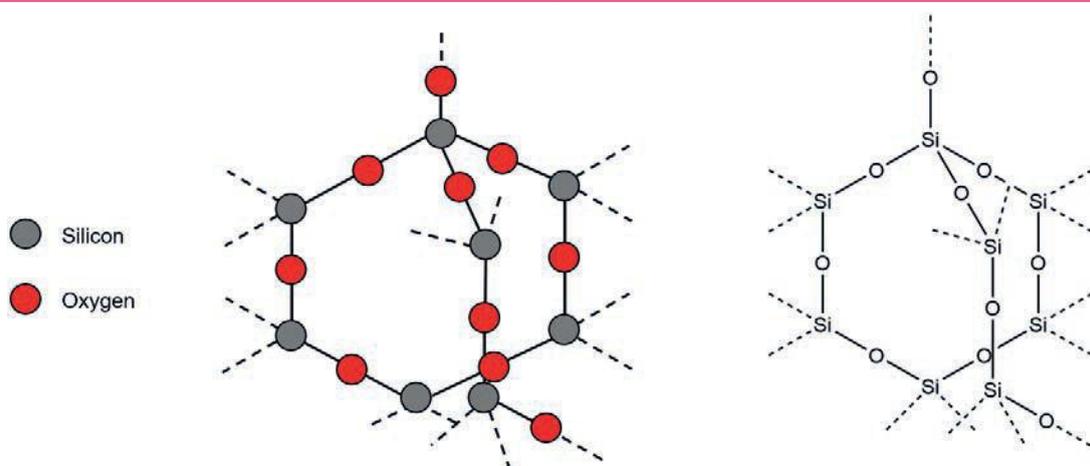
Worked examples

Silicate	Mineral	Anion	Oxidation number		Balancing charge		Charge
			Si	O			
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	$(\text{Si}_2\text{O}_5^{2-})_n$			Al^{3+}	OH^-	2-
			+4	-2	3+	1-	
			Total	$= 2(+4) + 5(-2)$ $= -2$	$= 2(3+) + 4(1-)$ $= 2+$		

Aluminosilicate	Mineral	Anion	Oxidation number			Balancing charge			Charge
			Al	Si	O				
Muscovite	$\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	$(\text{AlSi}_3\text{O}_{10}^{5-})_n$				K^+	Al^{3+}	OH^-	5-
			+3	+4	-2	1+	3+	1-	
			Total	$= (+3) + 3(+4) + 10(-2)$ $= -5$	$= (1+) + 2(3+) + 2(1-)$ $= 5+$				

Three-dimensional framework tetrahedra

Silicates also form three-dimensional frameworks of silicate tetrahedra in a 1:2 silicon–oxygen ratio (SiO_2)_n, where each silicon is bonded on each of the four corners containing an oxygen in the tetrahedron. Silicate minerals with a three-dimensional framework are referred to as **tectosilicates**. Tectosilicates make up approximately 75% of the Earth's crust and are predominantly aluminosilicates. These include the naturally occurring zeolites (refer to water softening using zeolites in Subtopic 4.2 page 285).



SiO_2 (Si:O, 1:2)



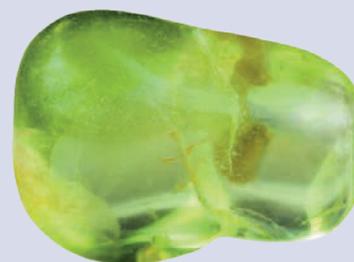
Science as a human endeavour

Carbon sequestration using olivine

Chemists and geoengineers are looking at applications of the mineral olivine in carbon sequestration (trapping carbon dioxide) from anthropogenic activities.

Natural weathering of olivine traps carbon dioxide in the chemical reactions that occur. When magnesium-rich olivine reacts with carbon dioxide and water, the resulting reaction forms magnesium carbonate as one of the products, storing carbon in the compound.

Weathering is a very slow process; however, scientists are proposing that the olivine be mined, crushed and spread in vast quantities over land and sea to accelerate the process. It is predicted that this process could store vast quantities of carbon dioxide that has been emitted into the atmosphere. One limitation in the application is that calculations have suggested that 5 gigatonnes of olivine would need to be processed and spread annually to absorb approximately 30% of our current carbon dioxide emissions.



Science understanding

Silicon dioxide, silicates, and aluminosilicates are important components of rocks and soils.

Soil silicates and aluminosilicates are able to adsorb H^+ and release cations.

Explain how cations on the surface of soil silicates and aluminosilicates become available to plants.

Nutrient cations on the surface of soil silicates and aluminosilicates are replaced if the concentrations of H^+ or Na^+ in soil water become too high.

Explain how acidic or saline conditions (i.e. high concentrations of H^+ or Na^+) deplete the nutrient value of soils.

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Clays

Clay minerals are commonly found in soils. Clay is typically defined by particle size as extremely fine (less than $2\ \mu m$) hydrated silicate or aluminosilicate minerals. Clay minerals form over extended geological timescales from chemical weathering (carbonic acid and water) and the chemical decomposition of rocks containing silicates. The fine clay minerals form deposits in the environment. Clays play an important role in soils, in the transfer of exchangeable ions as nutrients for plants.

Clays are composed of **phyllosilicates** (sheet silicates) which form parallel sheets of silicate tetrahedra. The surface of the sheets contains hydroxyl groups that are hydrated with attached water molecules. Clay minerals are classified as 1:1 or 2:1 depending upon the number of parallel layers of tetrahedral and octahedral layers.

Ratio	Structure	Example
1:1	Consist of one tetrahedral sheet of silica on one octahedral sheet of alumina. They have limited cation exchange capacity as few negatively charged sites exist within the structure.	kaolinite
2:1	Consist of an octahedral sheet of alumina in between two tetrahedral sheets of silica. The substitution of magnesium for aluminium in the alumina sheet provides a negatively charged surface. They have a high cation exchange capacity due to the abundance of negatively charged sites. The surface is coated with exchangeable cations. Water exists between layers.	montmorillonite

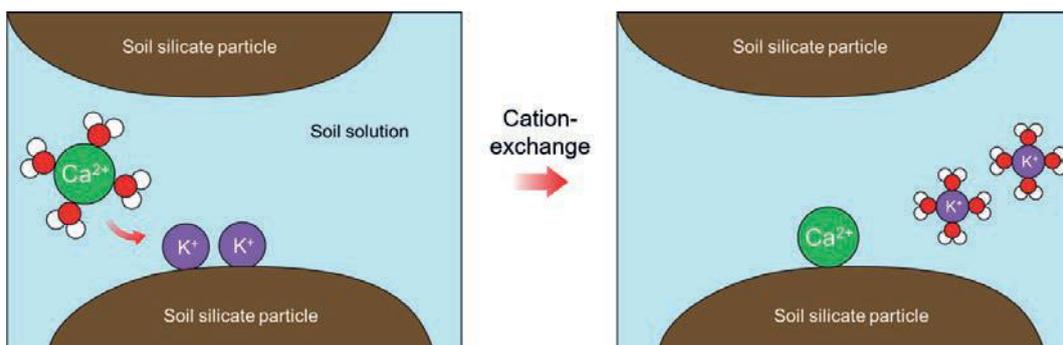


Figure 4.3.5: Layers of soil particles in clays.

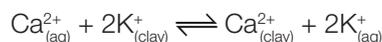
Cation exchange in soils

Cation exchange occurs between the soil surface and the soil solution establishing an equilibrium. The capacity for a particular soil to exchange cations is called the **cation exchange capacity (CEC)**. CEC determines how nutrients move through the soil and are retained. Low-CEC soils may require the addition of fertilisers. CEC is related to the clay content and composition (relative amounts of kaolinite and montmorillonite clays) in the soil. The fine particle size of clays offers exceptional capacity to bind cations.

Exchangeable ions are held weakly on the clay surface due to electrostatic interactions determined by the charge and size of the cations, summarised in the table below for selected ions.

Adsorption of cations					
(based on charge and hydrated radius)					
Strong			Weak		
Al^{3+}	H^+	Ca^{2+}	Mg^{2+}	K^+/NH_4^+	Na^+

Cations that form part of the covalent silicate structure, and those trapped within the structure, are unable to be exchanged. Cations held weakly on the surface of the clay can be replaced by similarly charged ions. Cation exchange is a reversible equilibrium maintaining charge.



Adsorption of these cations provides nutrients to the roots of plants that will not be leached away. (Cations in the soil solution can be washed away.)

Nutrient supply to plants

As water moves through the soil, ions are transported to the roots of plants and absorbed. Cations also undergo exchange on soil surfaces. Root tips in contact with the soil remove cations through osmosis. In each case cations are removed from the soil solution, impacting upon the equilibrium established.

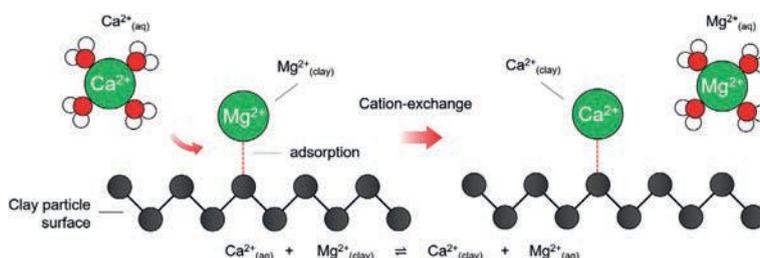


Figure 4.3.6: Cation exchange on the surface of clay particles in soils.

Removal of aqueous magnesium ions from soil solution by the plant places a stress on the equilibrium system. According to Le Châtelier's principle, the equilibrium system counters the change by shifting the position of equilibrium to favour the formation of products. Consequently, more magnesium ions (or equivalent cations) are exchanged from the clay surface and enter the soil solution.

Soil acidity

Soil acidity is present when the pH of the soil drops below 7. The optimal pH for the majority of plant growth is typically between 5.0 and 7.

Natural processes contribute to soil acidity. The weathering of rocks during soil formation, partial ionisation of carbonic acid present in rain, and cation exchange at the root tips of plants during growth, all result in increased hydrogen ion concentration in soil solution.

Human activities also contribute to, and accelerate, soil acidity. The main contributor to the acidity of soils used for agricultural activities is the extensive use of ammonium-based fertilisers, which result in the release of hydrogen ions through the nitrification of ammonium ions to nitrate ions. Accumulation of atmospheric pollutants may also result in the formation of acid rain and subsequent deposition of hydrogen ions in the soil solution from the ionisation of the acids present.

Increased acidity in soils leads to an increase in the concentration of aqueous hydrogen ions (H^+) in soil solution. This places a stress on the system at equilibrium. According to Le Châtelier's principle, the equilibrium system counters the change by shifting the position of equilibrium to favour the formation of products. This results in a shift of a high number of cations from the surface of the clay into the soil solution as hydrogen ions are exchanged onto the surface of the clay.

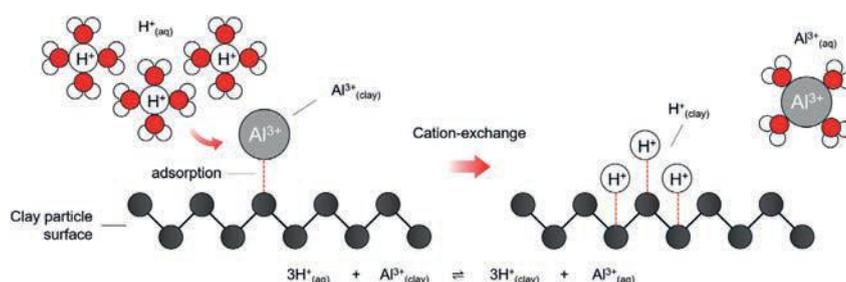


Figure 4.3.7: Removal of aluminium ions from the surface of clay particles in acidic conditions.

Increased acidity can lead to aluminium toxicity as well as magnesium and calcium deficiency in plants.

Aluminium ions are shifted into soil solution through cation exchange. Aluminium ions are toxic to plants, stunting root growth and inhibiting the transport of essential cations to the plant. The low pH and mobilised aluminium ions can also affect soil microbes, reducing the reactions that generate soil nutrients through decay processes.

Cations present in the soil solution are susceptible to leaching during periods of high rainfall. Essential cations such as magnesium and calcium are washed from the topsoil where they are accessible, moving into subsoil or washed out of the topsoil, leaving the soil nutrient deficient.

Soil salinity

Soil salinity is a measure of the dissolved salts contained in soil solution. Natural accumulation of salts occurs in soils due to the weathering of minerals from rocks. Salts are leached out of the soil by rainfall and effective drainage within soil structure. If these conditions are not present, soils may become saline.

Soil salinity is accelerated by human activities such as land clearing and irrigation (controlled watering of plants from a water source). Widespread land clearing for agriculture has removed deep-rooted plants (shrubs and trees) that have the ability to remove water through absorption and subsequent transpiration, preventing the (ground) water table from rising to the surface. Shallow-rooted crops (cereals and legumes) have replaced these plants in many regions; these crops are unable to remove water through absorption deep in the soil. Consequently, the (ground) water table rises. Groundwater contains a high concentration of dissolved salts and is described as highly saline. Saline water is brought to the surface via capillary action, with evaporation precipitating ionic salts. Irrigation and a lack of adequate drainage causes the water table to rise, also resulting in soil salinity.

Soil sodicity

Soil sodicity is a measure of the amount of sodium held on the surface of clays in the soil. When the concentration of sodium cations exceeds approximately 5% of all cations bound on the surface of clays, the soil is referred to as **sodic**. The ratio of salinity to sodicity is used to determine if soils are sodic. Saline soils may contain soil solutions with a high concentration of exchangeable sodium ions. Cation exchange under these conditions may lead to soil sodicity, as shown in the equation below.

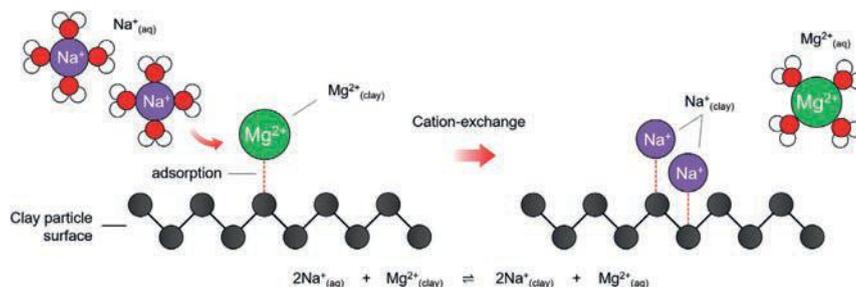


Figure 4.3.8: Removal of magnesium ions from the surface of clay particles forming sodic soils.

Cations of magnesium (Mg^{2+}) and calcium (Ca^{2+}) maintain flocculation in clays by binding the layers of clay within the soil. Replacing these cations with larger sodium ions (Na^+), through cation exchange, weakens the electrostatic attraction between layers of clay, resulting in their separation. The separation results in swelling of the layers of clay, leading to soil dispersion. (Montmorillonite clays are the most strongly affected by swelling and dispersion, with kaolinite clays less likely to swell and disperse.) Soil dispersion weakens aggregates in the soil, leading to structural collapse of the soil. When soil porosity and aeration are lost due to this collapse, the movement of water and gases through the soil is restricted. The root systems of plants are unable to obtain water and are unable to penetrate the soil and grow. The soil can become water-logged as drainage is reduced and a crust is formed on the surface.

A solution to soil sodicity is often found through the addition of gypsum (calcium sulfate (CaSO_4)). Gypsum increases the salinity of the water, which effectively reduces swelling in soils with a high clay content. Importantly, the calcium ions dissociated from gypsum undergo cation exchange with sodium ions causing the sodicity. The high concentration of calcium ions present in the soil solution forces the position of equilibrium to the right, shifting sodium ions into soil solution.

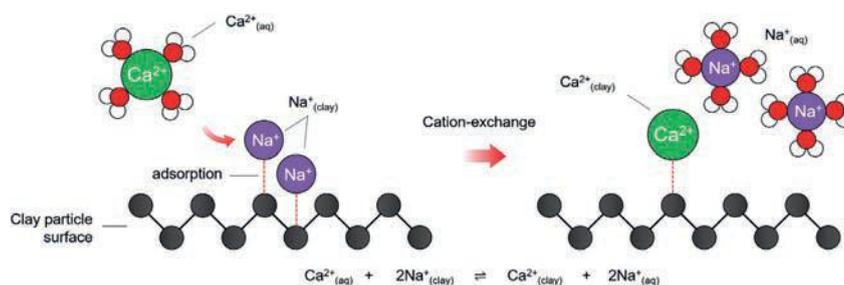
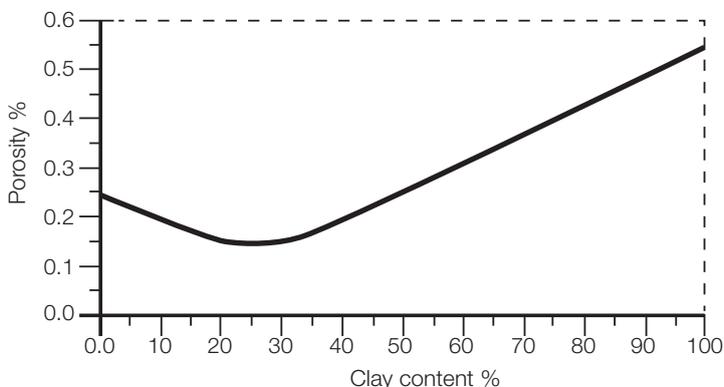


Figure 4.3.9: Removal of sodium ions from the surface of clay particles in sodic soils using calcium ions.

Question

15. Soils are prepared for the cultivation of grass for turf cricket pitches across Australia. Soils chosen are tested for pH, cation exchange capacity, and porosity (swelling).

(a) The clay content of prepared soils used for the growth of a turf cricket pitch are selected for desired levels of porosity.



(i) **Describe** the trend shown in the graph of clay content and porosity for the soil.

.....

 (2 marks) **IAE3**

(ii) **Suggest** why clay content is related to soil porosity.

.....

 (2 marks) **KA2**

(b) The pH values of clay soils used for cricket pitches are maintained between 6.5 and 7.5. Acidic soils, where pH values drop below 6, result in a reduction in the swelling of the clay leading to cracking of the pitch and poor growth of the turf (grass).

(i) **Calculate** the hydrogen ion (H^+) concentration for soil measuring a pH of 5.7.

(2 marks) **KA4**

(ii) **Explain**, with the aid of an equation, how an increased concentration of hydrogen ions present in soil solution leads to the removal of cations from the surface of clays.

.....

 (4 marks) **KA2**

- (iii) **Suggest** how cation exchange with hydrogen ions (H^+) leads to a loss of swelling in clays and the cracking of the pitch.

.....

 (2 marks) **KA2**

- (iv) **State** why acidic conditions result in the poor growth of turf.

.....
 (1 mark) **KA2**

- (v) Lime (hydrated calcium hydroxide, $Ca(OH)_2$) was once used to mark the white lines on cricket pitches, but has been replaced.

- (1) Calcium hydroxide can elevate the pH of soils through neutralisation.

Write a fully balanced chemical equation for the neutralisation of acidic water in soils.

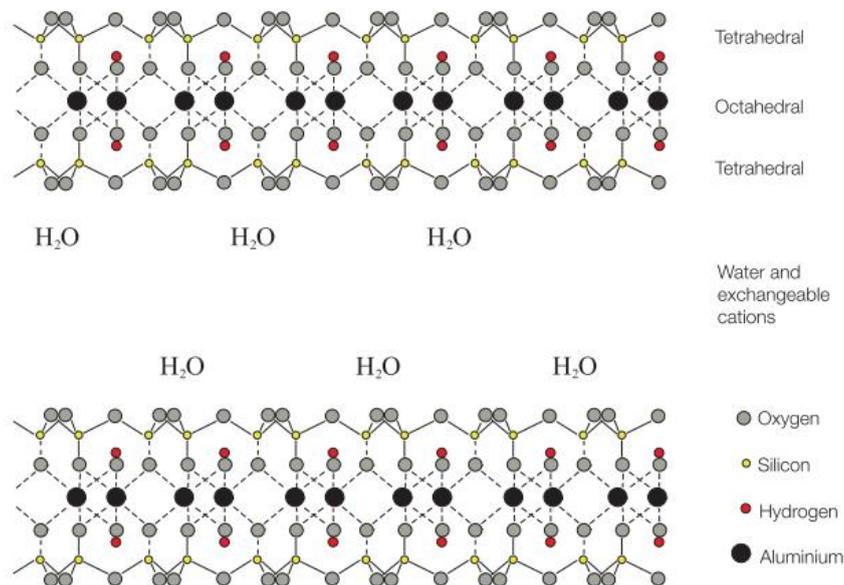
(2 marks) **KA4**

- (2) Calcium hydroxide is caustic.

Suggest one reason why it is no longer used for marking lines on pitches and sporting fields.

.....
 (1 mark) **KA3**

- (c) Montmorillonite clays make the greatest impact on the expansion and contraction of soils under a turf cricket pitch.



Explain, using the diagram above, why soil moisture content also determines the extent of expansion (swelling) and contraction (leading to cracking) in the soil of turf cricket pitches.

.....

 (2 marks) **IAE3**

4.4 Materials

Science understanding

Polymers are produced from monomers by addition or condensation reactions.

Identify the repeating unit of a polymer, given its structural formula

Identify a polymer as being the product of an addition polymerisation or a condensation polymerisation, given its structural formula.

Identify whether a molecule could undergo polymerisation, given its structural formula and, if so, the type of polymerisation.

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Monomers, polymers and repeating units

Polymers are large molecules (**macromolecules**) constructed from smaller molecular units termed **monomers**.

Polymerisation of monomer units results in the formation of a range of molecules of increased molar mass. Polymers exhibit **repeating units** within their structure (Figure 4.4.1). The repeating unit reflects the monomer(s) from which the polymers are constructed. The repeating unit is identified by placing square brackets around the repeating structure.

Polymer	Repeating unit
polytetrafluoroethylene (PTFE, Teflon™)	
polymethylmethacrylate (PMMA)	
polyethylene 2,6-naphthalate (PEN)	
polycarbonate (PC)	
polysiloxane (Silicone)	

Figure: 4.4.1: Repeating units in polymers.

Polymers are present in nature (refer to polysaccharides in Subtopic 3.4 (page 161) and polyesters and polyamides in Subtopics 3.7 and 3.10) and produced synthetically.

Addition polymers

Addition polymers are formed by addition reactions. The addition reaction occurs through the successive combination of monomers by the rearrangement of bonds without the loss of atoms. The formation occurs as a chain reaction (Figure 4.4.2).

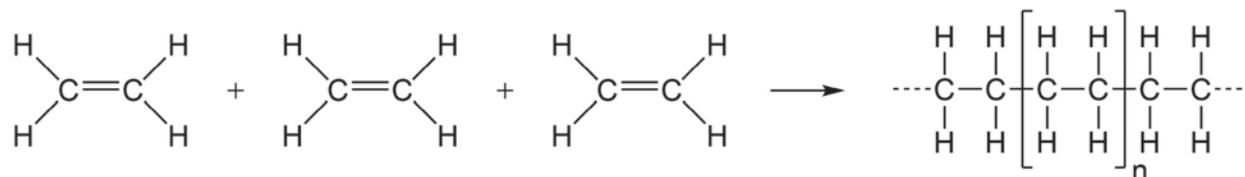


Figure 4.4.2: Polymerisation of the ethene monomer to polyethylene polymer.

Polymerisation occurs at elevated temperatures and pressures with the addition of a catalyst or initiator (to produce reactive species). Addition polymers are typically formed from unsaturated monomers containing carbon–carbon double bonds. The diversity of monomers results in many examples of addition polymers, some of which are shown below (Figure 4.4.3).

Monomer	Monomer name	Polymer	Polymer name
	propene		polypropylene (Plastic bags)
	vinyl chloride		polyvinyl chloride (PVC piping used for plumbing)
	styrene		polystyrene (Styrofoam packaging and cups)

Figure 4.4.3: Addition polymers.

Identification of addition polymers and derivation of monomer(s)

Addition polymers are characterised as having large molar mass and containing a continuous carbon chain (carbon backbone) running centrally through the polymer. Typically, monomers can be derived from one or more carbon–carbon double bonds with atoms or structures present at all four bonds.

Condensation polymers

Condensation polymers are formed in condensation reactions between monomers, with the elimination of a small molecule (often water). Polymerisation occurs in stages, with the formation of **dimers** (two units) which subsequently join to form polymers. Two classes of condensation polymers are **polyesters** and **polyamides**.

Polyesters are formed in condensation of monomers containing carboxyl (carboxylic acid) and hydroxyl (alcohol) functional groups. Polyesters are formed in the condensation of monomers through the formation of **ester** functional groups. Polyesters can be found in nature (cutin, a waxy polyester on the surface of leaves) or can be produced synthetically.

Polyesters can be formed from a single **hydroxycarboxylic acid** monomer containing both the hydroxyl and carboxy functional groups.

An example is the formation of polylactic acid (PLA), a biodegradable polyester derived from corn starch (Figure 4.4.4). The monomer is 2-hydroxypropanoic acid. (*Note: this nomenclature is beyond the scope of the course.*)

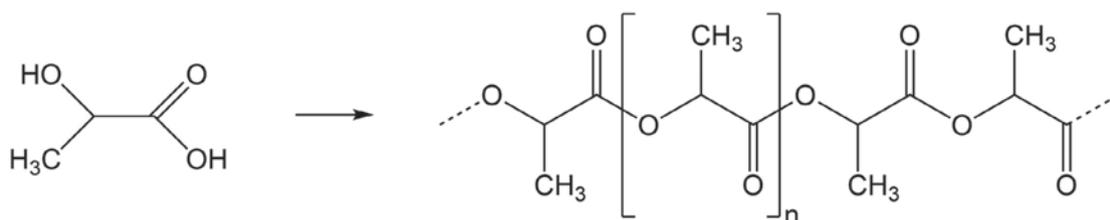


Figure 4.4.4: Condensation of the polyester, polylactic acid (PLA).

Polyesters are more commonly formed from two monomers, one a **dicarboxylic acid** and one a **diol**.

An example is the formation of polyethylene terephthalate (PET), used extensively for fibres in clothing and the formation of storage containers. The two monomers required are ethane-1,2-diol and benzene-1,4-dioic acid (terephthalic acid). (*Note: the nomenclature for the acid is beyond the scope of the course*) (Figure 4.4.5).

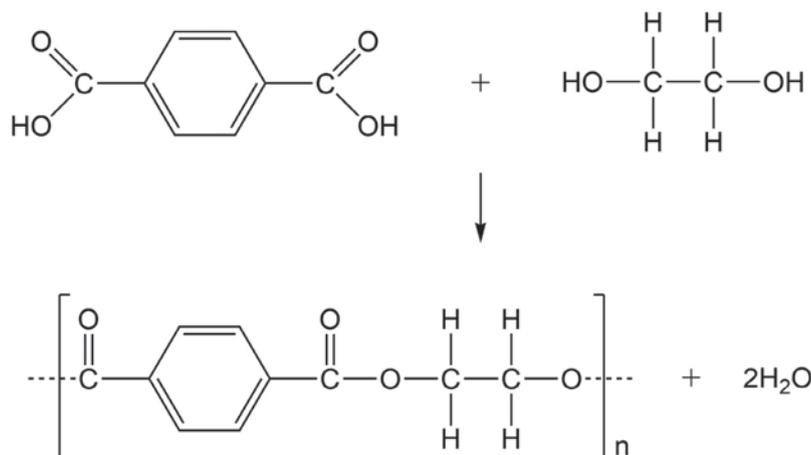


Figure 4.4.5: Condensation of a polyester, polyethylene terephthalate (PET).

Polyamides

Polyamides are formed by the condensation of monomers containing carboxyl (carboxylic acid) and amino (amine) functional groups. Polyamides are formed by the condensation of monomers through the formation of **amide** functional groups. Polyamides can be found in nature (proteins such as wool or silk) and are produced synthetically (nylons and aramids).

Polyamides can be formed from **aminocarboxylic acid (amino acid)** monomers containing both the amino and carboxyl functional groups.

Proteins are natural examples of these polymers, formed from amino acid monomers.

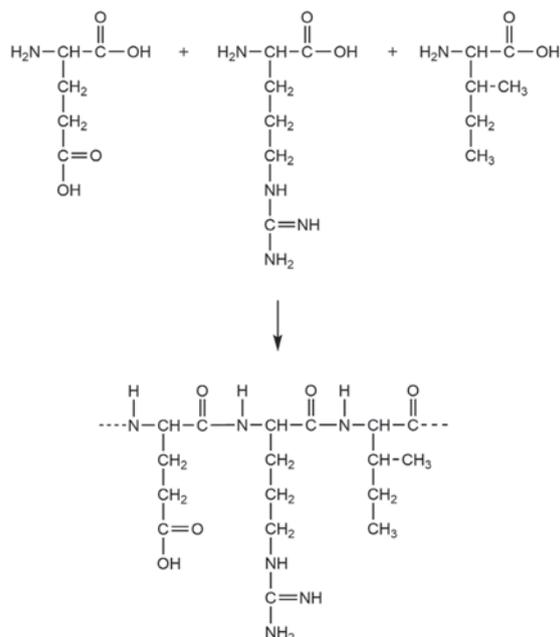


Figure 4.4.6: Condensation of amino acids to form a polypeptide.

Synthetic polyamides are more commonly formed from two monomers, one a **dicarboxylic acid** and one a **diamine**.

An example is the formation of nylon-6,6 used extensively for fibres and within resins. The two monomers required are hexanedioic acid and hexan-1,6-diamine (Figure 4.4.7).

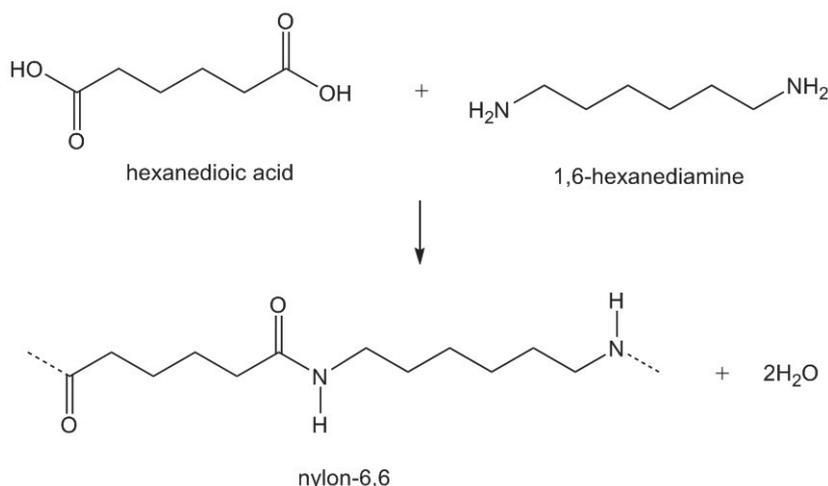


Figure 4.4.7: Condensation of a polyamide, nylon-6,6.

Identification of condensation polymers and derivation of monomer(s)

Condensation polymers are characterised by ester or amide groups linking monomers (or other functional groups resulting from condensation reactions). Typically, their monomer(s) can be derived by identifying the linking functional groups and splitting the polymer chain at these sites. The resulting divisions will reveal the monomer unit(s), which can be regenerated through the addition of H_2O (one end of the monomer will require H and the other OH).

Science understanding

The production of synthetic polymers allows the manufacture of materials with a diverse range of properties.

Discuss the advantages and disadvantages of synthetic polymers.

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Advantages and disadvantages of synthetic polymers

Polymers are produced in vast quantities and used in an unlimited number of applications due to the diversity of materials and desired properties that can be achieved. Synthetic polymers often replace traditional natural materials, such as wood and metal, due to the advantages they offer in physical and chemical properties. Many of their advantages and disadvantages are considered in the table below.

Advantages of polymers	Disadvantages of polymers
Synthetic polymers can be produced to offer a diverse range of structures and properties.	Synthetic polymers persist in the environment for tens to hundreds of years. On land and in the oceans, they are ingested by or entrap wildlife.
Synthetic polymers are relatively cheap to manufacture, compared to processed metals and timber. Synthetic polymers can also be processed in a variety of ways.	A large proportion of synthetic polymers offer limited degradability and ability to be recycled. They are also difficult to separate from composite materials.
Synthetic polymers can often mimic natural materials (glass, wool, cotton, metals, stone) and equal or better many of their physical and chemical properties, such as density, flammability, and thermal and electrical conductivity.	Synthetic polymers are used extensively worldwide for packaging and disposable products; at end of life, many are buried as wastes in landfill.
Synthetic polymers (through the inclusion of additives) can be produced with specific properties such as increased rigidity, durability, thermal stability, and chemical or UV resistance.	Synthetic polymers and their additives leach harmful chemicals into the soil and groundwater. Combustion of synthetic polymers and their additives can also result in the formation of toxic products.

4

Science understanding

Organic polymers can have different properties, such as rigidity, depending on the monomers and the degree of cross-linking between chains.

Compare the physical properties of polymers with different degrees of cross-linking and secondary interactions between polymer chains.

Compare the effects of heating on thermoplastic and thermoset polymers.

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Polymer properties

The molecular structure of polymers can be manipulated to develop synthetic polymers that vary in properties including density, hardness, rigidity, thermal and electrical conductivity, and opacity. This allows polymers to be created with unique chemical and physical properties.

Polymer properties vary widely due to differences in: the molecular size (chain lengths) of the resulting polymer, the types of monomers used, the degree of branching on polymer chains, and the extent of cross-linking between polymer chains. Additives can also alter properties such as UV resistance and thermal stability.

The molecular size of the polymer chains (molecular size varies for a polymer) affects the strength of dispersion forces experienced. Larger molecules experience stronger dispersion forces.

The monomers that the polymer is synthesised from determine the functional group chemistry present and the extent and type of branching that result. Polymers containing ester and amide groups, or branches with hydroxyl, carboxyl, or amino groups, can experience dipole–dipole interactions and hydrogen bonding between polymer chains, increasing the strength and number of interactions. Branching also affects the ability of chains to pack closely, changing the density of the polymer. Examples include LDPE (low-density polyethylene) which has extensive branching preventing molecules from stacking closely (plastic shopping bags), and HDPE (high-density

polyethylene) with minimal branching allowing the molecules to stack (garbage bins). The resulting increase in strength of dispersion forces makes HDPE stronger and more rigid.

The extent of cross-linking that occurs between polymer chains determines the rigidity of the polymer. Strong covalent bonds hold the polymer chains in position. With light cross-linking, the polymer is elastic and flexible; with extensive cross-linking, rigidity is increased.

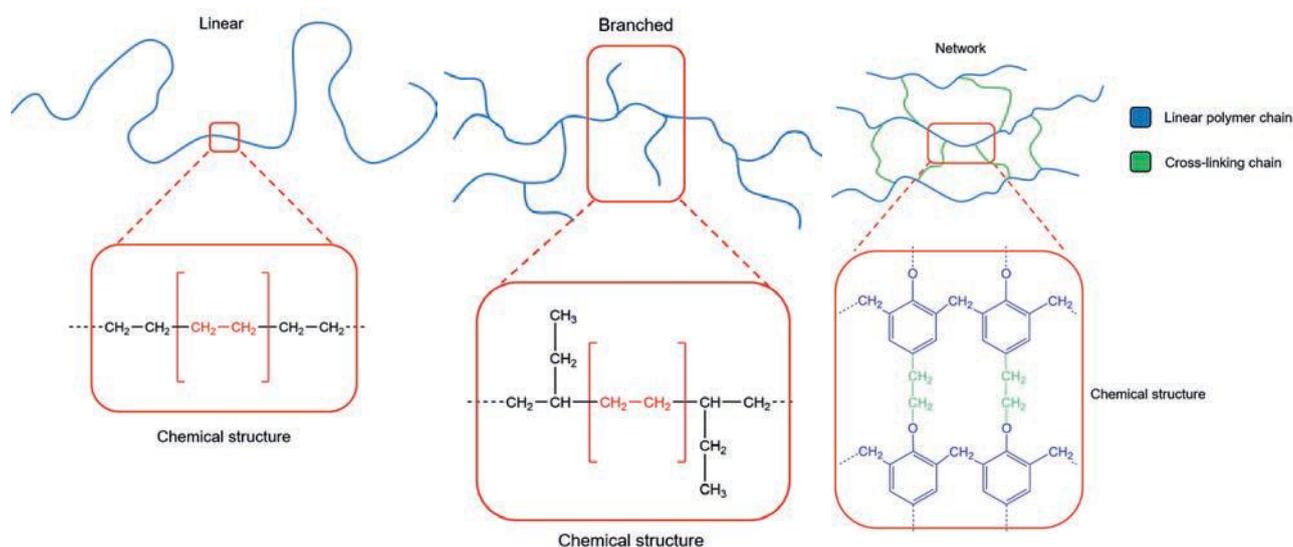


Figure 4.4.8: Polymers and intermolecular forces.

Thermoplastic polymers

Thermoplastic polymers soften and become fluid upon heating, and solidify when cooled. Polymer chains are typically linear or branched, are of large molecular mass, and exhibit little to no covalent cross-linking. Secondary interactions can be overcome when heat is applied, allowing polymer chains to slide past one another and flow. This is a reversible physical process allowing the polymers to be recycled.

Thermosetting polymers

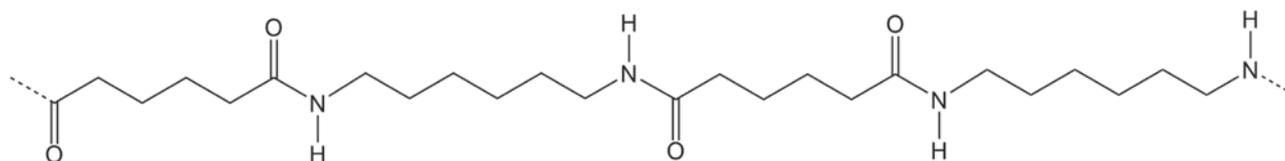
Thermoset or **thermosetting polymers** are formed during the curing, heating, or irradiation of a polymer (or the addition of a catalyst) to form cross-linking in polymers. Once formed, thermosets do not soften on heating; they tend to char and crack, decomposing rather than melting.

Curing introduces atoms that form covalent bridges or cross-links between polymer chains. Cross-links are generated during the formation of the polymer from monomers, or after formation through the addition of molecules capable of bridging polymer chains. This could include unsaturated carbon-carbon double bonds, opportunities for condensation, or formation of covalent sulfur-sulfur bonds (for example the vulcanisation of rubber).

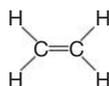
Thermosets are characterised by a high degree of covalent cross-linking to form three-dimensional networks with increased rigidity. When heat is applied, the chains are held in fixed positions. This makes them extremely difficult to recycle.

Question

16. Polymer development has had significant impact on materials applied to sporting equipment such as tennis racquets.
- (a) Tennis racquet strings were traditionally made from gut (animal intestines made of collagen). Modern strings are predominantly made of nylon, often braided with other synthetic polymers.
- (i) **Suggest** the name of the class of natural condensation polymers present in gut strings.
 (1 mark) **KA1**
- (ii) A section of the nylon-6,6 polymer used for modern strings is shown below.



(v) Polyolefin polymers offer the softest strings; they are made from the monomer shown below.



(1) **Identify** the type of polymer produced from the monomer above.

.....(1 mark) **KA1**

(2) **State** and **explain** whether the polymer produced from this monomer is classified as a thermoplastic or thermoset.

.....

(3 marks) **IAE3**

(3) **Suggest** why the polymer produced is a soft polymer.

.....
(1 mark) **KA2**

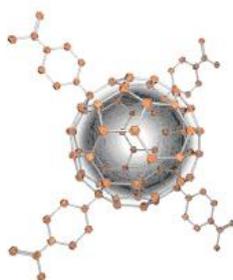
(b) Tennis grips and vibration dampeners in the frame of racquets are often made from the polymer polyurethane. Polyurethanes used in tennis racquets are elastic due to limited cross-linking in the polymer.

Explain how limited cross-linking leads to an elastic material, whereas an absence of cross-linking will not produce an elastic material.

.....

(3 marks) **KA2**

(c) New technologies used in the manufacture of racquet frames use carbon fullerenes (X-fullerenes) that have the ability to form cross-links. The structure of the fullerene is shown below.



(i) **Explain** how the inclusion of X-fullerenes increases the rigidity of the carbon polymer structure.

.....

(2 marks) **KA2**

(ii) **Suggest** one advantage of producing a tennis racquet with greater rigidity.

.....
(1 mark) **KA3**

Science understanding

Polymers can be made from fossil resources or from renewable materials.

Discuss the advantages and disadvantages of making polymers from fossil resources or from renewable materials.

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Polymer production

The majority of synthetic polymers are derived from **petrochemicals** (from petroleum) as a feed stock. The accelerated depletion of these reserves, and the need for more environmentally sustainable production, has led to greater research into and application of synthetic biopolymers as an alternative.

Synthetic biopolymers are derived from renewable plant material as a feedstock for raw materials. Polysaccharides (starch, cellulose and lignin from plant crops), proteins (zein from corn) and triglycerides (canola, castor and soybean oil) can all be used as raw materials in the production of biopolymers. The advantages and disadvantages of polymer production from both petrochemicals and biomass are considered in the table below.

Advantages of polymer production from petrochemicals	Advantages of polymer production from biomass
Petroleum and natural gas are a relatively abundant feedstock.	Carbohydrates, proteins and oils derived from biomass are relatively abundant as feedstock.
Petroleum and natural gas are easily extracted and processed into petrochemicals used as raw materials.	Raw materials are easily extracted and processed from biomass.
Well-established industries exist for a multitude of polymer products derived from petroleum and associated petrochemicals.	The source of biomass can often be a by-product or waste product of other industries such as agriculture.
A wide variety of polymers with varying polymer properties can be derived from petrochemicals.	Biomass is a renewable feedstock.

Disadvantages of polymer production from petrochemicals	Disadvantages of polymer production from biomass
Petroleum and natural gas reserves are being depleted at an accelerated rate. Their rate of depletion is much faster than their geological rate of formation.	A limited range of polymers derived from biomass are currently possible.
Petroleum and natural gas are non-renewable feedstock.	Use of biomass for polymer production may compete directly with land cropped for food production.

Science understanding

Some polymers are biodegradable — being able to be broken down by microorganisms and other living things.

Explain why some polymers are biodegradable but others are not.

Explain the advantages of polymers being biodegradable.

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Degradable polymers

Many conventional synthetic polymers persist in the environment for many years after their disposal. For example, the strong covalent carbon–carbon bonds present in many addition polymers are difficult to break down. This has led to the development of renewable and degradable synthetic polymers that impact less on the environment.

Degradable polymers are designed to maintain structural integrity and functionality during use, then break down over time in the environment after disposal. The polymers degrade due to chemical reactions in the environment (oxidation and hydrolysis), reactions of microorganisms, and, in some applications, absorption of sunlight (photodegradable polymers). Degradable polymers include natural polymers (carbohydrates, proteins, nucleic acids) and synthetic polymers derived from petroleum and biomass.

Biodegradable polymers

Biodegradable polymers degrade due to the enzyme-assisted reactions of microorganisms such as bacteria, fungi and algae (Figure 4.4.9).

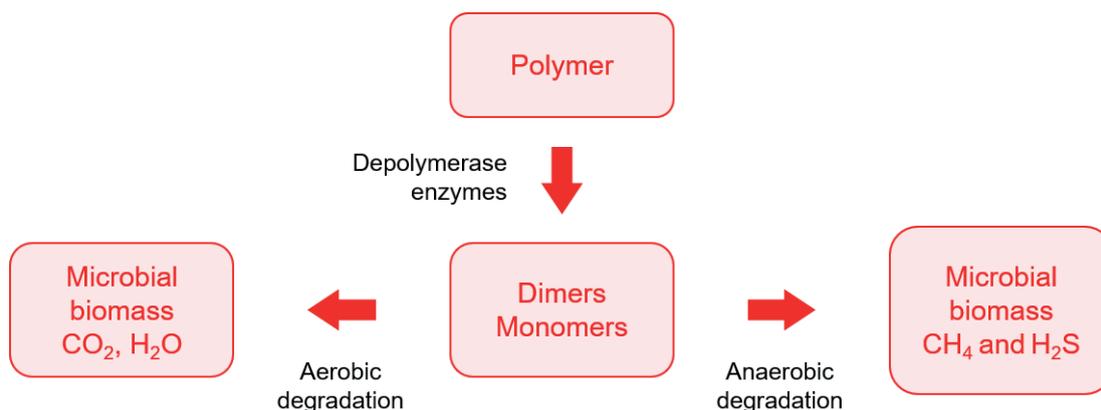


Figure 4.4.9: Biodegradation by microorganisms.

Many biodegradable polymers contain ester and amide groups (or other functional groups that may be hydrolysed). The bonds readily undergo hydrolysis to break down the polymer. Examples include polylactic acid (PLA, derived from corn starch, used for compostable bags) and polyglycolic acid (PGA, derived from sugar cane, used for dissolvable stiches) (Figure 4.4.10).

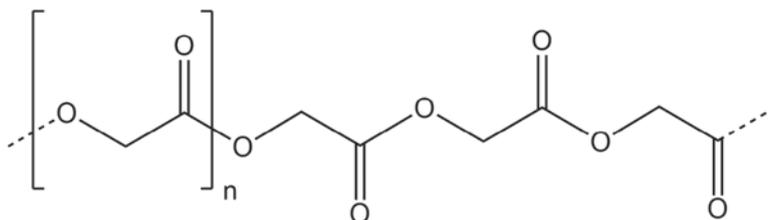


Figure 4.4.10: Polyglycolic acid PGA.

Photodegradable polymers

Photodegradable polymers are designed to become brittle and break down when exposed to sunlight. Carbonyl groups (C=O) can be incorporated into the polymer. These absorb radiation from sunlight and break down. Light-sensitive additives can also be incorporated to catalyse the reaction.



Science as a human endeavour

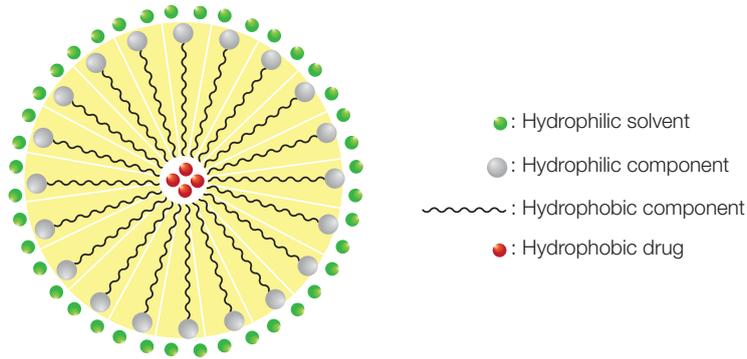
Limitations of degradable polymers

There is much debate between scientists whether the advantages offered by degradable polymers outweigh some of their disadvantages and whether recycling of non-degradable polymers is more effective in terms of the use of resources and in terms of environmental impact.

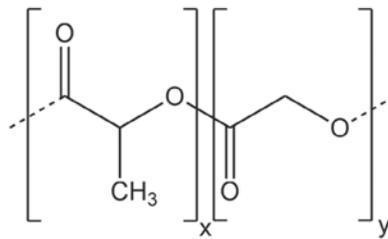
Many of the polymers we use end up in landfill. It is estimated that 20700 tonnes of plastic (polymer) are disposed of in landfill sites around Australia every year. In landfill, degradable synthetic polymers are exposed to limited oxygen, water and sunlight. Without sunlight, photodegradable reactions will not occur, halting the break down of photodegradable polymers. When these polymers are exposed to sunlight, they simply break down to smaller particles of polymer, which persist in the environment with unknown consequences. With limited exposure to water and oxygen in landfill, biodegradable polymers degrade at much slower rates and persist longer in the environment.

Question

17. Polylactic-co-glycolic acid (PLGA) is used in applications of drug delivery due to its degradability in the human body. The polymer surrounds the drug being delivered as shown in the diagram below.



(a) The PLGA polymer is shown below.



- (i) **Circle** one ester group in the section of polymer. (1 mark) KA1
- (ii) **State** whether PGLA is an addition or condensation polymer.

- (iii) **Draw** the structural formulae of the two monomers (lactic acid and glycolic acid) used to form the polymer. (1 mark) KA1

(4 marks) IAE3

(b) PGLA has hydrophilic regions, providing solubility in the human body, while also being degradable in this aqueous environment.

- (i) **State** the interaction that occurs between water and the hydrophilic regions.
 (1 mark) KA1
- (ii) **Explain** how the presence of ester groups in the PGLA polymer leads to the polymer's degradability in the human body.

 (2 marks) KA2
- (iii) **Suggest** one advantage of the use of a degradable polymer in drug delivery.

 (1 mark) KA3



- (c) The PGLA polymer can be altered with the inclusion of long non-polar (hydrophobic) monomers into the polymer structure to increase the solubility of non-polar drugs.

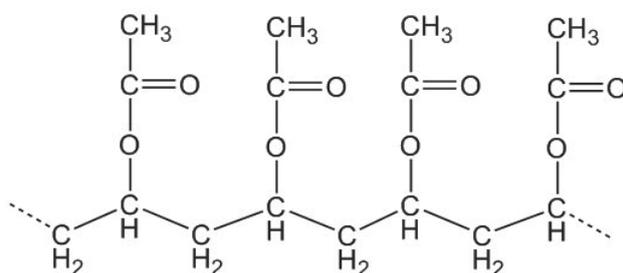
State and **explain** the effect of the inclusion of long non-polar monomers on the rate of degradation of the polymer in the human body.

.....

 (3 marks) **IAE3**

18. Laundry bags in hospitals are being made from soluble polymers to reduce the risk of infection from soiled garments. Polyethenol is one dissolvable polymer used for laundry bags.

- (a) The synthetic polymer, polyethenol, is made from another polymer, polyethenyl ethanoate. The structure of polyethenyl ethanoate is shown below.

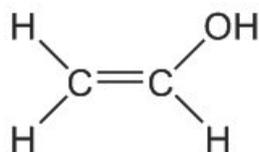


- (i) **State** whether polyethenyl ethanoate is formed through a condensation or an addition reaction.
 (1 mark) **KA1**

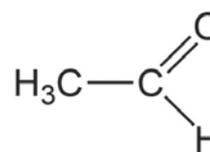
- (ii) **Draw** the structural formula of the monomer of polyethenyl ethanoate.

(2 marks) **KA4**

- (b) Polyethenol is made from an ester exchange rather than polymerisation due to the unstable nature of ethenol. Ethenol and the aldehyde it forms are shown below.



ethenol



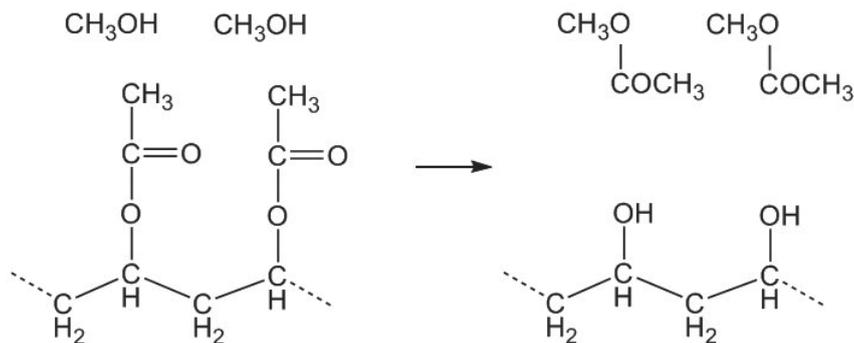
aldehyde

- (i) Ethenol and the aldehyde share the same molecular formula but have different structural formula. **State** the name given to this occurrence.
 (1 mark) **KA1**

- (ii) **State** the systematic name of the aldehyde.

..... (2 marks) **KA4**

(c) Methanol is the reactant used to generate the ester exchange. The ester exchange reaction is shown below.



- (i) **State** the systematic name of the ester that is formed as a product of the exchange.
 (2 marks) **KA4**
- (ii) The extent of ester exchange determines the percentage of hydroxyl groups that are formed on the surface of the polymer. The solubility in water for different percentages of exchange are summarised in the table below.

% of ester groups replaced	Solubility in water
100 – 99	Soluble
99 – 97	Soluble in warm water
96 – 90	Soluble in hot water
Less than 90	Insoluble

State and **explain** the trend in solubility shown in the table.

.....

 (3 marks) **IAE3**

- (iii) **Suggest** one alternative use for the polymer based on the information provided in the table and provide one reason for its use in this application.

 (2 marks) **KA3**



Science understanding

The occurrence of metals in combined or uncombined form in the Earth's crust is related to the reactivity of the metal.

Given the position of a metal in the activity series of metals:

Predict whether the metal is likely to occur in nature in a combined or uncombined form.

Predict and explain the likely method of reduction of the metal compound, including electrolysis of the molten compound, electrolysis of an aqueous solution of the metal compound, and use of carbon as a reducing agent.

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Occurrence of metals

The majority of metals in the Earth's crust occur as **minerals**, often found in **ores**. A mineral is a naturally occurring compound formed in the Earth's crust. Some minerals contain sufficient quantities of metal to be extracted economically. It is possible to find some metals in their **native** form as an element. Elemental gold, silver, copper, platinum, arsenic, bismuth, and alloys of these and other metals, occur uncombined in nature due to their low activity. The activity of selected metals in comparison to hydrogen are shown in the table below.

Activity	Metal		Reactivity	Ion	Reduction of ions
Most active metal → least active metal	potassium	K	Displaces H ₂ gas from water, steam and acids and forms hydroxides	K ⁺	Most difficult to reduce → most easily reduced
	sodium	Na		Na ⁺	
	lithium	Li		Li ⁺	
	calcium	Ca		Ca ²⁺	
	magnesium	Mg	Displaces H ₂ gas from steam and acids and forms hydroxides	Mg ²⁺	
	aluminium	Al		Al ³⁺	
	zinc	Zn		Zn ²⁺	
	iron	Fe	Displaces H ₂ gas from acids only and forms hydroxides	Fe ³⁺	
	nickel	Ni		Ni ²⁺	
	tin	Sn		Sn ²⁺	
lead	Pb	Pb ²⁺			
hydrogen	H ₂	Included for comparison			
copper	Cu	Combines with O ₂ to form oxides and cannot displace H ₂	Cu ²⁺		
mercury	Hg	May be found uncombined in nature. Oxides decompose with heating	Hg ²⁺		
silver	Ag		Ag ⁺		
gold	Au		Au ³⁺		

Methods of reduction

The method chosen for reduction of the metal ions to the metal (elemental form) is determined primarily by the activity of the chosen metal. Economics and the energy requirements for each stage of metal production also determine the method used. The costs associated with maintaining high-temperature furnaces and the release of vast quantities of pollutants during this process have favoured the use of electrolytic reduction (both molten and aqueous). The potential methods of reduction based on chemical activity are summarised for selected metals of economic importance in the table on the next page.

Activity	Metal		Methods of reduction	Compound in mineral	Reduction of ions
Most active metal → least active metal	potassium	K	Molten electrolytic reduction Water cannot be present, as it is reduced in preference to the metal ions	KCl	Most difficult to reduce → most easily reduced
	sodium	Na		NaCl	
	lithium	Li		LiCl	
	calcium	Ca		CaCl ₂	
	magnesium	Mg		MgCl ₂	
	aluminium	Al		Al ₂ O ₃	
	water	H ₂ O	Included for comparison		
zinc	Zn	Aqueous electrolytic reduction Reduction of an aqueous solution as the metal ions are reduced in preference to water or Chemical reduction Chemical reduction utilising carbon or carbon monoxide as a reducing agent	ZnO		
iron	Fe	Chemical reduction Reduction utilising carbon or carbon monoxide as a reducing agent	Fe ₂ O ₃		
nickel	Ni		NiO		
tin	Sn		SnO ₂		
lead	Pb		PbO		
copper	Cu	Chemical reduction Roasting in oxygen, utilising oxygen as the reducing agent	Cu ₂ S		
mercury	Hg		HgS		
silver	Ag	May be found uncombined in nature	Ag		
gold	Au		Au		

Production of metals

Once a body of ore has been identified, the geological and environmental impact of mining is considered for the region and a mine site may be established. Atomic absorption spectroscopy (AAS) (refer to Page 90) is commonly used to identify the concentration of metals present in minerals in the ore; this analysis is used to establish the viability of the mine. Typically, five stages may be undertaken in the production of metals. It must be noted that not all stages outlined are required, depending upon the percentage of mineral present in the ore, cost of processing, and the desired purity and applications of the final product. The five common stages involved in metal production are summarised in the table below.

Stage	Explanation
Extraction	An identified ore body must be economically viable to be mined. The ore deposit is extracted (mined) from the Earth's crust. Open-cut or underground mining techniques may be undertaken.
Concentration	The ore is crushed and ground and the mineral present is concentrated by removal of unwanted minerals and waste rock (gangue). Higher concentrations of mineral are achieved at the mine site to reduce costs associated with transportation and disposal of waste rock. This stage is not required if the percentage of the mineral present in the ore is substantial or conversion is viable with wastes present.
Conversion	One or more stages of chemical conversion may be required to convert the mineral to a compound suitable for the reduction stage. This stage is not required if the mineral already exists as a compound suitable for reduction.
Reduction	Chemical reduction at high temperatures or molten or aqueous electrolysis is used to reduce metal ions to the metal.
Refining	Electrolysis or further chemical reactions are undertaken to remove remaining impurities. The metal may also be alloyed at this stage to improve upon properties. This stage is not required if the reduction stage yields a metal of sufficient purity for its desired application.

Science understanding

The production of some metals requires the conversion of minerals to a form suitable for reduction.

Explain, with the aid of equations, the methods chosen for the conversion of a mineral to a metal, given sufficient information.

Explain the benefits of one method of reduction compared with another, given relevant information.

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Aluminium, iron, copper, zinc and titanium are five of the most commonly used metals. The stages required for the production of aluminium and zinc are outlined.

Example

Production of aluminium

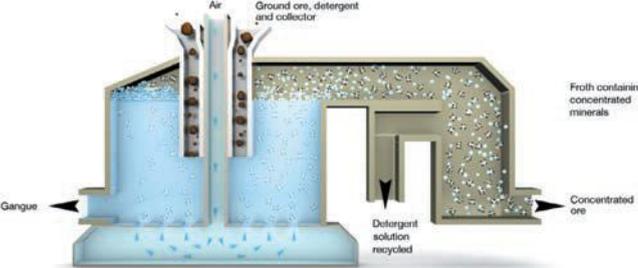
Stage	Explanation
Mining (Extraction)	Aluminium is extracted from the ore bauxite. Bauxite is one of the most abundant ores in the world. Aluminium occurs in the ore primarily as the mineral gibbsite (aluminium hydroxide $\text{Al}(\text{OH})_3$)
Concentration	A concentration stage is not required as the ore contains a sufficiently high percentage of the mineral containing aluminium.
Conversion	Powdered bauxite is mixed with sodium hydroxide and heated. $\text{Al}(\text{OH})_{3(\text{s})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaAlO}_{2(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})}$ Aluminium hydroxide is digested to form sodium aluminate. Oxides of iron remain insoluble and are settled as a waste product (red mud). The residual solution is seeded with aluminium hydroxide to allow crystallisation of solid aluminium hydroxide. $\text{NaAlO}_{2(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Al}(\text{OH})_{3(\text{s})} + \text{NaOH}_{(\text{aq})}$ Aluminium hydroxide is filtered off and heated in a kiln to produce aluminium oxide (alumina). $2\text{Al}(\text{OH})_{3(\text{s})} \rightarrow \text{Al}_2\text{O}_{3(\text{s})} + 3\text{H}_2\text{O}_{(\text{l})}$
	Reduction (electrolytic)
Refining	A refining stage is not required due to the high purity of the metal obtained from electrolysis.

Comparing methods of reduction for aluminium

Molten electrolytic reduction is required for aluminium ions, as aluminium is an active metal. This is a highly energy intensive process. If an aqueous electrolytic cell was employed, water would be reduced in preference to aluminium ions, thus producing hydrogen gas rather than aluminium. Chemical reduction is not suitable to reduce aluminium ions.

Example

Production of zinc

Stage	Explanation
Extraction	The majority of zinc is obtained from zinc sulphide ores (also containing lead, cadmium iron and silver). The most common ore mined to obtain zinc is sphalerite (ZnS).
Concentration	<p>The ore is mined, crushed, ground in a ball-mill and concentrated using froth flotation (see the following diagram).</p> <p>The powdered ore is mixed with water in a large tank to form a slurry. Detergent and collector (ions containing a charged region and a non-polar region) are added, and compressed air is forced through the mixture to generate bubbles. The zinc mineral adheres to the bubbles and is carried to the surface of the froth where it is skimmed off. Heavier clays and silicates settle at the bottom of the tank. This waste product is referred to as gangue. The purpose of froth flotation is to concentrate the mineral present in the ore.</p> 
Conversion	<p>The ore is roasted in a large furnace in the presence of a stream of air to achieve the high temperatures required for conversion of zinc sulphide to zinc oxide.</p> $2\text{ZnS}_{(s)} + 3\text{O}_{2(g)} \rightarrow 2\text{ZnO}_{(s)} + 2\text{SO}_{2(g)}$ <p>Sulfur dioxide gas is removed as a by-product. If released into the atmosphere it may contribute to environmental pollution. It is of greater environmental and economic benefit to generate sulfuric acid as a by-product for later stages of zinc production and to on-sell to the fertiliser industry.</p> $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$ $\text{SO}_{3(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)}$ <p>Zinc oxide is leached with sulfuric acid (as a by-product or regenerated during electrolysis) to allow conversion to aqueous zinc sulfate, a suitable electrolyte for electrolytic reduction.</p> $\text{ZnO}_{(s)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow \text{ZnSO}_{4(aq)} + \text{H}_2\text{O}_{(l)}$ <p>The mixture containing zinc sulfate is then filtered to remove suspended solids and treated with powdered zinc dust (offering large surface area) to precipitate less-active metals such as cadmium, copper, nickel and cobalt. Ions of less-active metals are displaced by relatively active zinc metal.</p> $\text{Cd}_{(aq)}^{2+} + \text{Zn}_{(s)} \rightarrow \text{Zn}_{(aq)}^{2+} + \text{Cd}_{(s)}$ <p>The precipitated metals are another valuable by-product of the process; this is the principal method of cadmium production.</p>
Reduction (electrolytic)	<p>In the final stage, zinc sulfate is electrolysed to produce purified zinc (99.96%).</p> <p>Zinc is reduced onto aluminium cathodes, periodically stripped from the electrodes, melted and cast.</p> $\text{Zn}_{(aq)}^{2+} + 2e^- \rightarrow \text{Zn}_{(s)}$ <p>At the anode, oxygen is evolved as the electrolyte is regenerated.</p> $2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}_{(aq)}^+ + 2e^-$
Refining	Refining is not undertaken due to the high purity of the metal obtained from electrolysis. Changing parameters in the electrolytic cell can yield zinc of even higher percentage purity.
Reduction (chemical)	<p>The thermal method uses a blast furnace charged with coke (carbon) to generate carbon monoxide (CO) as the chemical reducing agent.</p> $2\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow 2\text{CO}_{(g)}$ $\text{ZnO}_{(s)} + \text{CO}_{(g)} \rightarrow \text{Zn}_{(s)} + \text{CO}_{2(g)}$ <p>The zinc that forms is turned into a vapour at the high temperatures encountered. It is collected with gases and condensed.</p>

Comparing methods of reduction for zinc

Chemical reduction of zinc using the thermal process employs a blast furnace operating at approximately 1000°C. High temperatures needed for the reaction are generated and maintained by the combustion of fossil fuels. Large quantities of carbon dioxide gas and atmospheric pollutants are produced. Because of the high costs of production and emissions, most zinc production uses electrolytic reduction. More than 90% of world zinc production is from the electrolytic method. Electrolytic reduction of an aqueous zinc sulfate solution does not require elevated temperatures to allow operation of the cell. This provides a considerable cost saving when compared to the energy requirements of the thermal process or a molten cell.

Science understanding

Electrolytic cells are used to produce required substances.

Identify the anode and cathode and their charges, as well as the direction of ion and electron flow in an electrolytic cell, given sufficient information.

Write electrode half-equations for an electrolytic cell, given sufficient information.

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Electrolytic cells

Electrolytic cells are electrochemical cells that generate redox reactions when an electrical current is applied. Electrical energy is converted to chemical energy. A power supply is used to generate a potential difference between two electrodes (anode and cathode). Electric current flows between the anode and cathode; this current initiates non-spontaneous redox reactions at the surface of each electrode (Figure 4.4.11). Electrolysis is commonly used to decompose chemical compounds and to reduce metal ions to metals.

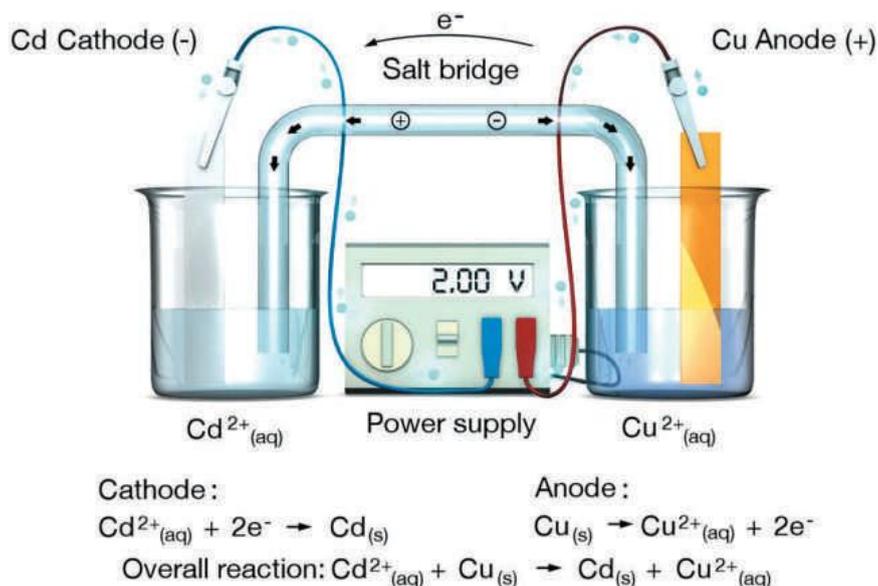


Figure 4.4.11: Copper-cadmium electrolytic cell

The operation of an electrolytic cell can be summarised as follows.

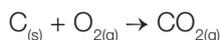
Electrolytic cell	
Energy conversion (forced)	Electrical energy to chemical
Anode reaction	Oxidation
Cathode reaction	Reduction
Electron flow	Anode to cathode
Sign of anode	Positive (+)
Sign of cathode	Negative (-)
Anion movement	Anode
Cation movement	Cathode

Electrolytic cells used in metal production

Electrolytic cells are often used for the reduction and refining stages in metal production.

Reduction of aluminium (molten cell)

The cell is lined with graphite (carbon) as the cathode (-). Blocks of graphite (carbon) are suspended in the molten electrolyte as the anode (+). Aluminium oxide (alumina, Al_2O_3) is introduced to the cell along with cryolite (acting as a flux to lower the melting point of the alumina) to form the electrolyte. The mixture is still required to be heated to above 1000°C to form a molten electrolyte. Strong ionic bonding is overcome in the compounds to provide a molten electrolyte capable of conduction due to free ions. Electrical current is applied for the reduction in the electrolytic cell. Aluminium ions are reduced to molten aluminium at the cathode. The molten aluminium is denser than the molten cryolite and settles as a layer in the bottom of the cell and can be periodically tapped off and cast. At the anode, oxide ions are oxidised to form oxygen. Combustion of the carbon occurs at the anode, which must be replaced periodically.



Reduction of aluminium is an extremely energy-intensive process that requires high temperatures to be maintained and an effective supply of electricity (Figure 4.4.12).

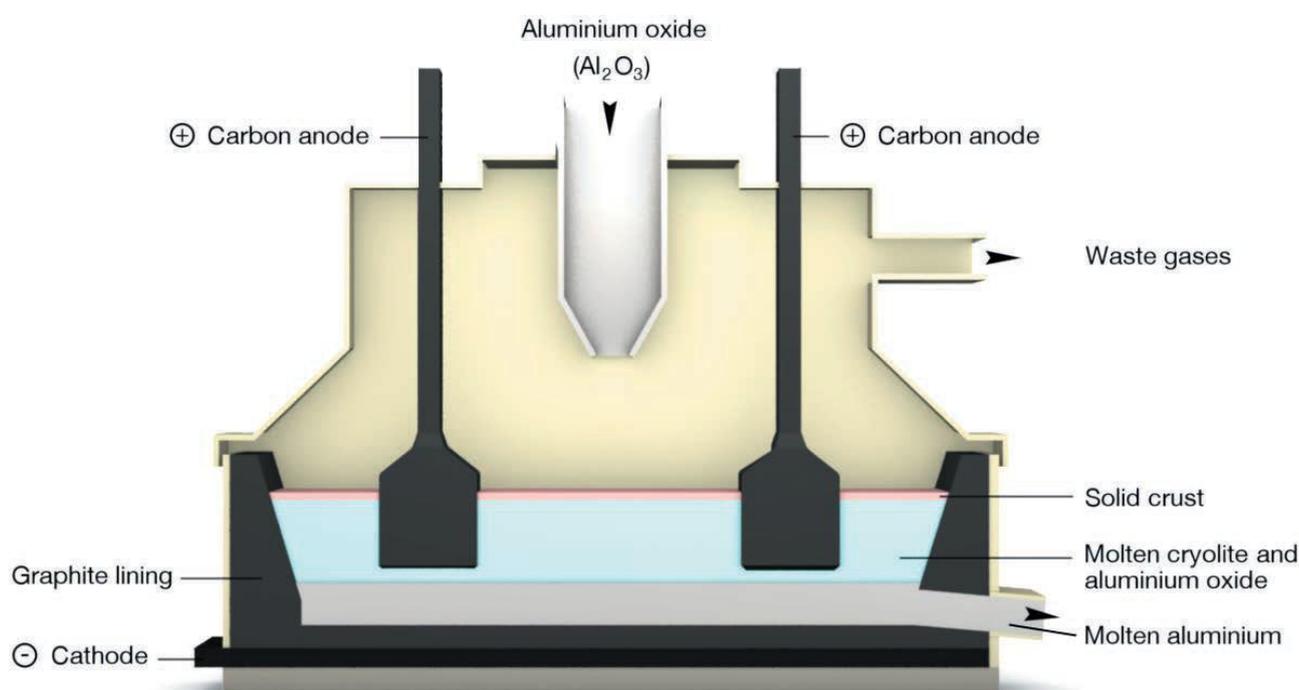


Figure 4.4.12: Aluminium production, electrolytic cell.

Cell features	
Electrolytic (molten cell)	
Anode (+)	$2\text{O}_{(\text{l})}^{2-} \rightarrow \text{O}_{2(\text{g})} + 4\text{e}^-$
Cathode (-)	$\text{Al}_{(\text{l})}^{3+} + 3\text{e}^- \rightarrow \text{Al}_{(\text{s})}$
Electron flow	Anode (+) to cathode (-)
Anion movement	$\text{O}_{(\text{l})}^{2-}$ ions migrate to the anode
Cation movement	$\text{Al}_{(\text{l})}^{3+}$ ions migrate to the cathode

Reduction of zinc (solution cell)

Lead is chosen as the anode due to the metal being relatively inert. Water in the cell is oxidised in preference to lead, eliminating the need to replace the anode. The direction of electron flow in the cell is from the lead anode (+) to the aluminium cathode (-), driven by the potential difference of the power supply. Zinc ions are reduced to high-purity zinc at the cathode. The relative activity of zinc compared to water allows zinc ions to be reduced using aqueous electrolysis. An aqueous cell is preferred to a molten cell because the process is less energy-intensive, as it does not require high temperatures to be maintained. The electrodes sit in a single container of zinc sulfate (ZnSO_4) as the electrolyte. Zinc cations migrate towards the cathode and water molecules migrate towards the anode (Figure 4.4.13).

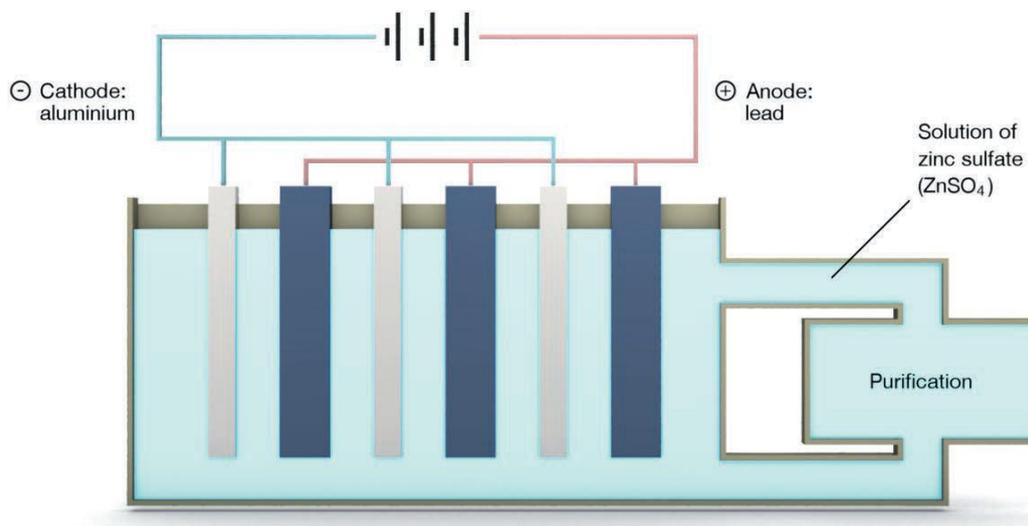


Figure 4.4.13: Zinc production, electrolytic cell.

Cell reactions	
Electrolytic (solution cell)	
Anode (+)	$2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 2\text{e}^-$
Cathode (-)	$\text{Zn}^{2+}_{(aq)} + 2\text{e}^- \rightarrow \text{Zn}_{(s)}$
Electron flow	Anode (+) to cathode (-)
Anion movement	H_2O molecules migrate to the anode
Cation movement	$\text{Zn}^{2+}_{(aq)}$ ions migrate to the cathode

Question

19. Copper is one of the most widely used metals in the world, used extensively in electrical wiring and in alloys.

- (a) Approximately 80% of the world's primary source of copper comes from copper ores containing sulfide minerals. Chalcopyrite is the most abundant copper ore.

Calculate the percentage composition of Cu in chalcopyrite (CuFeS_2).

(2 marks) **KA2**

- (b) The copper ore is crushed and ground and then undergoes froth flotation.

- (i) **State** the purpose of crushing and grinding the ore prior to froth flotation.

.....
 (1 mark) **KA1**

(ii) **State** the purpose of froth flotation.

.....
 (1 mark) **KA1**

(iii) Froth flotation is commonly undertaken at the mine site rather than during final processing.

(1) **Discuss** one advantage to the manufacturer of undertaking froth flotation at the mine site.

.....

 (2 marks) **KA3**

(2) **State** one advantage to the environment of undertaking froth flotation at the mine site.

.....
 (1 mark) **KA3**

(c) Copper is commonly produced using chemical reduction at elevated temperatures.

(i) Solid copper(II) sulfide, CuS, is heated in a blast furnace with oxygen-enriched air to form copper and sulfur dioxide gas.

Write a fully balanced chemical equation for this process.

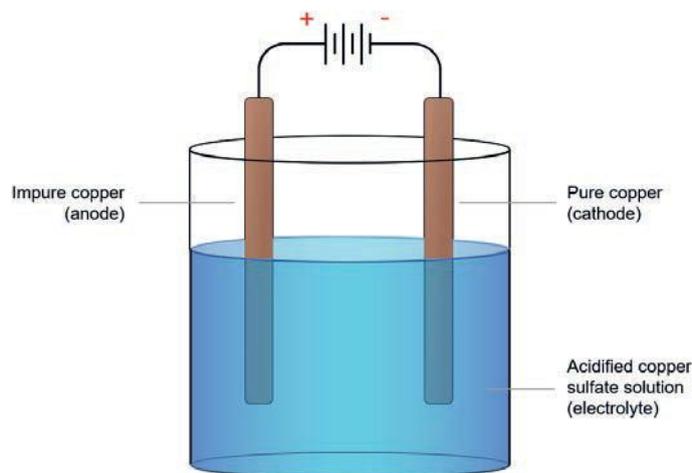
(2 marks) **KA4**

(ii) **Explain** why chemical reduction is used for the production of copper.

.....

 (2 marks) **IAE3**

(d) The product of chemical reduction is blister copper with a lower purity. This is placed at the anode of an electrolytic cell for refining. A simplified diagram of the cell is shown below.



(i) **State** how the refining stage increases the purity of copper.

.....
 (1 mark) **KA1**

(ii) **Suggest** why, in the application of electrical wiring, high-purity copper is required.

.....
 (1 mark) **IAE3**

(iii) **State** the charge on the electrode at which pure copper is produced.

..... (1 mark) **IAE3**

(e) Copper was produced via a different method from an ore containing a mixture of compounds containing copper and calcium. The ore was roasted in air and then digested in acid to produce an aqueous solution. The solution, containing $\text{Cu}_{(\text{aq})}^{2+}$ and $\text{Ca}_{(\text{aq})}^{2+}$, was then placed in an electrolytic cell to reduce the metals.

(i) **Write a half equation** for the reduction of $\text{Cu}_{(\text{aq})}^{2+}$ at the cathode.

(2 marks) **KA4**

(ii) After all of the copper had been reduced from aqueous solution, a different reaction began to occur at the cathode.

State and **explain** the reaction that occurred at the cathode at the conclusion of the reduction of copper.

.....

 (3 marks) **IAE3**

(f) Bacteria can be used to obtain copper. Acidified water is sprayed onto mining tailings (left over rock from mining processing) which contain low levels of copper minerals.

(i) As acidic water penetrates through the crushed rock, bacteria break down the iron sulfides and convert iron(II) to iron(III).

(1) **State** whether this conversion represents oxidation or reduction.

.....
 (1 mark) **IAE3**

(2) **Suggest** one reason why this method of obtaining copper is not adopted over conventional methods of copper production.

.....
 (1 mark) **KA3**

(ii) Iron(III) oxidises the sulfides of the copper sulphides to sulfates in tailings. Copper(II) sulfate remains in solution and can be recovered and reduced with the addition of scrap iron.

Explain, with the aid of an equation, how solid scrap iron can reduce copper.

.....

 (3 marks) **KA2**

Science understanding

There is a finite amount of materials on Earth. Materials that can be recycled reduce the amount of new materials that need to be produced from the Earth's crust.

Explain the advantages of recycling materials.

Some objects are difficult to recycle.

Explain the difference in the ease of recycling thermoplastic and thermoset polymers.

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Recycling

Recycling involves the processing of waste products to extract raw materials or make them suitable for reuse. Recycling materials means that finite resources extracted from the Earth can be reused. Recycling also reduces energy demands from the extraction and processing of raw materials.

Recycling of polymers

Polymers have become an essential material in everyday life, but also generate an abundance of waste products. Certain polymers may be recycled or converted into fuels. One of the most labour and energy-intensive stages in polymer-recycling is the sorting of polymer types prior to recycling. Polymers can be separated based on physical and chemical properties such as colour, IR absorption, and density.

Recycling thermoplastic and thermoset polymers

Thermoplastic polymers can be cleaned, ground, melted and used to form new materials. As temperatures are raised, the large molecular chains move freely past one another and flow, allowing them to be extruded and recast. The polymers may be recycled many times before the polymer chains begin to decompose.

As the degree and density of cross-linking is increased, the ease of recycling is reduced. As the polymers are heated, covalent cross-links hold the network of polymer chains in fixed positions, until eventually the polymer decomposes by combustion. Recycling codes have been established to assist in separating polymers. A higher recycling code indicates increased difficulty in recycling. The higher number reflects an increase in the extent of cross-linking in the polymer. This increase also represents a change in the type of polymer, from a thermoplastic to a thermoset, as extensive cross-linking is introduced.

4

Recycling code	Polymer	Category	Uses	Recycled products
 PET	polyethylene terephthalate (polyester)	Thermoplastic	Plastic soft-drink bottles	Polar fleece fabric
 HDPE	High-density polyethylene	Thermoplastic	Bottles	Plastic decking and benches
 PVC	polyvinyl chloride	Thermoplastic	Piping, detergent bottles, food wrap	Speed bumps
 LDPE	Low-density polyethylene	Thermoplastic	Shopping bags	Bin liners
 PP	polypropylene	Thermoplastic	Sauce and medicine bottles	Brooms and pallets
 PS	polystyrene	Thermoplastic	Packaging, cups, plates	Packaging and insulation
 OTHER	Melamine	Thermoset	Kitchen benchtops	Not easily or often recycled

(iii) Hydrogen bonding occurs between polymer chains. **Describe** hydrogen bonding.

.....

 (2 marks) **KA2**

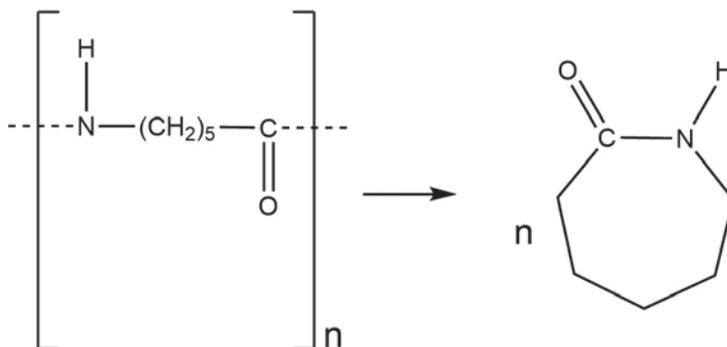
(iv) **State** and **explain** whether synthetic carpets made from nylon-6,6 would be expected to be easily recycled.

.....

 (3 marks) **IAE3**

(b) Nylon-6 used in carpets can be turned back into its monomer, caprolactam. The carpet is shredded and pulverised before heating to depolymerise the nylon-6.

The reaction for the process is represented below.



(i) **State** the feature of caprolactam that allows it to form the polymer nylon-6.

.....
 (1 mark) **IAE3**

(ii) **Discuss** two advantages to the manufacturer of recycling carpets made of nylon-6 using this process.

.....

 (4 marks) **KA3**

(iii) **Discuss** one advantage to the environment of recycling carpets using this method.

.....

 (2 marks) **KA3**



(b) Coal, which contains carbon, is introduced as a reducing agent.

(i) **Explain** why lead ions can be reduced using this method.

.....

 (2 marks) **KA1**

(ii) **State** why this method is preferable to electrolytic reduction.

.....
 (1 mark) **KA1**

(c) More than 50% of the lead used globally comes from recycled methods.

State one advantage to the manufacturer and one advantage to the environment of recycling lead.

.....

 (2 marks) **KA3**

Science understanding

Composite materials comprise two or more constituent materials to produce a material with properties different from the individual components.

Explain the advantages using of composite materials.

Explain the difficulties associated with recycling materials and objects comprising two or more different materials with different properties.

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Composite materials

Composite materials (composition materials) are composed of two or more different materials. Often the two materials have very different properties that complement one another and improve upon the properties offered by the original materials. The derived properties of the composite may not necessarily match the original properties offered by the individual materials. For example, mud bricks offer greater strength and flexibility than both the mud and straw they are made from. Within the composite material, the individual materials are often still visually distinguishable. For example, the glass fibres within fibreglass are still identifiable within the polymer resin. Composites exist in nature or can be produced synthetically.

Natural composites

Plants contain composite materials. Wood is an example of a **natural composite**. Wood consists of long chains of the polymer cellulose, combined with lignin. Individually the materials are weak, but together they make a strong composite.

Animals and humans also contain composite materials. Bones are an example of a composite material. Bones consist of hydroxyapatite (predominantly calcium phosphate) and the protein collagen. Hydroxyapatite is hard and brittle; when combined with soft and flexible collagen, the result is bones that are strong and flexible.

Synthetic composites

Synthetic composites are used in a wide range of applications in the automotive, aerospace, building, and renewable energy industries (batteries, solar panels and wind turbines). Synthetic composites are formed from processed materials.

Concrete is a widely used example of a composite. Concrete consists of aggregate, sand, cement and sometimes steel reinforcement. Together the materials generate a strong, versatile building material.

Modern synthetic composite materials are typically made of two components: the **matrix** (binder) and the material acting as the **reinforcement** (fibres). Many high-performance synthetic composites consist of a matrix of thermoplastic or thermosetting polymer and a reinforcement of fibres of carbon, aramid, glass, or metals such as titanium (Figure 4.4.15).

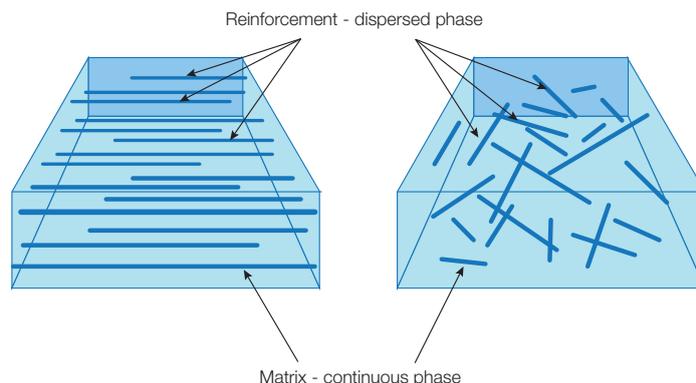


Figure 4.4.15: Matrix and reinforcement fibres in a synthetic composite.

Carbon fibre reinforced polymer (CFRP) is used in sporting goods, automotive racing, and aircraft. The matrix is often a thermoset resin such as epoxy or a thermoplastic polyester or polyamide. The reinforcement is typically carbon fibre (carbonised polymers such as rayon), sometimes mixed with metal fibres or even carbon nanotubes. The resulting composite can be moulded into a variety of shapes to suit its application, with the fibres set and woven in different arrangements to alter the properties offered. Carbon-fibre composites offer exceptional strength-to-weight and rigidity.

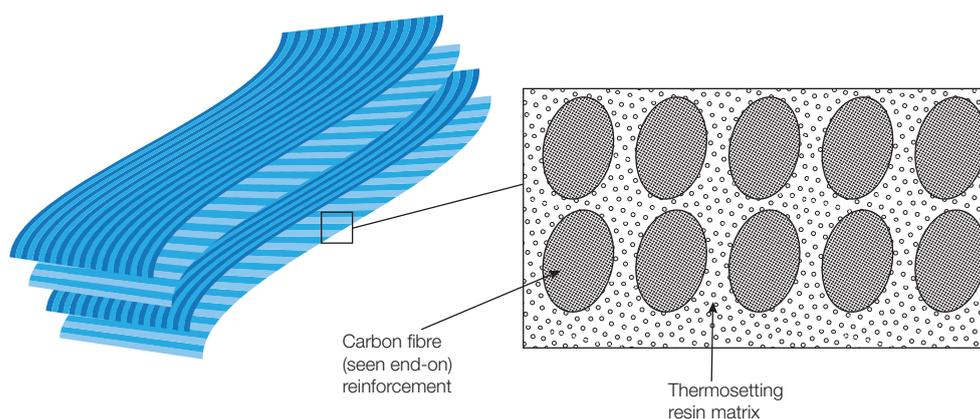


Figure 4.4.16: Synthetic composite, sheets of woven carbon fibres set in resin.

Recycling composite materials

Difficulties arise in recycling synthetic composite materials due mostly to the heterogeneity (mixing and incorporation of different components) of the resulting material. Composites that are made from thermosetting polymer resins cannot be heated to separate the matrix from the reinforcement.

Mechanical methods (grinding and chopping), thermal methods (melting and combustion), and chemical methods (hydrolysis) are currently used for separation, recycling, and energy production from some of the resulting products.

Recycling of composites is currently limited due to high associated costs, lower quality of separated components, and lack of incentives and infrastructure. As discussed, recycling results in savings to resources and energy, so recycling of composites will need to be pursued to a greater extent.



Science as a human endeavour

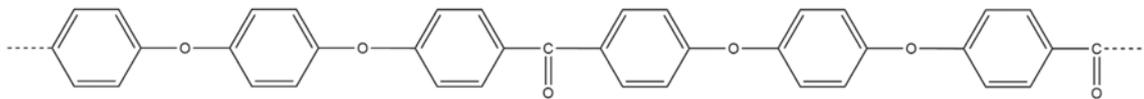
Smart composites

With the increase in fibre-reinforced composites being used in aircraft, aerospace and engineered structures, scientists are interested in real-time monitoring of materials, via sensors built into the composite material. Advancements in nanotechnology have allowed researchers to develop extremely small sensors that can be incorporated along with composite fibres. Embedded sensors are networked throughout the load-bearing structure and relay live data about forces and stresses experienced, leading to the early detection of potential failure. The ultimate goal in future composite technology is to produce lighter, stronger, self-diagnosing and self-healing composites with computational and communication abilities – robotic materials!

Question

22. Since the 1980s, polyaryletherketones (PAEKs) have been used as biomaterials for orthopaedic and spinal implants as the individual polymer and as a composite.

(a) The structure of a section of the PEAK polymer is shown below.



- (i) **Bracket** the repeating unit on the section of polymer above. (1 mark) KA4
- (ii) PEAK is a high-temperature thermoplastic.

Identify the predominant interaction that would occur between polymer chains.

..... (1 mark) IAE3

(b) PEAK can be used as the matrix added to carbon-fibre reinforcement in the creation of spinal implants.

- (i) **Explain** two advantages of creating an implant for the human spine made from a composite material containing carbon fibre and a polymer.

.....

 (3 marks) IAE3

- (ii) **Suggest** why a composite made from carbon fibre and PEAK polymer would be easily recycled.

.....
 (1 mark) IAE3

- (iii) **Suggest** one property required of a composite that is introduced to the human body.

.....
 (1 mark) KA3



Summary test 4: Managing resources

1. Motorsports have often been the testing ground for advancements in technologies, such as alternative fuels and materials, as manufacturers pursue greater performance with less impact on the environmental.

(a) In recent years, the V8 supercar series in Australia has substituted the use of high-octane petrol for E85, a blend of petrol with up to 85% bioethanol.

(i) Sucrogen[®], bioethanol used by the V8 supercar series, is produced from sucrose extracted from sugarcane. The disaccharide, sucrose, is converted into the monosaccharide, glucose, prior to fermentation.

Write a fully balanced chemical equation for the fermentation of glucose to produce ethanol.

(2 marks) **KA4**

(ii) Ethanol undergoes combustion in fuel blends or as a pure liquid.

Write a thermochemical equation for the complete combustion of ethanol, which releases 1371 kJ of energy for every mole of fuel.

(4 marks) **KA4**

(iii) **Calculate** the specific energy, in kJ g⁻¹, for ethanol.

(2 marks) **KA4**

(iv) Specific energy and energy density can be determined for a fuel.

Suggest why energy density is important to car racing.

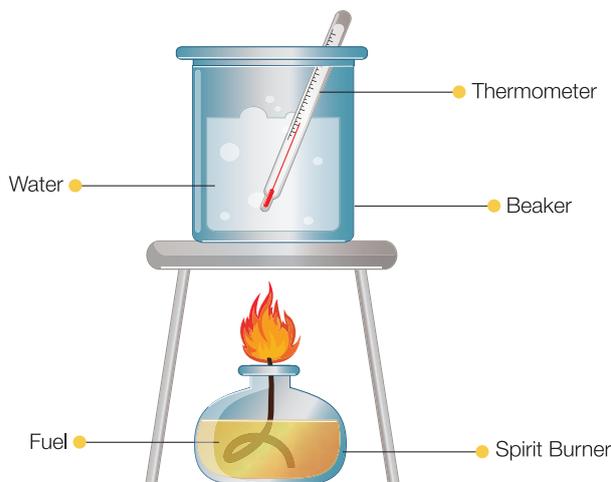
.....
 (1 mark) **KA3**

(v) **Discuss** one advantage of the production and use of an E85 bioethanol blend compared to high-octane petrol derived from crude oil.

.....

 (2 marks) **KA1**

- (b) Many drag-racing cars run on pure methanol as a fuel, to produce engine outputs well in excess of 1000 horsepower.
- (i) The molar enthalpy of combustion for pure methanol was determined experimentally using the apparatus shown below.



- (1) A sample of pure methanol was burnt in a spirit burner under a beaker containing 100 mL of distilled water. The burner remained alight until a temperature change of 30°C was obtained. The mass of the spirit burner decreased by 1.8 g. (Specific heat capacity of water $c = 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.)

Calculate the molar enthalpy of combustion of methanol in kJ mol^{-1} .

(4 marks) **KA4**

- (2) **Suggest** one reason why the value obtained was considerably lower than the expected reference value for methanol.

.....
 (1 mark) **IAE4**

- (ii) Methanol and octane, present in petrol, are both burnt in internal combustion engines in different categories of drag racing.

State why the combustion of methanol in air produces a larger proportion of the products of complete combustion, compared to the combustion of octane under the same conditions.

.....
 (1 mark) **KA2**

- (iii) Nitrous oxide (N_2O) is also added to the combustion of the fuels in the some drag cars. At elevated temperatures, nitrous oxide decomposes, releasing oxygen.

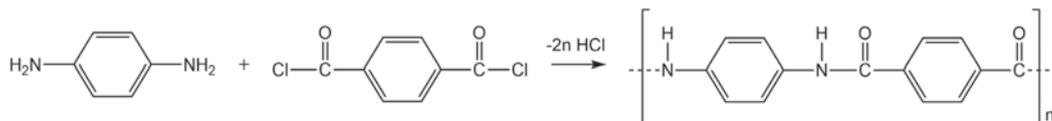
Explain how nitrous oxide allows fuel to undergo combustion at a faster rate, thus producing more power from the engine.

.....

 (3 marks) **KA2**



- (iv) The engines and transmission in drag cars are surrounded by a Kevlar blanket in the event of catastrophic failure.



- (1) **State** the name of the type of polymerisation reaction undertaken to form Kevlar.
 (1 mark) **IAE3**
- (2) As a fabric, the polymer fibres offer exceptional strength between polymer chains. **State** the name of the secondary interaction that accounts for this strength.
 (1 mark) **KA1**
- (c) Many advanced materials have been engineered for Formula One racing.
- (i) Alloys and composites of titanium used extensively in Formula One cars offer exceptional strength to weight. Most of the world's titanium is extracted from ores containing titanium dioxide.
- (1) Titanium can be mined economically from beach sand containing rutile (TiO₂) and ilmenite (FeTiO₃) as well as smaller quantities in the silicate zircon (ZrSiO₄).

State the charge on the silicate anion present in zircon.

(1 mark) **KA4**

- (2) Titanium dioxide is converted to titanium chloride, suitable for chemical reduction with magnesium according to the equation below.

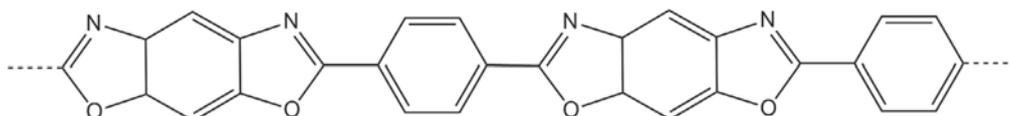


Explain how magnesium is able to reduce titanium ions.

.....

 (2 marks) **IAE3**

- (ii) The polymer Zylon® is used to create fibres. The fibres are used to tether wheels to the chassis of Formula One cars, and are also used in the formation of epoxy-composites to line the cockpit of the car. In both applications, the materials provide safety to the driver and spectators.



- (1) **Bracket** the repeating unit in Zylon® on the diagram above. (1 mark) **KA4**
- (2) Epoxy resins have the ability to form extensive cross-linking within the composite. **State** the effect of cross-linking on the rigidity of the composite.
 (1 mark) **KA1**
- (3) Zylon® fibres are used as reinforcement and combined with an epoxy resin polymer as the matrix, to form an impenetrable composite that lines the driver's cockpit.

State one advantage of using a composite in this application.

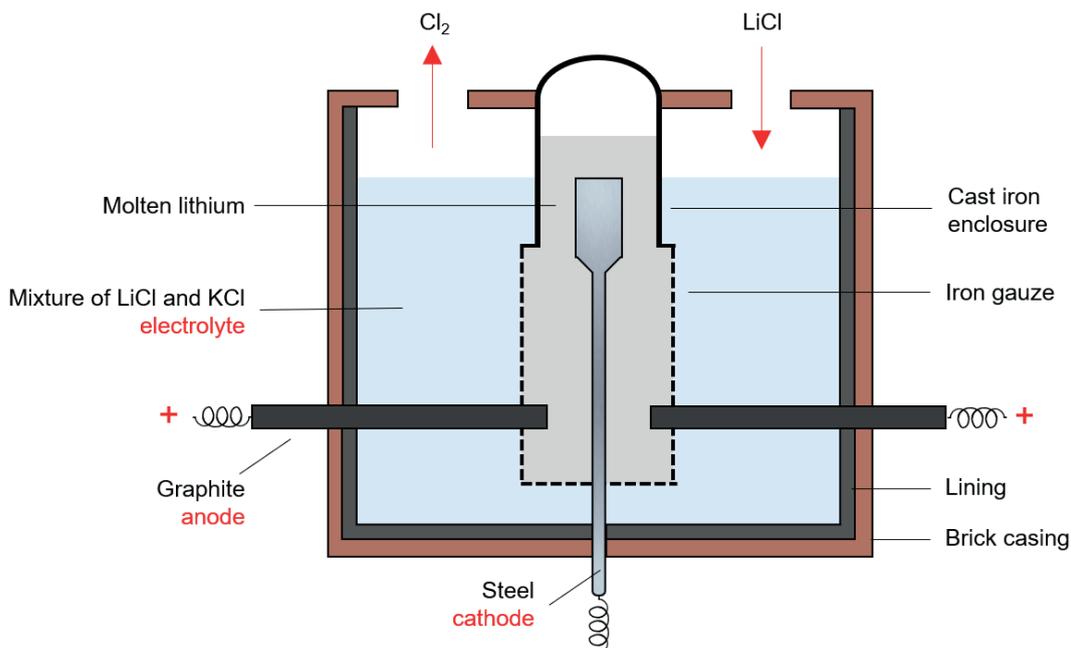
.....
 (1 mark) **KA1**

- (4) **Describe** one difficulty in recycling car components made of composites containing thermoset polymers.

.....

 (2 marks) **KA2**

(b) Lithium, used in batteries, is an element in worldwide demand. Lithium can be produced from the electrolysis of molten lithium chloride. A simplified diagram of the cell is shown below.



(i) **Suggest** why the product at the anode must be extracted carefully.

 (1 mark) **KA3**

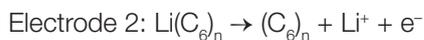
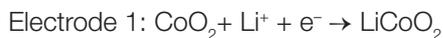
(ii) **Write a balanced half-equation** for the formation of lithium at the cathode.

 (2 marks) **KA4**

(iii) **Explain** why molten electrolytic reduction is chosen for the production of lithium.

 (2 marks) **IAE3**

(c) The lithium-ion battery is a rechargeable battery. Cell half-equations for the battery during discharging are shown below.



(i) **State** the type of cell during recharging.
 (1 mark) **KA1**

(ii) **State and explain** which electrode is the anode during recharging.

 (2 marks) **IAE3**



(iii) The battery is proposed to be built adjacent to a wind farm in rural South Australia.
 (1) **State** one advantage of electricity produced from wind turbines.
 ..
 .. (1 mark) KA1

(2) **Discuss** one advantage of establishing a battery in conjunction with a wind farm.
 ..
 ..
 ..
 .. (2 marks) KA3

(iv) Lithium-ion batteries are limited in their ability to be recharged over time, due to the formation of lithium oxide on overdischarge and cobalt oxide on overcharge. This build-up removes reactants from the battery.
 (1) **Suggest** one implication for the use of the proposed lithium-ion battery as a reserve power supply.
 ..
 .. (1 mark) KA3

(2) Flow batteries could also be used in this application.
State one advantage of a flow battery over a lithium-ion battery used for power storage and supply.
 ..
 .. (1 mark) KA2

3. Ingenuity is often found in farming practices, as resources become scarce and environmental consequences are recognised.

(a) In the arid lands north of Port Augusta in South Australia, a solar still has been employed for the irrigation and production of tomatoes. Sundrop Farm uses greenhouses and desalinated seawater for the year-round production of tomatoes.

(i) Desalination of seawater is achieved with a solar still, which uses more than 23000 mirrors to direct the Sun's thermal radiation to a tower containing seawater.
Explain how this method of thermal distillation produces potable water.
 .
 .
 .
 . (2 marks) KA1

(ii) **State** one advantage of desalination using this process compared to reverse osmosis.
 .
 . (1 mark) KA2

(iii) **Suggest** why, if this water was to be used for human consumption, the addition of chlorine would be advisable.
 .
 . (1 mark) KA3

(b) Biosolids have been produced from the Bolivar sewage treatment plant in South Australia since 1960. Farmers can access biosolids for the commercial production of cereal crops.

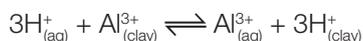
(i) **Explain** how nitrogen present in human waste can be made available to plants when biosolids are spread on the soil as a fertiliser.
 .
 .
 .
 . (2 marks) KA2

- (ii) Farmers near the township of Booleroo Centre in rural South Australia have been using biosolid fertilisers for many years in the production of cereals (wheat and barley).

State why intensive cropping in this region has required the use of fertilisers.

.....
 (1 mark) **KA1**

- (iii) The extensive use of synthetic fertilisers in the region has also led to soil acidity. Soil acidity is known to stunt root-growth in wheat and barley due to aluminium toxicity.



Explain, with reference to the equation above, how an increase in the aqueous concentration of hydrogen ions (H⁺) present in soil solution can lead to aluminium toxicity.

.....

 (3 marks) **KA2**

- (iv) The soils around the township contain a large component of clay.

- (1) Calcium and magnesium ions present in the soil flocculate clays.

State the feature of clays that allow them to be flocculated by calcium and magnesium cations.

.....
 (1 mark) **KA1**

- (2) Acidic soils containing clay exhibit poor drainage and soil structure. Gypsum (calcium sulfate, CaSO₄) is added to clay soils to increase aeration and drainage.

Explain, with the aid of an equation, how the addition of gypsum improves soil structure and drainage in acidic soils.

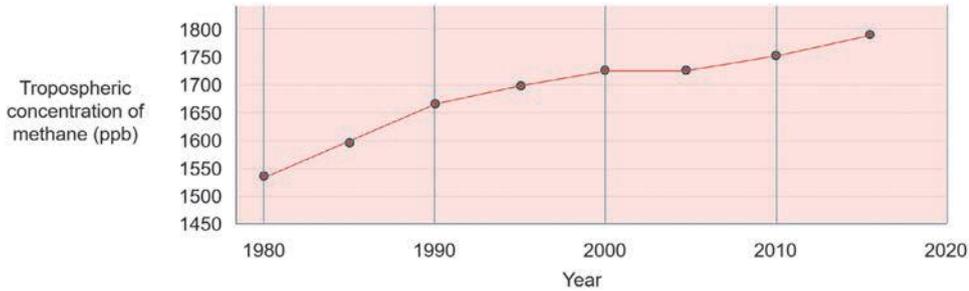
.....

 (3 marks) **KA2**

Topic 1 solutions: Monitoring the environment

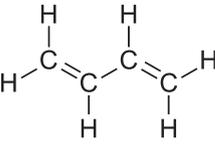
Question	Part	Author's response	Marks										
1	(a) (i)	-17°C	1										
	(ii)	Greenhouse gases such as carbon dioxide and methane are able to absorb and emit thermal IR radiation that has been reradiated from the surface of the Earth.	1										
		Thermal IR radiation is transferred between greenhouse gases, directed back to the surface, and lost to space.	1										
		A thermal balance is established, maintaining the average global temperature in the Earth's troposphere.	1										
	(b)	If there is greater reflectivity in the atmosphere and on the surface of the Earth, less energy from the Sun is absorbed at the surface of the Earth.	1										
		Hence, less energy is reradiated as thermal IR radiation, reducing warming.	1										
(c) (i)	The atmosphere of Venus contains an extremely high concentration of the greenhouse gas carbon dioxide (95%).	1											
	There is much stronger greenhouse warming due to this high concentration, as more thermal IR radiation is absorbed.	1											
	(ii) Although the concentration of carbon dioxide in the atmosphere is high, a very thin atmosphere results in a small amount present to absorb thermal IR radiation.	1											
2	(a) (i)	<table border="1"> <thead> <tr> <th>Factor</th> <th>Importance</th> </tr> </thead> <tbody> <tr> <td>Same 2L volume</td> <td>To allow comparisons to be made for the same volumes of gases</td> </tr> <tr> <td>Use the same carbon dioxide sensor, calibrated to the same value in ppm</td> <td>To ensure accurate readings of carbon dioxide</td> </tr> <tr> <td>Calibration of temperature sensors</td> <td>To ensure initial readings are consistent</td> </tr> <tr> <td>Same distance from the same lamp</td> <td>To ensure that each bottle receives the same radiant heat</td> </tr> </tbody> </table>	Factor	Importance	Same 2L volume	To allow comparisons to be made for the same volumes of gases	Use the same carbon dioxide sensor, calibrated to the same value in ppm	To ensure accurate readings of carbon dioxide	Calibration of temperature sensors	To ensure initial readings are consistent	Same distance from the same lamp	To ensure that each bottle receives the same radiant heat	1+1
		Factor	Importance										
		Same 2L volume	To allow comparisons to be made for the same volumes of gases										
		Use the same carbon dioxide sensor, calibrated to the same value in ppm	To ensure accurate readings of carbon dioxide										
	Calibration of temperature sensors	To ensure initial readings are consistent											
	Same distance from the same lamp	To ensure that each bottle receives the same radiant heat											
	(ii)	The concentration of carbon dioxide.	1										
	(iii)	Increasing the concentration of carbon dioxide will result in an increase in recorded temperature.	2										
	(iv)	Any one: <ul style="list-style-type: none"> Repeat the procedure with bottles at a range of increasing concentrations of carbon dioxide. Repeat the procedure for air and controlled concentrations of carbon dioxide. 	1										
	(b) (i)		1										
1													
1													
1													
1													
1													
(ii)	A higher concentration of carbon dioxide resulted in a higher final temperature achieved.	1											
	A higher rate of temperature increase was achieved at a higher concentration of carbon dioxide present.	1											
	Carbon dioxide gas absorbs thermal IR radiation from the lamp.	1											



Question	Part	Author's response	Marks
3	(a)	 <p>Data points and line of best fit.</p>	1 1
	(b) (i)	Increasing atmospheric temperatures have led to increased rates of thawing of land ice and permafrost.	1
	(ii)	Methane is a greenhouse gas able to absorb thermal IR radiation, reradiated from the surface of the Earth.	1
	(ii)	Increased methane levels lead to greater absorption of thermal IR radiation. Thermal IR radiation is trapped for longer before escaping, which leads to a thermal imbalance, increasing the average global temperature in the Earth's troposphere.	1 1
	(iii)	Methane is present in the atmosphere at significantly lower concentrations compared to carbon dioxide.	1
	(c) (i)	Any one: <ul style="list-style-type: none"> • Mining • Production of fuels derived from fossil fuels • Intensive farming of livestock • Rice growing 	1
(ii)	Advantage: methane, as a greenhouse gas, is collected rather than being released into the troposphere. Disadvantage: the combustion of methane as a fuel source results in the emission of carbon dioxide, a greenhouse gas.	1 1	
4	(a) (i)	$[H_3O^+] = 10^{-pH}$ $[H_3O^+] = 10^{-6.5}$ $[H_3O^+] = 3.16 \times 10^{-7} \text{ mol L}^{-1}$	1
	(a) (i)	$[H_3O^+] = 10^{-pH}$ $[H_3O^+] = 10^{-4}$ $[H_3O^+] = 1 \times 10^{-4} \text{ mol L}^{-1}$ Highest concentration of hydronium ions results from the lowest pH, a pH of 4.0.	1 1
	(ii)	Increase in acidity.	1
	(iii)	Each shift in pH value represents a 10-times change in concentration of hydronium ions.	2
	(b)	Any one: <ul style="list-style-type: none"> • The formation of acid rain from industrial activity. • The formation of acid rain from metal production. • The formation of acid rain from the oxides of sulfur and nitrogen formed during the combustion of fuels in motor vehicles. 	1
(c)	Frogs eggs made from calcium carbonate will undergo reaction with hydrogen ions from acid rain leading to their dissolution.	1	

Question	Part	Author's response	Marks
5	(a) (i)	Slightly acidic	1
	(ii)	$\text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{CO}_{3(aq)}$	2
	(b) (i)	$\text{Na}_2\text{CO}_{3(s)} + 2\text{H}^+_{(aq)} \rightleftharpoons \text{H}_2\text{O}_{(l)} + \text{CO}_{2(g)} + 2\text{Na}^+_{(aq)}$	2
	(ii)	$\begin{aligned} \text{pOH} &= 14 - \text{pH} \\ &= 14 - 10.5 \\ &= 3.5 \end{aligned}$	1
		$\begin{aligned} [\text{OH}^-] &= 10^{-\text{pOH}} \\ [\text{OH}^-] &= 10^{-3.5} \\ [\text{OH}^-] &= 3.16 \times 10^{-4} \text{ mol L}^{-1} \end{aligned}$	2
6	(a) (i)	Covalent bond (triple).	1
	(ii)	$\text{N} \equiv \text{N}$	2
	(b)	High temperatures encountered during the combustion of fuels in an aircraft engine allow nitrogen and oxygen to react to form nitric oxide.	1
		$\text{N}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{(g)}$	1
		Nitric oxide oxidises further in the atmosphere, reacting with oxygen to form nitrogen dioxide.	1
		$2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$	1
	(c) (i)	Endothermic (photochemical)	1
	(ii)	Nitrogen dioxide photodissociates on absorption of ultraviolet radiation, forming nitric oxide and an oxygen radical.	1
		The oxygen radical reacts with oxygen forming ozone.	1
		$\text{NO}_{2(g)} \xrightarrow{\text{UV}} \text{NO}_{(g)} + \text{O}$ or $\text{O}_{(g)} + \text{O}_{2(g)} \rightarrow \text{O}_{3(g)}$	1
(d) (i)	Changes to the altitude and flight path result in different distances and times of flight, which result in the formation of more or less emissions of NOx.	1	
(ii)	Carbon dioxide is a greenhouse gas.	1	
	Increased concentration of atmospheric carbon dioxide has led to global warming.	1	
	Any one (or other relevant consequences): Global warming has been linked to: <ul style="list-style-type: none"> • rising sea levels • extreme weather events. 	1	

Question	Part	Author's response	Marks
7	(a) (i)	Greater volumes of air containing pollutants are inhaled into the lungs during physical activity.	1
	(ii)	Any two: <ul style="list-style-type: none"> • Ozone affects respiratory function. • Individuals with existing respiratory illness are more susceptible to exposure to ozone. • Increased exposure to higher concentrations of ground-level ozone is detrimental to human health. 	2
	(b) (i)	$\text{SO}_{3(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)}$	2
	(ii)	pH decreases	1
		7–8 am Disadvantage: Concentration of primary pollutants would increase due to peak hour traffic, increasing exposure. Advantage: Concentrations of secondary pollutants (such as ozone) are low, as little sunlight is available to generate photochemical reactions.	1 1
		12 am –1 pm Disadvantage: Primary pollutants have had the opportunity to form secondary pollutants.	1
	(c)	UV concentrations are high, leading to the formation of ozone and a peak in concentration (as long as sunlight is available). Advantage: Primary pollutants may have been able to disperse depending on weather conditions.	1 1
		8–9 pm Disadvantage: Evening peak-hour traffic would lead to increased concentrations of primary pollutants, increasing exposure. Advantage: Without sunlight, ozone levels will decrease. limiting exposure.	1 2
		Communication: spelling, sentence structure, and logical sequence.	

Question	Part	Author's response	Marks																				
8	(a) (i)	(1) Trigonal planar	1																				
		(2) Oxygen has a higher electronegativity than carbon, with a stronger affinity for valence electrons. The difference in electronegativity between carbon and oxygen results in an uneven electron distribution, forming a polar bond ($O\delta^-$ and $C\delta^+$).	1 1																				
		(3) Methanal molecules are relatively small and polar. Methanal molecules experience dipole–dipole interactions between the $C=O$ bonds in the polar molecules. At room temperature, there is sufficient energy to overcome the interactions, therefore methanal is volatile (low boiling point), existing as a gas.	1 1 1																				
	(ii)	$NO_{2(g)} \xrightarrow{UV} NO_{(g)} + O$ $O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$	2 2																				
	(b) (i)	To disperse and remove the pollutants.	1																				
	(ii)	Ozone is a respiratory irritant.	1																				
	(c) (i)	Addition	1																				
	(ii)		2																				
	(iii)	Ozone, as an oxidising agent, breaks carbon–carbon double bonds present in the polymer. This leads to cracking and degradation of the function of the polymer.	1 1																				
	(iv)	Carbon–carbon double bonds are not present in the main chain, hence not as susceptible to degradation by ozone	1																				
9	(a) (i)	Oxides of nitrogen are precursors to the formation of photochemical smog. Reducing their concentration reduces the formation of secondary pollutants such as ozone.	1 1																				
	(ii)	$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$	2																				
	(b) (i)	Oxidation The oxidation number of nitrogen increases from +4 in NO_2 to +5 in NO_3^- .	1 1																				
	(ii)	Incomplete combustion	1																				
	(iii)	Large surface area to expose pollutants to the catalyst material.	1																				
	(iv)	$2NO_{(g)} + 2CO_{(g)} \rightarrow 2CO_{2(g)} + N_{2(g)}$	2																				
10	(a)	<table border="1" data-bbox="411 1668 1289 1877"> <thead> <tr> <th>Element</th> <th>Symbol</th> <th>Atomic mass</th> <th>m (g)</th> <th>n (mol)</th> </tr> </thead> <tbody> <tr> <td>platinum</td> <td>Pt</td> <td>195.1</td> <td>2.93</td> <td>0.0150</td> </tr> <tr> <td>palladium</td> <td>Pd</td> <td>106.4</td> <td>3.46</td> <td>0.0325</td> </tr> <tr> <td>rhodium</td> <td>Rh</td> <td>102.9</td> <td>8.61</td> <td>0.0837</td> </tr> </tbody> </table>	Element	Symbol	Atomic mass	m (g)	n (mol)	platinum	Pt	195.1	2.93	0.0150	palladium	Pd	106.4	3.46	0.0325	rhodium	Rh	102.9	8.61	0.0837	3
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rhodium	Rh	102.9	8.61	0.0837																			
(b)	Nanoparticles offer greater surface area to catalyse the reaction, therefore less of these rare metals are required.	1																					

Question	Part	Author's response					Marks		
11	(a)		Atomic mass	Concentration units				4	
			g mol⁻¹	mol L⁻¹	g L⁻¹	ppm	ppb		
		lead	Pb	207.2	9.65 × 10⁻⁷	0.00020	0.20		200
		cadmium	Cd	112.4	9.65 × 10 ⁻⁷	0.00011	0.11		110
		arsenic	As	74.92	6.67 × 10⁻⁷	0.00005	0.05		50
		mercury	Hg	200.6	8.97 × 10⁻⁷	0.00018	0.18		180
		zinc	Zn	65.38	6.12 × 10⁻⁵	0.0040	4.0		4000
		selenium	Se	78.96	1.90 × 10⁻⁵	0.0015	1.5		1500
		sodium	Na	22.99	6.05 × 10 ⁻⁴	0.0139	13.9		13900
		calcium	Ca	40.08	2.07 × 10 ⁻⁴	0.0083	8.3		8300
		magnesium	Mg	24.31	5.64 × 10 ⁻⁴	0.0137	13.7	13700	
11	(b) (i)	Lethal level = 763 ppm = 763 mg L ⁻¹ = 763 × 55 mg in a 55 kg adult = 41965 mg Bottled water = 0.0500 ppm = 0.0500 mg L ⁻¹ $= \frac{41965}{0.0500}$ = 839300 L = 8.4 × 10 ⁵ L					1 2		
		(ii)	Other elements may reach a concentration which is detrimental to human health.					1	
	12	(a)	0.995 ppm = 0.995 mg L ⁻¹ = 0.995 mg kg ⁻¹ = 0.995 × 10 ⁻³ mg g ⁻¹ = 0.995 × 10 ⁻³ × 150 mg = 0.149 mg					1 2	
(b)		0.149 mg of mercury in 150 g of swordfish ∴ 0.149 mg in 75 kg $= \frac{0.149}{75} \text{ mg kg}^{-1}$ = 1.99 × 10 ⁻³ ppm					1 2		
(c)		Larger deep-sea fish contain higher levels of mercury, building from the consumption of smaller fish, hence reduced consumption is recommended.					1		
		Young children and the unborn foetus of pregnant women are more susceptible to mercury exposure due to their small mass for absorption, leading to high concentrations of the element. Even less frequent consumption is recommended.					1		

Question	Part	Author's response	Marks
13	(a) (i)	$m(\text{CO}_2) = 21.8 \times 10^3 \text{ g}$ $M(\text{CO}_2) = 44.01 \text{ g mol}^{-1}$ $n(\text{CO}_2) = \frac{m}{M}$ $n(\text{CO}_2) = \frac{21.8 \times 10^3}{44.01}$ $n(\text{CO}_2) = 495 \text{ mol}$ <p>mole ratio $n(\text{CO}_2) : n(\text{C}_6\text{H}_{12}\text{O}_6) = 6 : 1$</p> $\frac{n(\text{C}_6\text{H}_{12}\text{O}_6)}{n(\text{CO}_2)} = \frac{1}{6}$ $\therefore n(\text{C}_6\text{H}_{12}\text{O}_6) = \frac{495}{6}$ $n(\text{C}_6\text{H}_{12}\text{O}_6) = 82.6 \text{ mol}$ $M(\text{C}_6\text{H}_{12}\text{O}_6) = 180.156 \text{ g mol}^{-1}$ $m(\text{C}_6\text{H}_{12}\text{O}_6) = n \times M$ $m(\text{C}_6\text{H}_{12}\text{O}_6) = 82.6 \times 180.156$ $m(\text{C}_6\text{H}_{12}\text{O}_6) = 14873 \text{ g}$ $m(\text{C}_6\text{H}_{12}\text{O}_6) = 14900 \text{ g}$ $m(\text{C}_6\text{H}_{12}\text{O}_6) = 14.9 \text{ kg (3 sig. fig.)}$	2
			2
			2
			2
	(ii)	<p>mole ratio $n(\text{CO}_2) : n(\text{O}_2) = 1 : 1$</p> $\therefore n(\text{O}_2) = 495 \text{ mol}$ $M(\text{O}_2) = 32.00 \text{ g mol}^{-1}$ $m(\text{O}_2) = n \times M$ $m(\text{O}_2) = 495 \times 32.00$ $m(\text{O}_2) = 15851 \text{ g}$ $m(\text{O}_2) = 15900 \text{ g (3 sig. fig.)}$	3
	(b) (i)	$\text{CO}_{2(\text{vehicle emission for one car})} = 4.7 \times 10^3 \text{ kg}$ $\text{CO}_{2(\text{absorbed by single tree})} = 21.8 \text{ kg}$ $\text{Total number of mature trees} = \frac{4700}{21.8}$ $= 216 \text{ mature trees}$	2
	(ii)	Through photosynthesis, trees offset considerable quantities emissions of carbon dioxide.	1

Question	Part	Author's response	Marks
14	(a)	$m(\text{O}_2) = 0.300 \text{ g}$ $M(\text{O}_2) = 32.00 \text{ g mol}^{-1}$ $n(\text{O}_2) = \frac{0.300}{32.00}$ $n(\text{O}_2) = 9.38 \times 10^{-3} \text{ mol}$ $m(\text{N}_2) = 1.60 \text{ g}$ $M(\text{N}_2) = 28.02 \text{ g mol}^{-1}$ $n(\text{N}_2) = \frac{1.60}{28.02}$ $n(\text{N}_2) = 5.17 \times 10^{-2} \text{ mol}$ <p>Mole ratio $n(\text{O}_2) : n(\text{N}_2) = 1 : 1$ $\therefore \text{O}_2$ is the limiting reagent</p>	2 2 1
	(b)	<p>Mole ratio $n(\text{O}_2) : n(\text{NO}) = 1 : 2$</p> $\frac{n(\text{NO})}{n(\text{O}_2)} = \frac{2}{1}$ $n(\text{NO}) = 2 \times 9.375 \times 10^{-3}$ $n(\text{NO}) = 1.875 \times 10^{-2} \text{ mol}$ $M(\text{NO}) = 30.01 \text{ g mol}^{-1}$ $m(\text{NO}) = 1.875 \times 10^{-2} \times 30.01$ $m(\text{NO}) = 0.563 \text{ g (3 sig. fig.)}$	2 2
15	(a)	$c_{(\text{DCMU})} = 900 \text{ g L}^{-1}$ $\frac{\text{g}}{\text{L}} \div M \frac{\text{mol}}{\text{L}}$ $= \frac{900}{233.1}$ $= 3.86 \text{ mol L}^{-1}$	2
	(b)	$c_1 \times V_1 = c_2 \times V_2$ $c_2 = \frac{c_1 \times V_1}{V_2}$ $c_2 = \frac{3.861 \times 40}{6000}$ $c_{(\text{diluted DCMU})} = 0.0257 \text{ mol L}^{-1} \text{ (3 sig. fig.)}$	3

Question	Part	Author's response	Marks
16	(a) (i)	Alkaline	1
	(ii)	Anhydrous sodium carbonate eliminates the need to account for water molecules in weighing the mass and during calculations.	1
	(iii)	Less impurities may affect the weighed mass or interact with the reagents, altering the desired concentration or products of the reaction.	1
	(b) (i)	$m(\text{NaOH}) = 4.002 \text{ g}$ $M(\text{NaOH}) = 39.998 \text{ g mol}^{-1}$ $n(\text{NaOH}) = \frac{4.002}{39.998}$ $n(\text{NaOH}) = 0.1001 \text{ mol}$	2
	(ii)	$m(\text{H}_2\text{O}) = 7.601 - 4.002$ $m(\text{H}_2\text{O}) = 3.599 \text{ g}$ $M(\text{H}_2\text{O}) = 18.016 \text{ g mol}^{-1}$ $n(\text{H}_2\text{O}) = \frac{3.599}{18.016}$ $n(\text{H}_2\text{O}) = 0.1998 \text{ mol}$	1 2
	(iii)	$\text{Ratio } n(\text{NaOH}) : n(\text{H}_2\text{O})$ $= 0.1001 : 0.1998$ $\approx 1 : 2$ $\therefore \text{NaOH} \cdot 2\text{H}_2\text{O}$	2
	(iv)	The sodium hydroxide solid would have absorbed water.	1
		Less moles of sodium hydroxide would be present due to the mass of water.	1
		With less moles present, the final concentration of the sodium hydroxide solution would be lower than expected.	1
	(v)	Sodium carbonate does not absorb water from the air as readily as sodium hydroxide.	1
17	(a)	Method 1	
		Using a beaker eliminates the need to deliver the solid solute to the flask.	1
		This technique does introduce the possibility of moles of solute being lost from residues left on the stirring rod.	1
		There is also the potential for some of the residual solution to remain adhered to the surface of the beaker.	1
		Method 2	
		Care must be taken to ensure that when transferring the solid solute from the watch glass none is lost.	1
		Reweighting removes the potential of moles of dissolved solute remaining on the watch glass during rinsing.	1
	There is the potential for some residual solution to remain adhered to the surface of the funnel.	1	

Question	Part	Author's response	Marks
18	(a)	White wine	1
	(b) (i)	Averaging the values reduces the effect of random error.	1
	(ii)	Higher degree of accuracy	1
		11.75 is closer to the group average of 11.80 and therefore can be considered more accurate than the average titre obtained for the original group.	1
	(c) (i)	Random error	1
	(ii)	It is difficult to see the permanent colour change thought the coloured suspension of orange juice.	1
	(d)	Carbon dioxide gas is being lost from the supersaturated solution.	1
19	(a)	$c(\text{NaOH}) = 0.00200 \text{ mol L}^{-1}$ $V(\text{NaOH}) = 10.2 \text{ mL} = 0.0102 \text{ L}$ $n(\text{NaOH}) = c \times V$ $n(\text{NaOH}) = 0.00200 \times 0.0102$ $n(\text{NaOH}) = 2.04 \times 10^{-5} \text{ mol}$	2
	(b)	Mole ratio $n(\text{OH}^-) : n(\text{NH}_4^+) = 1 : 1$ $\therefore n(\text{NH}_4^+) = 2.04 \times 10^{-5} \text{ mol}$	1
	(c)	$c = \frac{n}{V}$ $c(\text{NH}_4^+) = \frac{2.04 \times 10^{-5}}{0.0200}$ $c(\text{NH}_4^+) = 1.02 \times 10^{-3} \text{ mol L}^{-1} \text{ (3 sig. fig.)}$	3
20	(a)	$c(\text{EDTA}) = 0.010 \text{ mol L}^{-1}$ $V(\text{EDTA}) = 30.0 \text{ mL} = 0.0300 \text{ L}$ $n(\text{EDTA}) = c \times V$ $n(\text{EDTA}) = 0.010 \times 0.0300$ $n(\text{EDTA}) = 3.0 \times 10^{-4} \text{ mol}$	2
	(b) (i)	$c(\text{Zn}^{2+}) = 0.00100 \text{ mol L}^{-1}$ $V(\text{Zn}^{2+}) = \frac{(52.90 + 52.80 + 52.70)}{3}$ $= 52.80 \text{ mL} = 0.0528 \text{ L}$ $n(\text{Zn}^{2+}) = c \times V$ $n(\text{EDTA}) = 0.0010 \times 0.0528$ $n(\text{EDTA}) = 5.3 \times 10^{-5} \text{ mol}$	3
	(ii)	Mole ratio $n(\text{Zn}^{2+}) : n(\text{EDTA}_{\text{excess}}) = 1 : 1$ $\therefore n(\text{EDTA}_{\text{excess}}) = 5.3 \times 10^{-5} \text{ mol}$	1
	(iii)	$n(\text{EDTA}_{\text{reacted}}) = n(\text{EDTA}_{\text{original}}) - n(\text{EDTA}_{\text{excess}})$ $n(\text{EDTA}_{\text{reacted}}) = 3.0 \times 10^{-4} - 5.28 \times 10^{-5}$ $n(\text{EDTA}_{\text{reacted}}) = 2.472 \times 10^{-4} \text{ mol}$ $n(\text{EDTA}_{\text{reacted}}) = 2.5 \times 10^{-4} \text{ mol}$	2
	(iv)	Mole ratio $n(\text{EDTA}_{\text{reacted}}) : n\text{Al}^{3+} = 1 : 1$ $\therefore n(\text{Al}^{3+}) = 2.5 \times 10^{-4} \text{ mol}$ $c = \frac{n}{V}$ $c(\text{Al}^{3+}) = \frac{2.472 \times 10^{-4}}{0.025}$ $c(\text{Al}^{3+}) = 9.9 \times 10^{-3} \text{ mol L}^{-1} \text{ (2 sig. fig.)}$	1 2

Question	Part	Author's response	Marks
20	(v)	$M(\text{Al}^{3+}) = 26.98 \text{ g mol}^{-1}$ $\frac{\text{mol}}{\text{L}} \times M \rightarrow \frac{\text{g}}{\text{L}} \times 10^3 \rightarrow \frac{\text{mg}}{\text{L}} = \text{ppm}$ $= 9.888 \times 10^{-3} \times 26.98 \times 10^3$ $= 266.7 \text{ ppm}$ $= 270 \text{ ppm}$	
21	(a)	Mn +2 changes to Mn +3, indicating an increase and oxidation, hence this represents the reducing agent.	1 1
	(b)	$\text{Mn}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Mn}^{3+} + 3\text{H}_2\text{O}$	2
	(c) (i)	$c(\text{S}_2\text{O}_3^{2-}) = 0.0200 \text{ mol L}^{-1}$ $V(\text{S}_2\text{O}_3^{2-}) = 20.2 \text{ mL} = 0.0202 \text{ L}$ $n(\text{EDTA}) = c \times V$ $n(\text{S}_2\text{O}_3^{2-}) = 0.0200 \times 0.0202$ $n(\text{S}_2\text{O}_3^{2-}) = 4.04 \times 10^{-4} \text{ mol}$	2
	(ii)	$\text{Mole ratio } n(\text{S}_2\text{O}_3^{2-}) : n(\text{I}_2) = 2 : 1$ $\frac{n(\text{I}_2)}{n(\text{S}_2\text{O}_3^{2-})} = \frac{1}{2}$ $\therefore n(\text{I}_2) = \frac{4.04 \times 10^{-4}}{2}$ $\therefore n(\text{I}_2) = 2.02 \times 10^{-5} \text{ mol}$	2
	(iii)	Iodine formed from Equation 4 is reacted in Equation 5. $\therefore n(\text{I}_2) = 2.02 \times 10^{-5} \text{ mol}$	
	(1)	$\text{Mole ratio } n(\text{S}_2\text{O}_3^{2-}) : n(\text{I}_2) : n(\text{Mn}^{3+}) : n(\text{Mn}(\text{OH})_3) : n(\text{O}_2)$ $= 2:1, 1:2, 1:1, 1:4$ $\frac{n(\text{O}_2)}{n(\text{Mn}(\text{OH})_3)} = \frac{1}{4}$ $\therefore n(\text{O}_2) = \frac{2.02 \times 10^{-5}}{4}$ $\therefore n(\text{O}_2) = 5.05 \times 10^{-5} \text{ mol}$	1 2
	(iv) (2)	$c = \frac{n}{V}$ $c(\text{O}_2) = \frac{5.05 \times 10^{-5}}{0.100}$ $c(\text{O}_2) = 5.05 \times 10^{-4} \text{ mol L}^{-1} \text{ (3 sig. fig.)}$	2
(3)	$\frac{\text{mol}}{\text{L}} \times M = \frac{\text{g}}{\text{L}} \times 10^3 = \frac{\text{mg}}{\text{L}} = \text{ppm}$ $M(\text{O}_2) = 32.00 \text{ g mol}^{-1}$ $= 5.05 \times 10^{-4} \times 32.00 \times 1000$ $= 16.2 \text{ ppm}$	3	
(4)	2–8 ppm indicates moderately polluted water, therefore this water sample is polluted, as it is above that value.	1	

Question	Part	Author's response	Marks
22	(a) (i)	$R_{rA} = \frac{3.4}{5} = 0.68$	2
		$R_{rB} = \frac{2.9}{5} = 0.57$	2
	(ii)	$TcO_4^- = A$ $TcO_2 = B$	2
	(b)	As the stationary phase is shorter, the duration of the separation is shorter, leading to a faster analysis. Although the components have moved different distances, the rate of movement remains constant. The R_f values will be the same (accounting for experimental error). Therefore the validity is still maintained.	1 1 1 1
23	(a) (i)	Band C	1
		The component in band C has moved at the fastest rate.	1
		This indicates it was least strongly adsorbed to the polar stationary phase and most soluble in the mobile phase, therefore moving with it.	1
	(ii)	Increase the length of the column and, therefore, the stationary phase. Repeat the procedure altering the polarity of the solvent chosen.	1
(b)	Band C	1	
	The component in band C would move at the fastest rate, and therefore, the appear closest to the solvent front at the top of the chromatogram.	1	
	As a ratio (of the distance the component travelled compared to the solvent) it would generate the largest value, which is closest to 1.	1	
24	(a)	Tanker A	1
		The majority of the peaks for tanker A match the retention times, but do not for tanker B.	1
		The peaks demonstrate a lower relative abundance due to decomposition for tanker A but remain at the same retention times.	1
	(b)	Any one: The same oil may be used by other tankers. Peaks for components may have been lost as the hydrocarbons break down in the ocean or volatile components are lost.	1
25	(a)	14.7 minutes (3 significant figures)	1
	(b) (i)	Methamphetamine contains one extra carbon methyl group compared to amphetamine.	2
	(ii)	Methamphetamine is less polar than amphetamine.	1
		Methamphetamine has a larger retention time, as it was adsorbed more strongly to the stationary phase. Therefore, the stationary phase is likely to be non-polar.	1 1

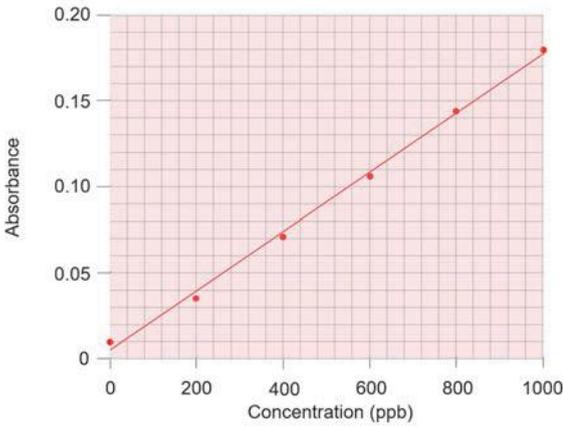
Question	Part	Author's response	Marks
26	(a) (i)	Ammonium and nitrate ions are soluble ions.	1
	(ii)	Anion exchange column	1
	(b)	The single negative charge of nitrate offers a lower charge-density compared to the double negative charge of the sulfate ions.	1
		Nitrate ions are less strongly adsorbed to the positively charged binding sites.	1
		Nitrates are more easily removed from binding sites. They travel at a faster rate along the column, hence a shorter retention time results.	1
	(c)	The high concentration of borate ions places a stress on the system at equilibrium.	1
The position of equilibrium shifts to the right to counteract the change.		1	
Nitrate ions are exchanged from the surface of the resin, replaced with borate ions.		1	
27	(a) (i)	Be $1s^2 2s^2$ C $1s^2 2s^2 2p^2$ O $1s^2 2s^2 2p^4$ F $1s^2 2s^2 2p^5$ Na $1s^2 2s^2 2p^6 3s^1$ Al $1s^2 2s^2 2p^6 3s^2 3p^1$ Si $1s^2 2s^2 2p^6 3s^2 3p^2$ P $1s^2 2s^2 2p^6 3s^2 3p^3$ Ar $1s^2 2s^2 2p^6 3s^2 3p^6$ K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	10
	(b)	The element is located in the block of the periodic table indicated by the highest energy subshell occupied.	1
28	(a) (i)	$= \frac{100}{13} \times 150$ $= 1153.8 \text{ mL}$ $= 1.1 \text{ L}$	2
	(ii)	Iodine is present in higher concentrations in other foods consumed daily.	1
	(b) (i)	$1s^2 2s^2 2p^6 3s^1$	2
	(ii)	$1s^2 2s^2 2p^6$	2
	(iii)	$1s^2 2s^2 2p^6 3s^2 3p^6$	2
	(iv)	In chloride and iodide, the final p subshell has been filled with the addition of one electron.	1

Question	Part	Author's response	Marks
29	(a) (i)	The highest energy subshell to contain electrons is the d subshell which is common to all of these elements.	1
	(ii)	2+	1
	(iii)	$1s^22s^22p^63s^23p^64s^13d^{10}$	2
	(iv)	$Cu^+ 1s^22s^22p^63s^23p^63d^{10}$	2
		$Cu^{2+}1s^22s^22p^63s^23p^63d^9$	2
	(b)	In both cases the actual configuration allows for a completely filled d subshell, which is a more stable configuration.	1
	(c) (i)	$2Ag_{(s)} + H_2S_{(g)} \rightarrow Ag_2S_{(s)} + H_{2(g)}$	2
		(ii)	H ₂ S or hydrogen sulfide
	(d) (i)	Electronics are imported from many regions around the world. They contain metals and raw materials extracted and refined from various regions of the world.	1
		Products that have become redundant in Australia become landfill or are exported back overseas for processing.	1
(ii)		Froth flotation, employed in metal production, can be used to collect the precious metals on the surface of bubbles.	1
30	(a) (i)	p	1
	(ii)	$1s^22s^22p^63s^23p^64s^23d^{10}4p^3$	2
	(b) (i)	Arsenic was present.	1
		The line emission spectra of arsenic is present in the spectra for the unknown sample.	1
	(ii)	lead	1
	(c)	$606 \text{ ppb} = 606 \mu\text{g L}^{-1}$ $= 0.606 \text{ mg L}^{-1}$ $= 6.06 \times 10^{-4} \text{ mg g}^{-1}$ $= 6.06 \times 10^{-4} \times 1.02 \text{ mg}$ $= 6.18 \times 10^{-4} \text{ mg}$	1
			1
		1	

Question	Part	Author's response	Marks
	(a)	It must contain lead, the element under investigation.	1
	(b) (i)	The electrons are able to absorb the energy incident in the beam, as the wavelengths present match the transitions in lead, promoting electrons to an excited state.	1
		The electrons return to lower energy levels in the atoms resulting in the emission of electromagnetic radiation.	1
	(ii)	Lead is toxic to humans if inhaled in high concentrations, extraction limits exposure.	
	(1)	The AAS apparatus has not been calibrated.	1
	(c) (i)		1
	(ii)	<p>42.4 mg L⁻¹ (plotted on the graph)</p>	2
	(iii)	<p>0.13 (plotted on the graph)</p>	1 1
	(d) (i)	The lead lamp provides an incident beam containing energies and corresponding wavelengths of radiation emitted by lead. One unique wavelength is chosen for detection.	1
		This selected wavelength does not match the energy transitions in cadmium, arsenic and chromium.	1
		These elements are unable to absorb radiation at this wavelength, and therefore do not interfere with the analysis.	1
	(ii)	Preparation of cadmium standard solutions and the construction of a calibration graph for cadmium.	1
		A unique wavelength present for cadmium would be selected for detection.	1

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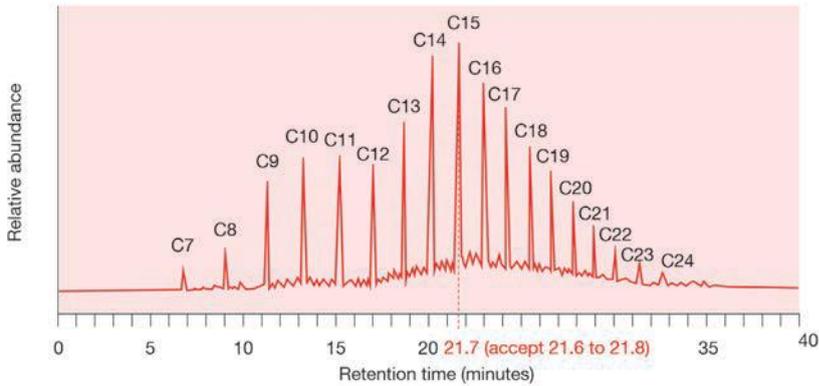


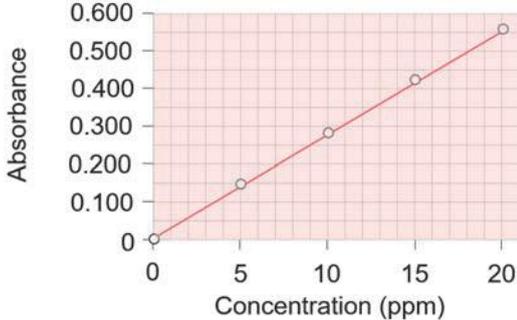
Question	Part	Author's response	Marks
32	(a)	Volumetric flask is rinsed with distilled water to remove contaminants.	1
		Mass of calcium salt required for the desired concentration is weighed out and transferred to the flask.	1
		Distilled water is added, the flask swirled to dissolve the salt and is then made up to the mark with the bottom of the meniscus on the calibration line.	1
		The process is repeated in the preparation of a range of solutions of increasing concentration.	1
		A blank of distilled water is introduced to the AAS to calibrate the apparatus.	1
		Solutions are introduced sequentially in order of increasing concentration. Absorbance values are recorded.	1
		A calibration graph is constructed, plotting absorbance values versus concentration.	
		A line of best fit is applied.	
		Communication: spelling, sentence structure, and logical sequence.	2
33	(a) (i)	p	1
	(ii)	$1s^22s^22p^63s^23p^2$	2
	(iii)	Covalent network	1
	(iv)	Strong primary covalent bonds exist between silicon and oxygen atoms in the extended network producing a hard material.	1
		A large amount of energy is required to overcome the bonds, thus ensuring a high melting point.	1
	(v) (1)	$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$	2
	(2)	Acidic oxide	1
	(b)	$0.326 \mu g mL^{-1} = 326 \mu g L^{-1}$ $= 326 \text{ ppb}$	2
	(c) (i)	Metal	1
	(ii)	$1s^22s^22p^63s^23p^6$	2
(iii) (1)		1	
			1
			1
			1
			1
			1
(2)	A low degree of scatter around the line of best fit.		

Summary test 1 solutions: Monitoring the environment

Question	Part	Author's response	Marks
	(a) (i)	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	2
	(ii)	Any one: Combustion of fossil fuels in internal combustion engines. Combustion of fossil fuels during the production of electricity in power stations. Deforestation and land-clearing.	1
	(iii)	Carbon dioxide is a greenhouse gas. Increased levels of carbon dioxide in the atmosphere leads to an increase in the infrared thermal radiation that is absorbed from the surface of the Earth. This creates a thermal imbalance between the radiation lost and absorbed from the lower atmosphere, resulting in an increased average temperature in the Earth's troposphere.	1 1 1
	(b)	$= 0.927 \times 4.18 \times 10^9 \times 10^3$ $= 3.87 \times 10^{12} \text{ kg}$	2
1	(c) (i)	Any four: <ul style="list-style-type: none"> The concentration of dissolved carbon dioxide in the oceans has increased and is predicted to show further increase. This increase is exponential. pH decreases accordingly as the concentration of dissolved carbon dioxide increases. Carbon dioxide dissolves in water to form carbonic acid. Carbonic acid partially ionises, increasing the concentration of H^+, thus decreasing the pH. 	4
	(ii)	Highest concentration H^+ , is represented by the lowest pH. $[\text{H}^+] = 10^{-7.85}$ $= 1.41 \times 10^{-8} \text{ mol L}^{-1}$	1 2
	(iii)	Increasing the concentration of H^+ results in the formation of hydrogen carbonate ions. The formation of hydrogen carbonate reduces the available concentration of carbonate ions. (Note: <i>simplified description, equilibrium is covered in Topic 2.</i>)	1 1

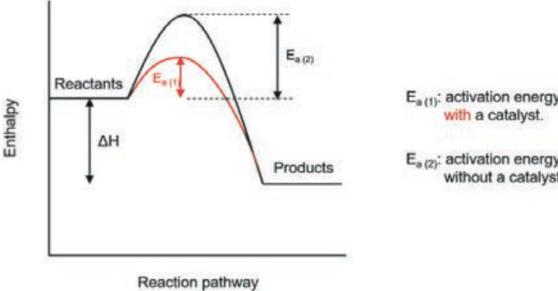
Question	Part	Author's response	Marks
	(d)	<p>Any four of the following points (or alternatives). The science must be clearly identified, and explicit links made to society (people).</p> <p>Influence:</p> <p>Environmental</p> <p>Mining practices to obtain raw materials for renewable energy infrastructure contribute significantly to atmospheric emissions of carbon dioxide. Energy requirements, processing, and transportation of products also contribute.</p> <p>Elevated concentrations of atmospheric carbon dioxide have led to global warming and climate change. Climate change impacts humans and native ecosystems.</p> <p>Mining practices also significantly impact upon native plant and animal species and their associated ecosystem in the location of the mine site.</p> <p>Researchers have mapped mine sites for renewable materials and important regions of natural biodiversity to influence planning for sustainability.</p> <p>Economic</p> <p>Australia has a substantial body of natural resources required for renewable energy production. Mined materials are a valuable export for Australia, with significant economic contribution. Economic decisions may not consider impact on biodiversity.</p> <p>Researchers have mapped mine sites for renewable materials and important regions of natural biodiversity to influence economic decisions.</p> <p>Social/Political</p> <p>Social pressures from the community with regards to environmental concerns of impact upon ecosystems and biodiversity may influence political decisions on where mining takes place and the extent of mining allowed.</p> <p>The findings outlined from researchers mapping of mine sites for renewable materials and important regions of natural biodiversity, may influence social understanding and subsequent political decisions.</p>	4
2	(a) (i)	High temperatures are experienced during the combustion of fuels in the engine. Nitrogen and oxygen are both present in air in the air-fuel mixture.	1
	(ii)	$2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$	2
	(b) (i)	Any one: The reaction is photochemical, requiring the absorption of UV light. The absorption of UV light provides the energy required to achieve the activation energy.	1
	(ii)	$\text{NO}_{2(g)} \xrightarrow{\text{UV}} \text{NO}_{(g)} + \text{O}_{(g)}$ $\text{O}_{(g)} + \text{O}_{2(g)} \rightarrow \text{O}_{3(g)}$	2 2
	(iii)	Human exposure to ozone may cause eye irritation and respiratory distress.	1
		3 significant figures	1
	(c) (i)	Yellow	1
	(ii)	$n(\text{NaOH}) = 0.100 \times 9.16 \times 10^{-3}$ $= 9.16 \times 10^{-4}$ $= 9.16 \times 10^{-4} \text{ mol}$	2
(iii)	<p>mole ratio $n(\text{NaOH}) : n(\text{HNO}_3)$</p> <p>1:1</p> <p>$\therefore n(\text{HNO}_3) = 9.16 \times 10^{-4} \text{ mol}$</p>	1	

Question	Part	Author's response	Marks
2	(iv)	mole ratio $n(\text{HNO}_3) : n(\text{NO}_2)$ $2:2 = 1:1$ $\therefore n(\text{NO}_2) = 9.16 \times 10^{-4} \text{ mol}$	1
	(v)	$C(\text{NO}_2) = \frac{9.16 \times 10^{-4}}{5.00}$ $= 1.832 \times 10^{-4} \text{ mol L}^{-1}$ $= 1.832 \times 10^{-4} \times 46.01 \text{ g L}^{-1}$ $= 1.832 \times 10^{-4} \times 46.01 \times 10^3 \text{ mg L}^{-1}$ $= 8.43 \text{ ppm (3 sig. fig.)}$	2 2
3	(a) (i)	Octane	1
	(ii)	 <p style="text-align: center;">21.7 (+/- 0.1) min (3 sig. fig.)</p>	1 1
	(iii)	As carbon chain length increases, the retention time increases.	1
	(iv)	Non-polar The non-polar alkanes are adsorbed to a non-polar stationary phase.	1 1
	(v)	Any one: <ul style="list-style-type: none"> • Shorter chain alkanes present are volatile and may be lost when temperatures rise. • Longer chain alkanes are decomposed, breaking down to volatile products which are lost. 	1
(b) (i)	Positive	1	
(ii)	Phosphate Phosphate ions have a 3- charge compared to 1- for nitrate. Overall, they have a higher negative charge density, resulting in stronger electrostatic attraction to the zeolite surface. They would be more difficult to remove from the surface and shift across the stationary phase. This therefore results in a longer retention time.	1 1 1	

Question	Part	Author's response	Marks
4	(a) (i)	d	1
	(ii)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	2
	(iii)	+6	2
	(b) (i)	Absorbance	1
	(ii)	 <p>Axes, labelled, unites, scale, data points, line of best fit.</p>	1 1 1 1 1 1
	(iii)	Low degree of scatter.	1
	(iv)	The wavelength of copper selected for detection is unique to copper.	1
		The transitions in chromium and arsenic do not match the detected wavelength, and therefore they are unable to absorb radiation incident from the lamp at this wavelength.	1
	(c)	Acid rain increases the mobilisation of cations, including toxic species.	1

Topic 2 solutions: Managing chemical processes

Question	Part	Author's response	Marks
1		<p>At t=5 seconds there is a greater concentration of reactants than at t=50 seconds when more of the reactants have been converted into carbon dioxide gas.</p> <p>The greater concentration leads to an increased frequency of collisions between HCl and CaCO₃.</p> <p>More collisions occur between reacting particles and as a result a larger number of successful collisions occur.</p> <p>Therefore, a larger number of successful collisions occur per unit time at t=5 seconds resulting in a higher instantaneous rate of reaction.</p>	4
2	(a)	<p>If the surface area of CaCO₃ is increased, exposing more particles, and altering the surface area to volume ratio.</p> <p>The frequency of collisions between HCl and CaCO₃ increases as more particles of CaCO₃ are exposed.</p> <p>More collisions occur and as a result a larger number of successful collisions occur between HCl and CaCO₃. Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.</p>	3
	(b)	<p>If the concentration of HCl is reduced there are less H⁺ ions in the system available to react with CaCO₃ and the frequency of collisions is decreased.</p> <p>Less collisions occur and as a result less successful collisions occur between H⁺ ions and CaCO₃. Therefore, less successful collisions occur per unit time resulting in a decrease in the rate of reaction.</p>	3
	(c)	<p>A mass of CaCO₃ is added to a conical flask.</p> <p>A specific volume of HCl is poured into a conical flask.</p> <p>The time taken for the CaCO₃ to completely react and no longer being visible is measured using a timer.</p>	3
3	(a)	<p>Lactase provides an alternative pathway with a lower E_a for the lactose to digest in the human gut.</p> <p>This results in a larger proportion of collisions between reacting particles reaching or exceeding the Activation Energy.</p> <p>There is an increased frequency of successful collisions occurring.</p> <p>Therefore, a larger number of successful collisions occur per unit time increasing the rate of digestion of lactose.</p>	3
	(b)	<p>If the temperature of the milk is increased this results in the average kinetic energy of all particles in the milk increasing and exhibiting more thermal energy.</p> <p>Therefore, there is a larger proportion of collisions between reacting particles in the milk reaching or exceeding the Activation Energy.</p> <p>There is an increased frequency of successful collisions occurring between these particles.</p> <p>Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of formation by products in the milk.</p>	3

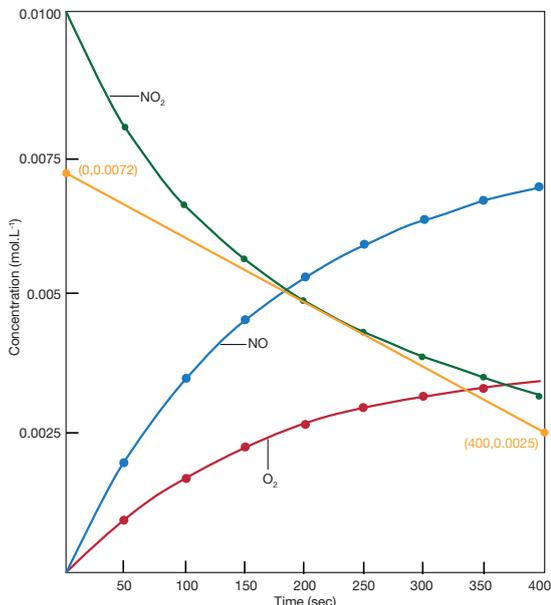
Question	Part	Author's response	Marks
4	(a)	$2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$	2
	(b)	<p>The surface area of magnesium is increased when using a powder instead of strips, exposing more particles, and altering the surface area to volume ratio.</p> <p>The frequency of collisions between magnesium and oxygen increases as more particles of magnesium are exposed.</p> <p>More collisions occur and as a result a larger number of successful collisions occur between magnesium and oxygen.</p> <p>Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.</p>	3
	(c)	<p>The fuse releases a large amount of energy that is provided to the system, this results in the average kinetic energy of the magnesium and oxygen increasing and exhibiting more thermal energy.</p> <p>Therefore, there is a larger proportion of collisions between magnesium and oxygen reaching or exceeding the Activation Energy.</p> <p>There is an increased frequency of successful collisions occurring between the particles.</p> <p>Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction</p>	3
	(d)	The reaction between magnesium and oxygen is exothermic and the energy produced is transferred to unreacted magnesium and oxygen.	2
	(e)	 <p>$E_{a(1)}$: activation energy with a catalyst.</p> <p>$E_{a(2)}$: activation energy without a catalyst.</p>	3

Question	Part	Author's response	Marks																				
5	(a)	$K_c = \frac{[\text{CH}_3\text{COOCH}_3] \cdot [\text{H}_2\text{O}]}{[\text{CH}_3\text{OH}] \cdot [\text{CH}_3\text{COOH}]}$	1																				
	(b)	<table border="1"> <thead> <tr> <th></th> <th>CH₃OH</th> <th>CH₃COOH</th> <th>CH₃COOCH₃</th> <th>H₂O</th> </tr> </thead> <tbody> <tr> <td>Initial moles</td> <td>1.2</td> <td>1.2</td> <td>0.00</td> <td>0.00</td> </tr> <tr> <td>Change in moles</td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>Equilibrium moles</td> <td></td> <td></td> <td>0.50</td> <td></td> </tr> </tbody> </table>		CH ₃ OH	CH ₃ COOH	CH ₃ COOCH ₃	H ₂ O	Initial moles	1.2	1.2	0.00	0.00	Change in moles					Equilibrium moles			0.50		3
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	(b)	$K_c = \frac{[\text{HI}]^2}{[\text{H}_2] \cdot [\text{I}_2]}$ $\therefore K_c = \frac{(2)^2}{4 \times 2}$ $\therefore K_c = \frac{4}{8}$ $\therefore K_c = 0.5$	3																																																																
	(c)	<p>A decrease in the volume to 50 mL leads to an increase in the pressure of the system at equilibrium. According to Le Châtelier's principle the system will counteract the introduced change placed on the equilibrium mixture by attempting to decrease the pressure.</p> <p>The decrease in pressure is achieved by shifting to the side of the equation which results in the formation of the least moles of gaseous particles until equilibrium is re-established. In this reaction the right hand side has 2 moles of gas whilst the left hand side has 1 mole of gas. Therefore, the position of equilibrium would shift to the left in the backward direction as this creates the least moles of gas. Therefore, decreasing the concentration of HI and increasing the concentrations of H₂ and I₂.</p>	3																																																																

Question	Part	Author's response	Marks
6	(d)	<p>The enthalpy given for this reaction is negative, indicating that the forward reaction is exothermic and the backward reaction is endothermic.</p> <p>According to Le Châtelier's principle, the endothermic reaction is favoured when the temperature of the reaction mixture is increased.</p> <p>This will result in the backward reaction being favoured in order to absorb the additional energy, shifting the position of equilibrium in the backward direction until equilibrium is re-established.</p> <p>Therefore, increasing the concentrations of H₂ and I₂ and decreasing the concentration of HI.</p>	3
	(e)	<p>No change to K_c value</p> <p>NOTE: The K_c value is only affected by changes to temperature</p>	1
7	(a)	Manure, straw or H ₂ O	1
	(b)	$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] \cdot [\text{H}_2]^2}$	1
	(c)	<p>The enthalpy given for this reaction is negative, indicating that the forward reaction is exothermic.</p> <p>According to Le Châtelier's principle, the exothermic reaction is favoured when the temperature of the reaction mixture is decreased.</p> <p>This will result in the forward reaction being favoured in order to release energy, shifting the position of equilibrium in the forward direction until equilibrium is re-established.</p> <p>Therefore, favouring the production of methanol.</p>	3
	(d)	<p>A high reaction temperature increases the average kinetic energy of reacting particles, leading to an increase in the rate of the reaction.</p> <p>However, a high reaction temperature would favour the backward reaction according to Le Châtelier's principle, decreasing the yield of methanol.</p> <p>Therefore, it is evident that by increasing the rate of reaction through an increase in temperature, this would result in a reduction of yield of methanol due to equilibrium principles. Therefore, using a higher temperature is a compromise for industry.</p>	3
	(e)	<p>If a catalyst is used, this would provide an alternative reaction pathway for the reacting particles with a lower Activation Energy.</p> <p>Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of reaction.</p> <p>Therefore, the system would reach a state of equilibrium faster. However, it would have no effect on the yield of methanol at equilibrium.</p>	3

Summary test 2 solutions: Managing chemical processes

Question	Part	Author's response	Marks
	(a)	Reacting particles meeting or exceeding the Activation Energy E_a	1
	(b) (i)	Time (sec)	1
	(b) (ii)	 <p>Instantaneous rate of decomposition = $\frac{\text{change in concentration}}{\text{time elapsed}}$</p> <p>$\therefore$ Instantaneous rate of decomposition = $\frac{0.0072 - 0.0025}{0 - 400}$</p> <p>$\therefore$ Instantaneous rate of decomposition = $\frac{0.0047}{-400}$</p> <p>\therefore Instantaneous rate of decomposition = $-1.2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$</p> <p>Therefore, at approximately $t = 200$ seconds the rate of decomposition of nitrogen dioxide gas is 1.2×10^{-5} moles per litre per second.</p>	3
	(b) (iii)	<p>At the start of the experiment the concentration of nitrogen dioxide is higher. Therefore, the frequency of collisions between nitrogen dioxide molecules is higher than later in the experiment when more NO_2 has been decomposed.</p> <p>More collisions occur and as a result a larger number of successful collisions occur between nitrogen dioxide molecules.</p> <p>Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of decomposition of nitrogen dioxide.</p>	3
	(b) (iv)	<p>If the pressure of the reaction vessel is increased, more collisions occur between nitrogen dioxide molecules.</p> <p>The frequency of collisions between nitrogen dioxide molecules is increased and as a result a larger number of successful collisions between nitrogen dioxide molecules occur.</p> <p>Therefore, a larger number of successful collisions occur per unit time resulting in an increase in the rate of decomposition of nitrogen dioxide.</p>	1

1

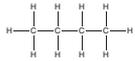
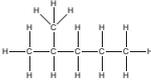
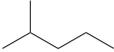
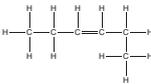
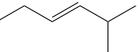
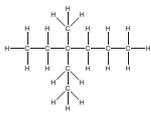
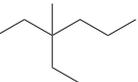
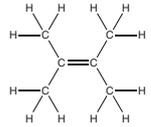
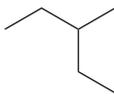
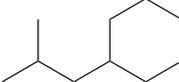
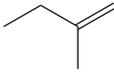
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	(c) (ii) (1)	<p>From the data provided, the K_c value is higher at a higher temperature. This indicates that at higher temperatures the position of equilibrium shifts to favour the products.</p> <p>According to Le Châtelier's principle, the endothermic reaction is favoured when the temperature of the reaction mixture is increased.</p> <p>Therefore, the decomposition of NOCl is an endothermic process.</p>	3																																																																												
	(c) (ii) (2)	<p>reaction at 127°C were:</p> $K_c = \frac{[\text{NO}]^2 \cdot [\text{Cl}_2]}{[\text{NOCl}]^2}$ $\therefore K_c = \frac{(0.0199)^2 \cdot (0.965)}{(0.0199)^2}$ $\therefore K_c = \frac{3.82 \times 10^{-4}}{3.96 \times 10^{-4}}$ $\therefore K_c = 0.965$ <p>At 127 the theoretical K_c value for this reaction is 5.6×10^{-6}. The K_c value at this point in the reaction is 0.965 which indicates that the reaction is not in a state of equilibrium.</p>	3																																																																												
1	(c) (iii) (1)	<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>NOCl</th> <th>NO</th> <th>Cl₂</th> </tr> </thead> <tbody> <tr> <td>Initial moles</td> <td>0.513</td> <td>0</td> <td>0</td> </tr> <tr> <td>Change in moles</td> <td></td> <td></td> <td></td> </tr> <tr> <td>Equilibrium moles</td> <td></td> <td></td> <td>0.0160</td> </tr> </tbody> </table> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>NOCl</th> <th>NO</th> <th>Cl₂</th> </tr> </thead> <tbody> <tr> <td>Initial moles</td> <td>0.513</td> <td>0</td> <td>0</td> </tr> <tr> <td>Change in moles</td> <td></td> <td></td> <td>+0.0160</td> </tr> <tr> <td>Equilibrium moles</td> <td></td> <td></td> <td>0.0160</td> </tr> </tbody> </table> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>NOCl</th> <th>NO</th> <th>Cl₂</th> </tr> </thead> <tbody> <tr> <td>Initial moles</td> <td>0.513</td> <td>0</td> <td>0</td> </tr> <tr> <td>Change in moles</td> <td>-0.0320</td> <td>+0.0320</td> <td>+0.0160</td> </tr> <tr> <td>Equilibrium moles</td> <td></td> <td></td> <td>0.0160</td> </tr> </tbody> </table> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>NOCl</th> <th>NO</th> <th>Cl₂</th> </tr> </thead> <tbody> <tr> <td>Initial moles</td> <td>0.513</td> <td>0</td> <td>0.00</td> </tr> <tr> <td>Change in moles</td> <td>-0.0320</td> <td>+0.0320</td> <td>+0.0160</td> </tr> <tr> <td>Equilibrium moles</td> <td>0.481</td> <td>0.0320</td> <td>0.0160</td> </tr> </tbody> </table> <p style="text-align: center;">$v = 1 \text{ L}$</p> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>NOCl</th> <th>NO</th> <th>Cl₂</th> </tr> </thead> <tbody> <tr> <td>Equilibrium moles</td> <td>0.481</td> <td>0.0320</td> <td>0.0160</td> </tr> <tr> <td>Concentration at equilibrium (mol L⁻¹)</td> <td>$\frac{0.481}{1}$ = 0.481 mol L⁻¹</td> <td>$\frac{0.0320}{1}$ = 0.0320 mol L⁻¹</td> <td>$\frac{0.0160}{1}$ = 0.0160 mol L⁻¹</td> </tr> </tbody> </table>		NOCl	NO	Cl ₂	Initial moles	0.513	0	0	Change in moles				Equilibrium moles			0.0160		NOCl	NO	Cl ₂	Initial moles	0.513	0	0	Change in moles			+0.0160	Equilibrium moles			0.0160		NOCl	NO	Cl ₂	Initial moles	0.513	0	0	Change in moles	-0.0320	+0.0320	+0.0160	Equilibrium moles			0.0160		NOCl	NO	Cl ₂	Initial moles	0.513	0	0.00	Change in moles	-0.0320	+0.0320	+0.0160	Equilibrium moles	0.481	0.0320	0.0160		NOCl	NO	Cl ₂	Equilibrium moles	0.481	0.0320	0.0160	Concentration at equilibrium (mol L ⁻¹)	$\frac{0.481}{1}$ = 0.481 mol L ⁻¹	$\frac{0.0320}{1}$ = 0.0320 mol L ⁻¹	$\frac{0.0160}{1}$ = 0.0160 mol L ⁻¹	
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1	(c) (iii) (2)	$K_c = \frac{[\text{NO}]^2 \cdot [\text{Cl}_2]}{[\text{NOCl}]^2}$ $\therefore K_c = \frac{(0.0320)^2 \cdot (0.160)}{(0.0481)^2}$ $\therefore K_c = \frac{1.638 \times 10^{-5}}{0.231}$ $\therefore K_c = 7.08 \times 10^{-5}$	2
	(c) (iii) (3)	No change to K_c value	1
	(c) (iv) (1)	<p>At t_1 the concentration of NO was increased which introduces a change to the system at equilibrium.</p> <p>According to Le Châtelier's principle the system will attempt to counteract the change in concentration by reducing the concentration of NO.</p> <p>Resulting in the backward reaction being favoured in order to convert products into reactants, shifting the position of equilibrium to the left until equilibrium is re-established. Therefore, resulting in the concentration of NO and Cl_2 decreasing and the concentration of NOCl increasing as can be seen in the diagram.</p>	4
	(c) (iv) (2)		

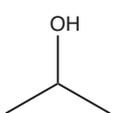
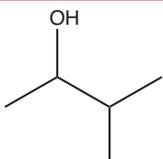
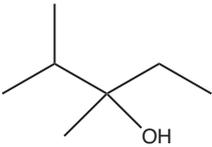
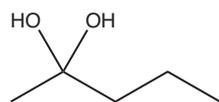
Question	Part	Author's response	Marks									
	(a)	<p>A triple covalent bond exists between nitrogen atoms within the nitrogen molecule.</p> <p>A triple covalent bond is very strong and requires large amounts of thermal energy to break this bond.</p> <p>A chemical reaction can only occur once this triple covalent bond within the nitrogen molecule is broken, the thermal energy required means the temperature provided to the reaction needs to be high.</p>	3									
	(b)	<p>Temperature</p> <p>The enthalpy given for this reaction is negative, indicating that the forward reaction is exothermic.</p> <p>According to Le Châtelier's principle, the exothermic reaction is favoured when the temperature of the reaction mixture is decreased.</p> <p>This will result in the forward reaction being favoured in order to release energy, shifting the position of equilibrium in the forward direction until equilibrium is re-established.</p> <p>In this reaction the left hand side has 4 moles of gas whilst the right hand side has 2 moles of gas.</p> <p>According to Le Châtelier's principle, the production of the least moles of gas is favoured when the pressure is increased.</p> <p>Therefore, the use of low temperature and high pressure would favour the production of ammonia.</p>	5									
	(c)	Methane, coal, oil or N ₂	1									
2	(d) (i)	<table border="1"> <thead> <tr> <th>Theoretical conditions</th> <th>Actual Conditions</th> <th>Explanation</th> </tr> </thead> <tbody> <tr> <td>Low Temperature</td> <td>450°C – 500°C (moderate temp)</td> <td>A low temperature will lead to a slow rate of reaction, resulting in higher production costs. A moderate temperature is used as a compromise between rate and equilibrium.</td> </tr> <tr> <td>High Pressure</td> <td>150 – 200 atm (moderate pressure)</td> <td>Reaction vessels required for high pressures are costly to the manufacturer. OR Achieving high pressure is an energy intensive process therefore energy costs are high. A moderate pressure is used as a compromise between equilibrium and manufacturer costs.</td> </tr> </tbody> </table> <p>From this example it is evident that by increasing the yield through a decrease in temperature, this would result in a slow rate of reaction. Therefore, industry finds a compromise between rate and equilibrium in order to maximise yield and subsequently maximise the profits.</p>	Theoretical conditions	Actual Conditions	Explanation	Low Temperature	450°C – 500°C (moderate temp)	A low temperature will lead to a slow rate of reaction, resulting in higher production costs. A moderate temperature is used as a compromise between rate and equilibrium.	High Pressure	150 – 200 atm (moderate pressure)	Reaction vessels required for high pressures are costly to the manufacturer. OR Achieving high pressure is an energy intensive process therefore energy costs are high. A moderate pressure is used as a compromise between equilibrium and manufacturer costs.	3
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	(d) (ii)	<p>$E_a(1)$: activation energy with a catalyst. $E_a(2)$: activation energy without a catalyst.</p>	4									

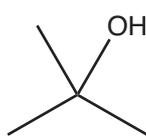
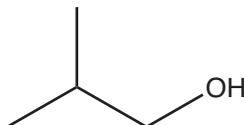
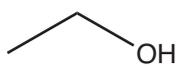
Question	Part	Author's response	Marks
2	(d) (iii)	<p>The application of scientific understanding to develop the catalyst for manufacturers that lowers temperatures needed</p> <p>or</p> <p>Society influences scientists to find the catalyst solution to reduce combustion of fossil fuels in order to reduce global warming</p> <p>The reduction in temperatures needed for the production of ammonia would result in lower energy requirements for the industry.</p> <p>Lower energy requirements leads to CO₂ produced through energy production.</p> <p>Lower CO₂ production leads to lower concentrations of CO₂ in the atmosphere and less infrared radiation being absorbed, reducing the impact on the enhanced greenhouse effect.</p>	4
	(d) (iv)	$\text{H}^+ + \text{F}^- \rightarrow \text{HF}$ <p>Fluoride ions are able to accept protons, basic substances are proton acceptors.</p>	2
	(d) (v)	<p>Lower temperatures favour the production of ammonia according to Le Châtelier's principle.</p> <p>Leading to an increased yield of ammonia.</p> <p>Increased yield would result in larger profits for the manufacturer.</p>	3

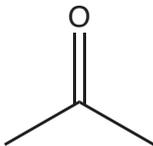
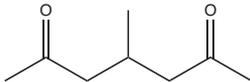
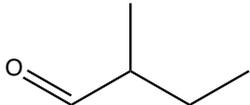
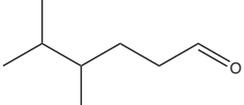
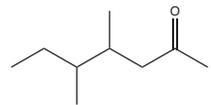
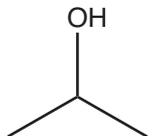
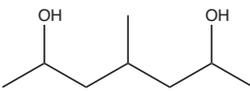
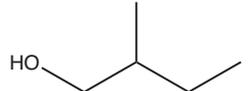
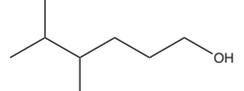
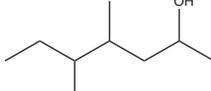
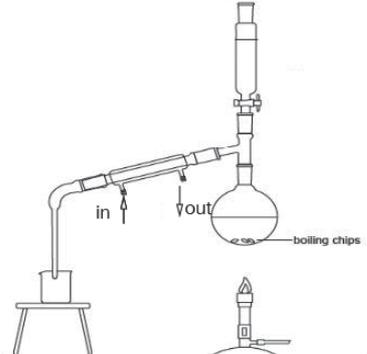
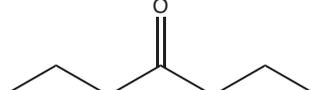
Topic 3 solutions: Organic and biological chemistry

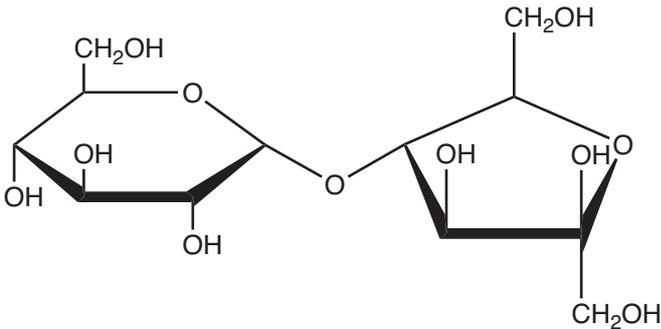
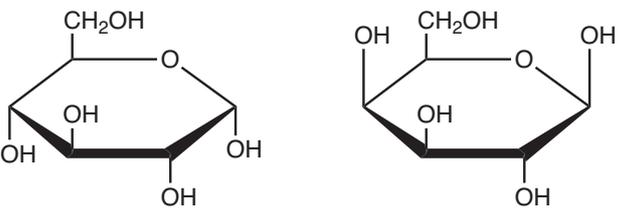
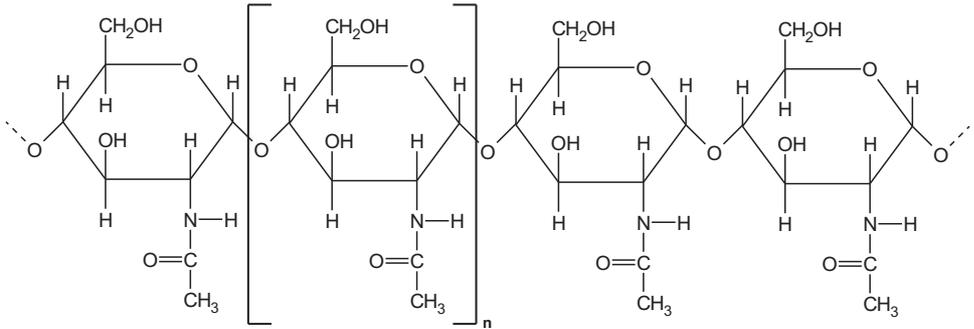
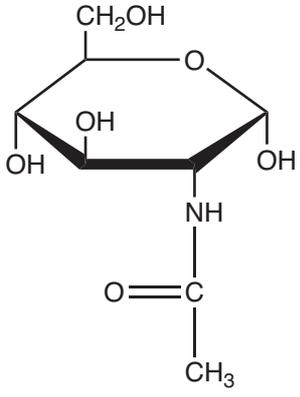
Question	Part	Author's response					Marks
1	(a)	Name	Molecular formula	Empirical formula	Complete structural formula	Condensed structural formula	Skeletal structure
		butane	C_4H_{10}	C_2H_5		$CH_3-CH_2-CH_2-CH_3$	
		2-methylpentane	C_6H_{14}	C_3H_7		$CH_3-CH(CH_3)-CH_2-CH_2-CH_3$	
		2-methyl-3-hexene	C_7H_{14}	CH_2		$CH_3-CH_2-CH=CH-CH(CH_3)-CH_3$	
		3-ethyl-3-methylhexane	C_9H_{20}	C_3H_{20}		$CH_3-CH_2-C(CH_3)(CH_2-CH_3)-CH_2-CH_2-CH_3$	
		2,3-dimethyl-2-butene	C_6H_{12}	CH_2		$CH_3-C(CH_3)=C(CH_3)-CH_3$	
	(b)	Compound	Correct name	Structure			
		3-ethylbutane	3-methylpentane				
		1-methyl-4-propylhexane	4-ethyl-2-methylheptane				
	3-methyl-3-butene	2-methyl-1-butene					

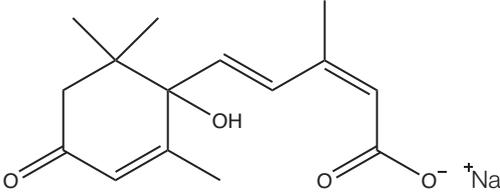
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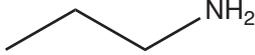
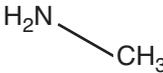
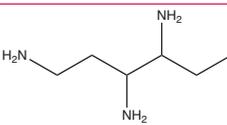
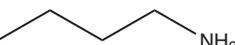
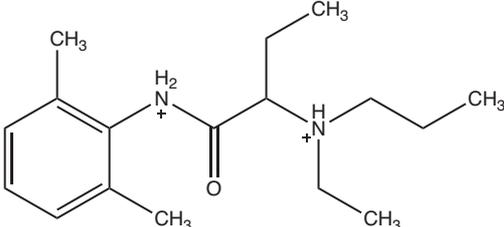
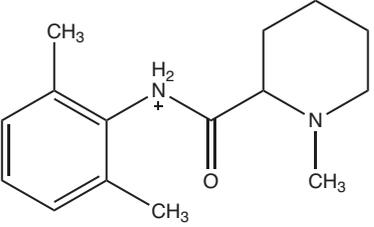
Question	Part	Author's response	Marks	
2	(a)	1 Propane (lowest b.p.) < 2 diethyl ether < 3 ethanol (highest b.p.)	3	
	(b)	The boiling points of covalent molecular substances are determined by their molecular weight and the strength of the intermolecular forces between the molecules. These compounds have similar molecular weights.	1	
		Plus any two of:	2	
	(c)	– Ethanol molecules can form hydrogen bonds with each other; ethanol will have a high boiling point.	1	
		– Diethyl ether molecules are slightly polar, and will experience dipole-dipole interactions; diethyl ether will have a moderate boiling point.		
		– Propane molecules experience only dispersion forces; propane will have a low boiling point.		
	(d)	Butan-1-ol molecules can form hydrogen bonds with each other, while pentane molecules are only attracted to one another by dispersion forces.	1	
		Hydrogen bonds are much stronger than dispersion forces.	1	
	(e)	It takes significantly more energy to overcome the hydrogen bonds, so a higher temperature is necessary for butan-1-ol to boil.	1	
		Ethanol will have the greatest solubility in water.	1	
The hydroxyl functional group (–OH) present in ethanol can form hydrogen bonds with water.		1		
The other compounds are unable to form hydrogen bonds with water.		1		
i) Alcohols contain the hydroxyl functional group (–OH). Hydroxyl functional groups can form hydrogen bonds with water, increasing the solubility of the overall molecule.		1		
(e)	ii) Hydrocarbon chains are non-polar and do not form strong intermolecular bonds with polar water molecules.	1		
	As the length of the hydrocarbon chain increases, the non-polar aspect of the molecule comes to dominate and the effect of hydroxyl group(s) on solubility diminishes.	1		
3	(a)	i) 3,4-dimethylheptan-3-ol	2	
		ii) prop-2-en-1-ol	2	
		iii) 3,3-dimethylpentan-2,2-diol	2	
		iv) 2-methylpropan-1,2,3-triol	2	
	(b)	i) tertiary	1	
		ii) primary	1	
		iii) tertiary	1	
		iv) Left to right – primary, tertiary, primary	1	
	(c)	a	propan-2-ol	2
				
b		3-methylbutan-1-ol	2	
				
c	2,3-dimethylpentan-3-ol	2		
				
d	pentane-2,2-diol	2		
				

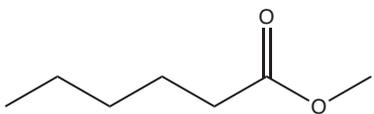
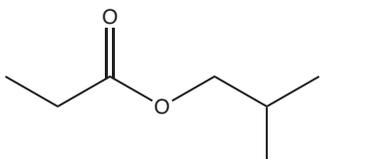
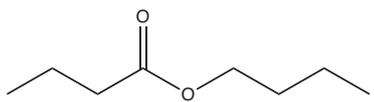
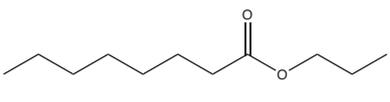
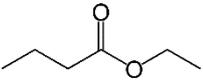
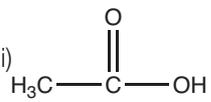
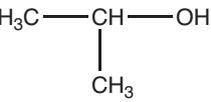
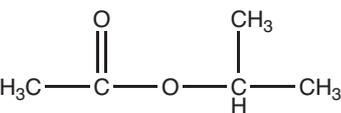
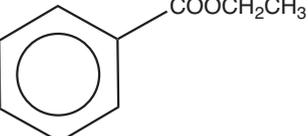
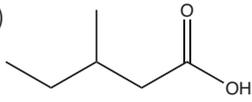
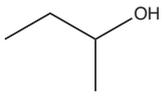
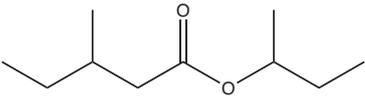
Question	Part	Author's response	Marks
		$\begin{array}{c} \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{O} \end{array}$	2
	(a)	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{C}=\text{O} \\ \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{C}=\text{O} \\ \\ \text{OH} \end{array}$	2+2
4	i)	 2-methylpropan-2-ol	2
		 2-methylpropan-1-ol	2
	ii)	A small amount of acidified dichromate solution is added to a sample of both compounds.	1
		2-methylpropan-1-ol is a primary alcohol and will oxidise in the presence of acidified dichromate.	1
		This results in the reduction of dichromate to chromium ions changing the solution from orange to green.	1
		$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	
		2-methylpropan-2-ol is a tertiary alcohol and will not be oxidised, therefore remaining orange.	1
	(c)	$3\text{C}_5\text{H}_{12}\text{O} + 8\text{H}^+ + \text{Cr}_2\text{O}_7 \rightarrow 3\text{C}_5\text{H}_{10}\text{O} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	4
5	(a)	Compound Y contains both a hydroxyl and carbonyl group (together forming a carboxyl group). Compound X contains only a hydroxyl group and also has a longer hydrocarbon chain.	1
		The additional carbonyl group provides an additional site for dipole-dipole bonding to occur with water, enhancing solubility.	1
	(i)		2
	(b)	(ii) primary	1
		(iii) acidified dichromate	1
6		$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{C}=\text{O} \\ \quad \\ \text{H} \quad \text{H} \end{array} \quad \text{or} \quad \begin{array}{c} \diagup \\ \diagdown \\ \text{O} \end{array}$	
7	(a)	i) 2-ethyl-3-methylpentanal	2
		ii) 2-methylbutanal	2
		iii) ethanedial	2
		iv) 3-methylpentan-2-one	2
		v) butan-2,3-dione	2
		vi) 3,3-dimethylbutan-2-one	2

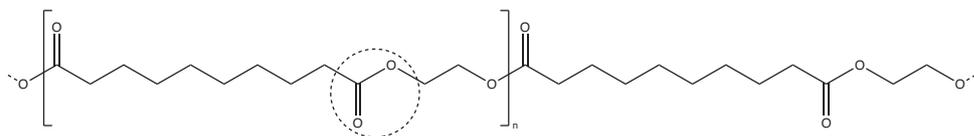
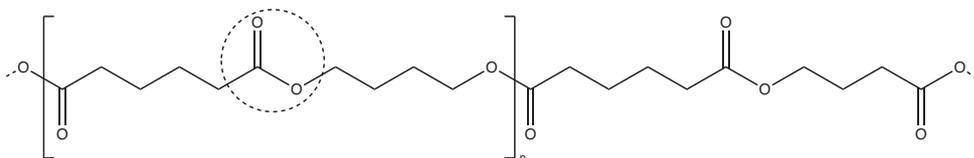
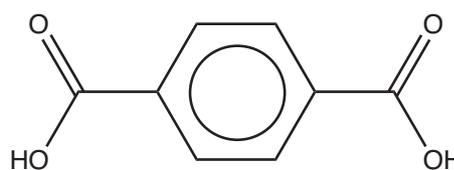
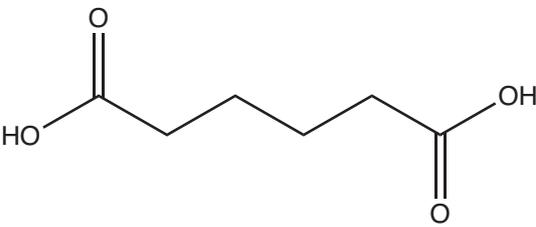
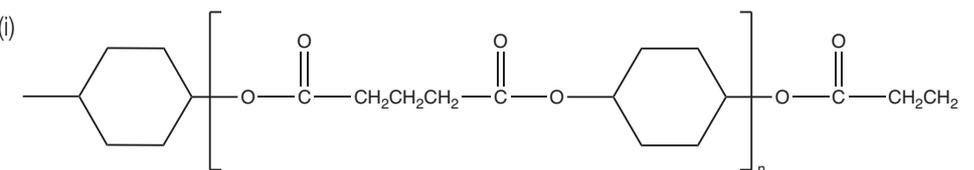
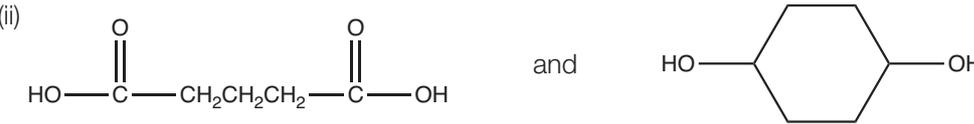
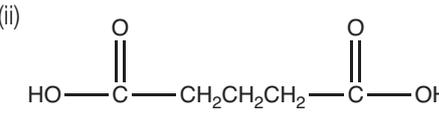
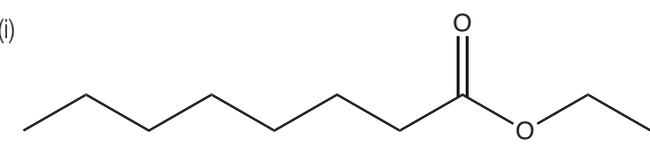
Question	Part	Author's response	Marks
(b)	i)		6 6
	ii)		
(b)	iii)	$\text{H}_2\text{C}=\text{O}$	6 6
	iv)		
(b)	v)		6 6
	vi)		
(c)	Tollen's test (using ammoniacal silver nitrate)		1
	Add a small amount of Tollen's reagent to separate test tubes containing a sample of both compounds and heat.		1
	The terminal carbonyl group present in compound iii) will oxidise resulting in the reduction silver diamine ion, producing a silver mirror on the inside of the reaction vessel.		1
	Compound ii) contains two ketone (non-terminal carbonyl) groups which do not oxidise and therefore will produce no observable reaction.		1
(d)	(i)		6 6
	(ii)		
(d)	(iii)	$\text{H}_3\text{C}-\text{OH}$	6 6
	(iv)		
(d)	(v)		6 6
	(vi)		
7	i)	A: addition funnel or dropper funnel, B: Liebig condenser	
(e)	ii)		1+1 1 2 1
	iii)	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	
	iv)	carboxyl	
(f)	i)	 heptan-4-one	1 2
	ii)	e.g., (Heptan-2-one, heptan-3-one and heptan-4-one are all isomers of the aldehyde shown).	
	iii)	In its ionic form the carboxylate anion contains a full negative charge.	1
		The negative charge on the oxygen atom is able to form strong ion-dipole bonds with water.	1
	This allows water molecules to successfully surround and separate the carboxylate salt facilitating its solubility.	1	

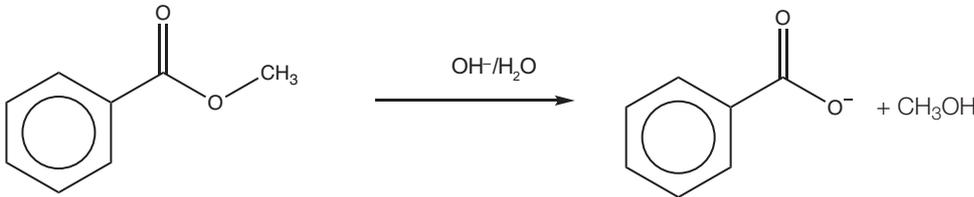
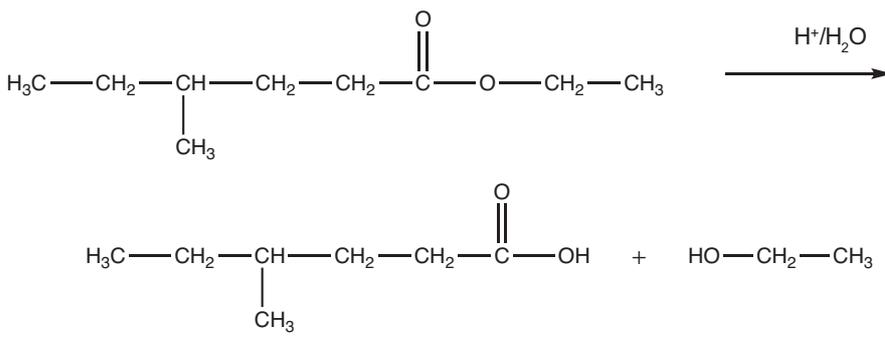
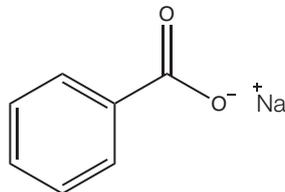
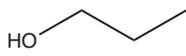
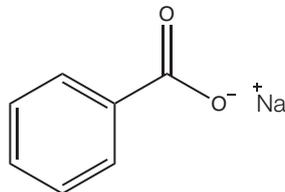
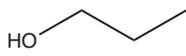
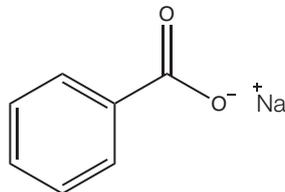
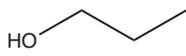
Question	Part	Author's response	Marks
8	(a)	Polyhydroxy ketone	1
	(b)	Molecules with the same molecular formulae, but differing structural formula containing different functional groups. Changes to structural formulae results in changes to chemical properties.	1 1
	(c)		2
	(d)	Condensation	1
	(e)	Addition of Tollen's reagent. The straight-chain glucose has a terminal carbonyl group which can be oxidised by Tollen's reagent resulting in the formation of a silver mirror on the inside of the reaction vessel.	1 1 1
	(f)	(i) $C_{12}H_{22}O_{11}$  (ii)	2 2+2
9	(a)		1
	(b)		2
	(c)	Polysaccharide	1

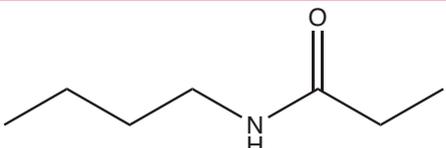
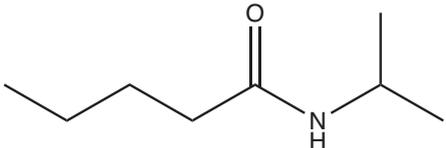
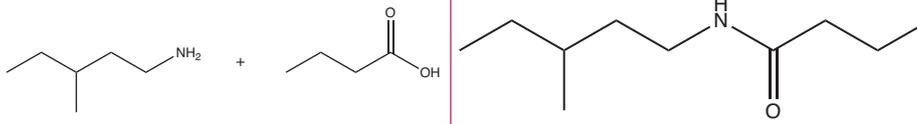
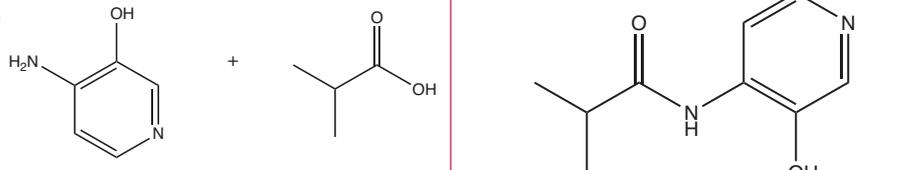
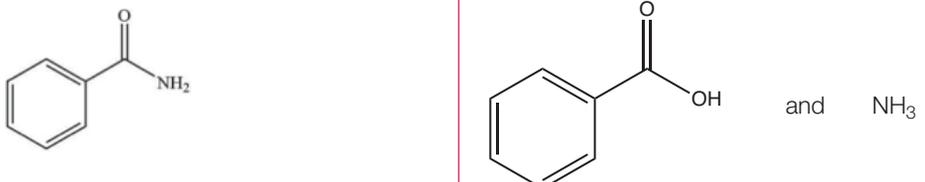
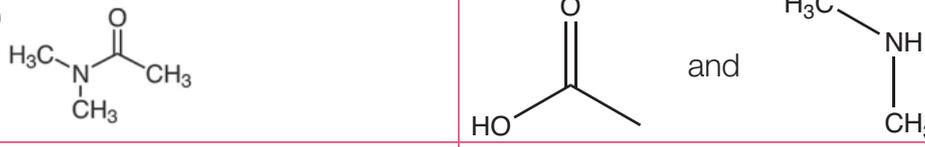
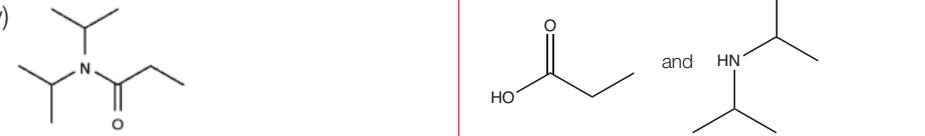
Question	Part	Author's response	Marks											
10	(a)	Ethane-1,2-dioic acid	1											
	(b)	$C_2O_4H_2$	1											
	(c)	(i) $RCOOH + OH^- \rightarrow H_2O + RCOO^-$ The oxalic acid (a solid) at room temperature with react with sodium hydroxide solution to produce a soluble carboxylate salt. The resulting solution will be miscible.	1 1 1											
		(ii) $2RCOOH + CO_3^{2-} \rightarrow H_2O + 2RCOO^- + CO_2$ The oxalic acid (a solid) at room temperature with react with sodium carbonate solution to produce a soluble carboxylate salt. The resulting solution will be miscible and produce effervescence due to the carbon dioxide produced.	1 1 1											
	(d)	(i)	2											
		1. Methanoic acid 2. Butanoic acid 3. Propane-1,3-dioic acid	2 2 2 2 2											
	11	(a)	$C_{15}H_{20}O_4$	1										
		(b)	Carbonyl, hydroxyl, carboxyl and alkene. Any three are acceptable.	1 + 1 + 1										
		(c)	<table border="1"> <thead> <tr> <th>Abcsicic acid tested with...</th> <th>Observations</th> </tr> </thead> <tbody> <tr> <td>Bromine water (Br_2)</td> <td>Orange to colourless colour change</td> </tr> <tr> <td>Acidified dichromate ($Cr_2O_7^{2-}/H^+$)</td> <td>Orange to green colour change</td> </tr> <tr> <td>Tollens' reagent</td> <td>No observable change seen</td> </tr> <tr> <td>Sodium bicarbonate solution ($NaHCO_3$)</td> <td>Effervescence</td> </tr> </tbody> </table>	Abcsicic acid tested with...	Observations	Bromine water (Br_2)	Orange to colourless colour change	Acidified dichromate ($Cr_2O_7^{2-}/H^+$)	Orange to green colour change	Tollens' reagent	No observable change seen	Sodium bicarbonate solution ($NaHCO_3$)	Effervescence	1 1 1 1
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	This allows water molecules to successfully surround and separate the carboxylate salt facilitating its solubility.	1												
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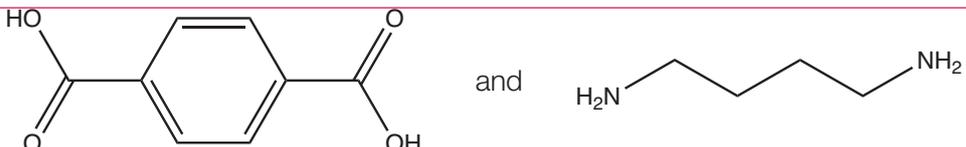
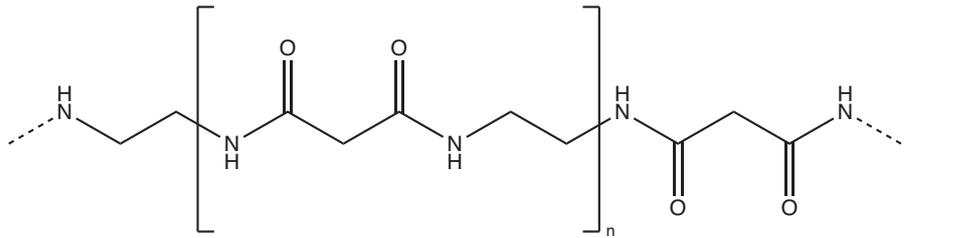
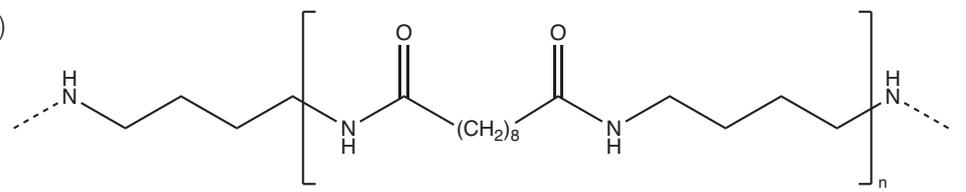
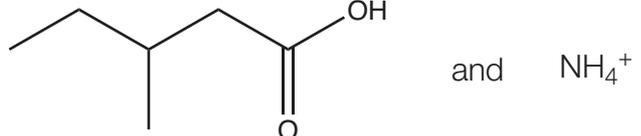
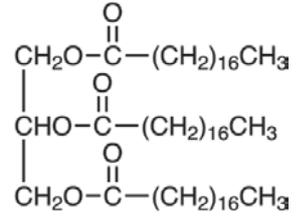
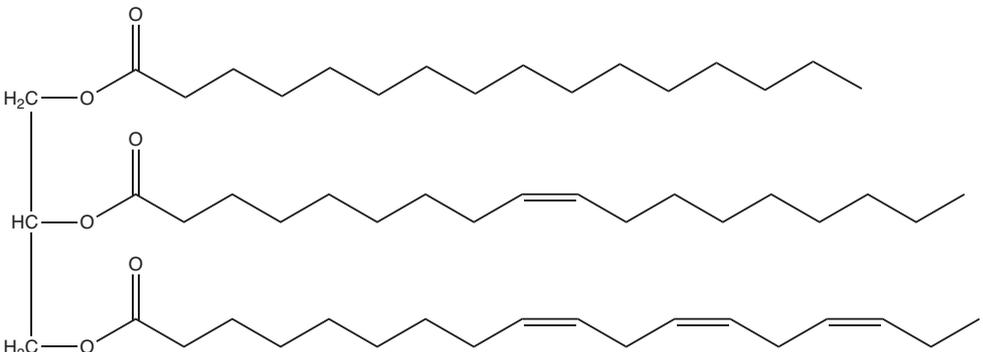
Question	Part	Author's response	Marks		
12		Ketogenic diets have been used in children with severe epilepsy since the 1990s.	1 1 1		
		A fatty acid, decanoic acid, directly binds to a molecule that is found on the surface of brain cells and is known to be involved in spreading electrical impulses between different neurons.			
		Through research at the University of London scientists are developing a ketogenic diet high in decanoic fatty acid following a wide range of evidence from many sources and across disciplines.			
		The development of new dietary regimes is revealing new evidence that may modify previous general ketogenic diets.			
13	(a)	(i) Secondary	(ii) Primary and Secondary	(iii) Primary	1 1 1
		(iv) Tertiary	(v) Secondary	(vi) Secondary	
		(i) 	(ii) 	(iii) 	2 2 2
	(b)	(iv) 	(v) 	(vi) 	
	(a)	(i) 	2		
		(ii) 	2		

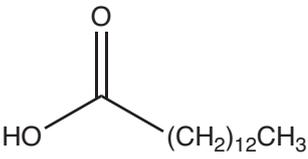
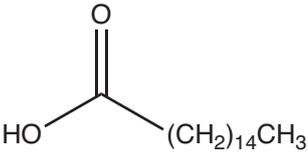
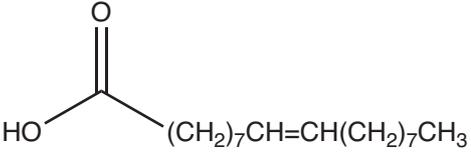
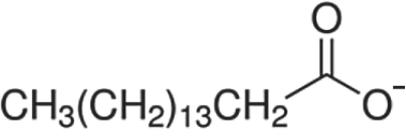
Question	Part	Author's response	Marks			
	(a)	(i) Ester: ethyl ethanoate Alcohol: ethanol Carboxylic acid: ethanoic acid	(ii) Ester: methyl butanoate Alcohol: methanol Carboxylic acid: butanoic acid	3 3 3		
		(iii) Ester: propyl methanoate Alcohol: propanol Carboxylic acid: methanoic acid	(iv) Ester: ethyl propanoate Alcohol: ethanol Carboxylic acid: propanoic acid	3 3		
		(v) Ester: methyl propanoate Alcohol: methanol Carboxylic acid: propanoic acid	(vi) Ester: ethyl 4-methylpentanoate Alcohol: ethanol Carboxylic acid: 4-methylpentanoic acid	3 3		
		15	(b)	(i) methyl hexanoate 	(ii) 2-methylpropyl propanoate 	2 2
				(iii) butyl butanoate 	(iv) propyl octanoate 	2 2
				(i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons$ 		2
				(ii)  +  \rightleftharpoons 		2
		(c)	(iii) $\text{CH}_3\text{CH}_2\text{OH} +$  \rightleftharpoons 		2	
			(iv)  +  \rightleftharpoons 		2	

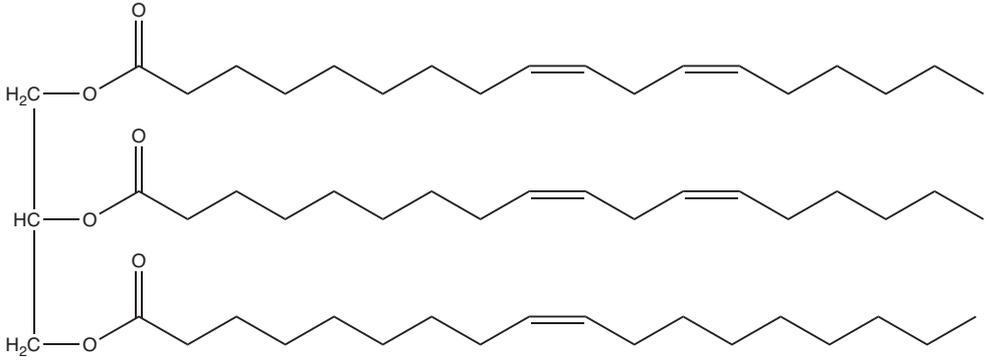
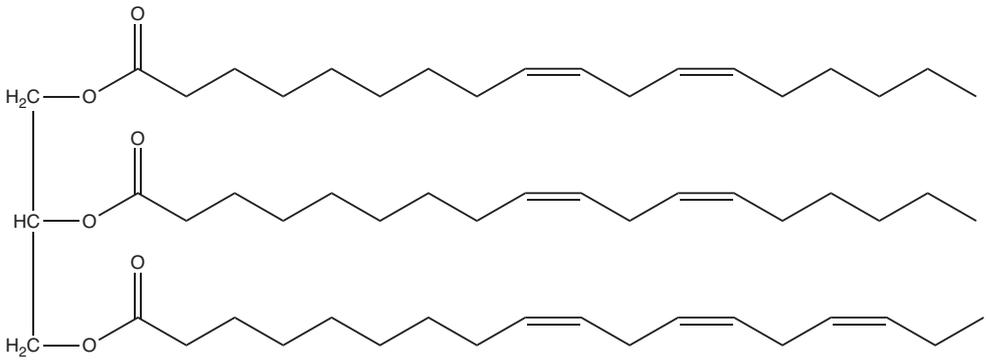
Question	Part	Author's response	Marks
16	(a)		4
	(b)		4
17	(a)	HO-CH ₂ -CH ₂ -OH and 	2 2
	(b)	 and HO-CH ₂ -CH ₂ -OH	2 2
	(c)	(i)  (ii)  and 	1 2 2
18	(a)	Octanoic acid	2
	(i)		2
	(ii)	ethyl octanoate	2
	(iii)	Acts as a catalyst, providing an alternate reaction pathway of lower activation energy, increasing the rate of reaction.	1
	(iv)	Reflux allows the reaction to take place at the highest temperatures with minimal loss of reactants.	1
	(b)	Increases kinetic energy of particles, allowing more particles to possess the necessary activation energy. This leads to a greater number of successful collisions per unit time, thus increases rate of reaction.	1 1
	(v) Esterification is an example of an equilibrium reaction. Adding excess ethanol increases the concentration of reactants. This stresses the reaction system, and in accordance to Le Chatelier's principle the system will adjust to oppose the change. This favours the forward reaction, increasing the yield of the ester produced.	1 1 1	

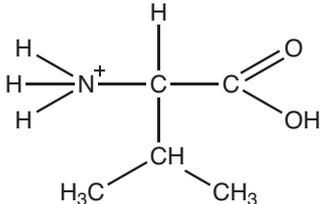
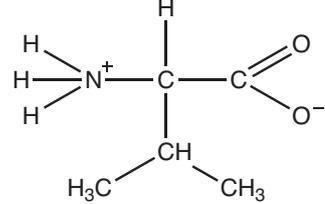
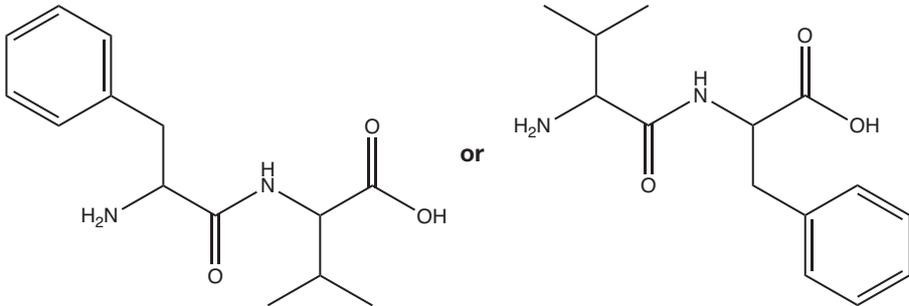
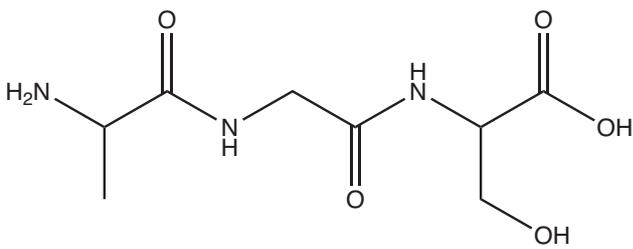
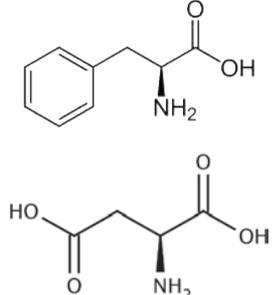
Question	Part	Author's response	Marks				
	(a)		2 2				
	(b)	<p>(i)</p>  <p>(ii) 4-methylhexanoic acid and ethanol</p>	2 2 2				
19	(c)	<p>(i)</p> <table border="1" data-bbox="365 895 1356 1168"> <tr> <td>  </td> <td>  </td> </tr> <tr> <td>Carboxylate salt</td> <td>Alcohol</td> </tr> </table> <p>(ii) In its ionic form the carboxylate anion contains a full negative charge. The negative charge on the oxygen atom is able to form strong ion-dipole bonds with water. This allows water molecules to successfully surround and separate the carboxylate salt facilitating its solubility. The original ester can only form weaker dipole-dipole associations with water which are not significant enough to allow it to be soluble.</p>			Carboxylate salt	Alcohol	2 2 1 1 1
							
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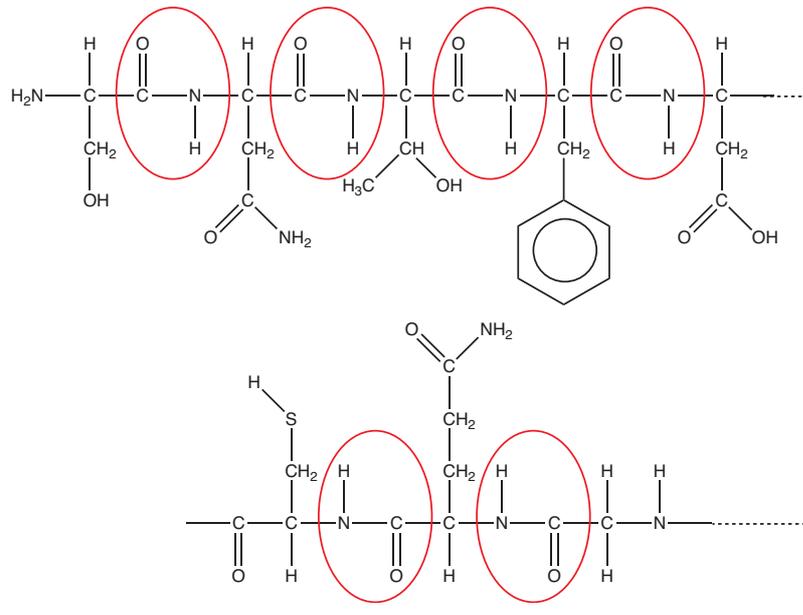
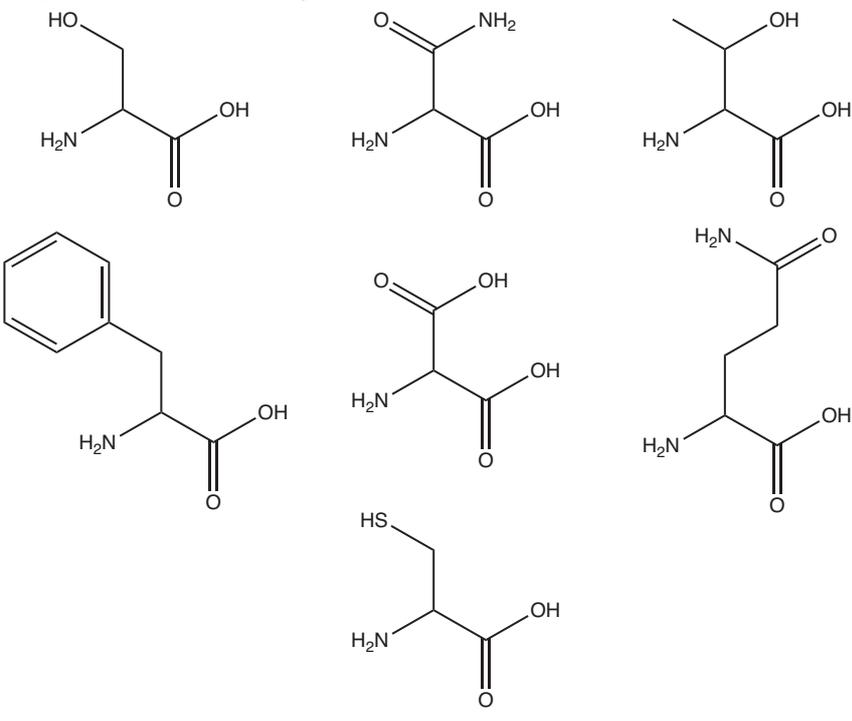
Question	Part	Author's response	Marks
20	(a)	(i) Butan-1-amine and propanoic acid 	2
		(ii) Pentanoic acid and propan-2-amine 	2
		(iii) 	2
		(iv) 	2
	(b)	(i) 	2
		(ii) 	2
		(iii) 	2
		(iv) 	2
21	(a)	Tertiary	1
	(b)	Secondary	1
	(c)	Tertiary	1
	(d)	Secondary	1
	(e)	Primary	1
22	Niacinamide contains a polar amide group.		1
	The N-H group is capable of forming strong hydrogen bonds with adjacent polar water molecules, and the carbonyl group will form dipole-dipole interactions with water molecules.		1
	These interactions allow water molecules to surround and separate niacinamide providing its water soluble and skin absorbing properties.		1

Question	Part	Author's response	Marks
	(a)		2 2
	(b)		2 2
23	(c)	i)  ii) 	2 2
	(a)		2 2
24	(b)		2 2
	(c)		2 2
25			2
26			2

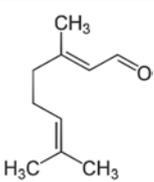
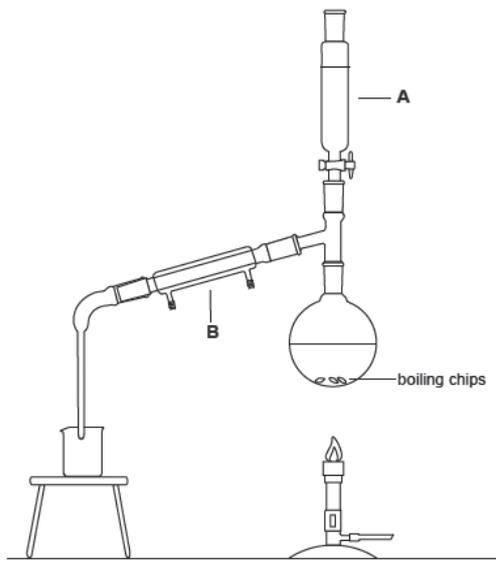
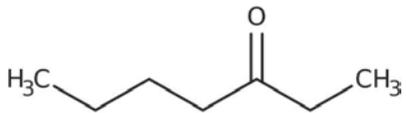
Question	Part	Author's response	Marks	
27	(a)		2	
			2	
			2	
	(b)		2	
28		$n_{(\text{iodine})} = \frac{m}{M}$ $n = \frac{85}{253.81}$ $n = 0.33 \text{ mol}$ $n_{(\text{ricinoleic acid})} = \frac{100}{298.46}$ $n = 0.34 \text{ mol}$ <p>If 0.33 mol of iodine reacts with 0.34 of ricinoleic acid, and x mol of iodine reacts with 1 mol of ricinoleic acid then:</p> $\frac{x}{1} = \frac{0.33}{0.34}$ $x = \frac{0.33}{0.34} \times 1$ $x = 1 \text{ mol}$ <p>1 mole of iodine are needed for every 1 mole of ricinoleic acid. Therefore, ricinoleic acid has 1 carbon-carbon double bond.</p>	1	
			1	
				1

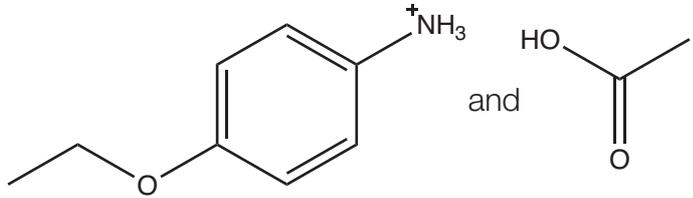
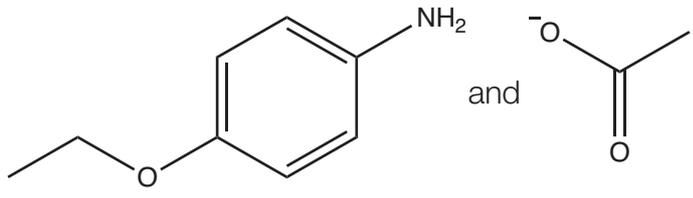
Question	Part	Author's response	Marks
29	(a)	(i) Oleic acid: $C_{18}H_{34}O_2$ (ii) Linoleic acid: $C_{18}H_{32}O_2$	1 1
	(b)		2
	(c)		2
	(d)	Hydrogen, H_2	1
	(e)	High temperature	1
		High pressure	1
		Nickel catalyst	1
	(f)	Flaxseed oil is a unsaturated triglyceride which is a liquid at room temperature, whereas margarine is a saturated triglyceride which is a solid at room temperature.	
	(g)	The melting points of edible fats and oils are dependent on the strengths of the intermolecular forces between triglyceride molecules.	1
		Edible saturated triglycerides such as margarine are solid at room temperature due to the greater proportion of triglyceride molecules with saturated carbon chains.	1
Shorter distance separates triglycerides with saturated carbon chains which increases the strength of the dispersion forces between molecules.		1	
The lower melting point of the oils that make up margarine, are attributed to the greater proportion of triglyceride molecules with unsaturated carbon chains.		1	
30	Each double bond introduces a "kink" to the chain increasing the distance between hydrocarbon chain decreasing the strength of attractive forces between them.	1	
	Scientific knowledge, understanding, and inquiry is enabling scientists to develop a possible solution for disorders of the central nervous system.	1	
	Scientists application of core-shell nanoscopic carriers for the treatment of such disorders may have advantageous applications due to their size, ease of preparation, ease of sterilization and the possibility of surface modification.	1	

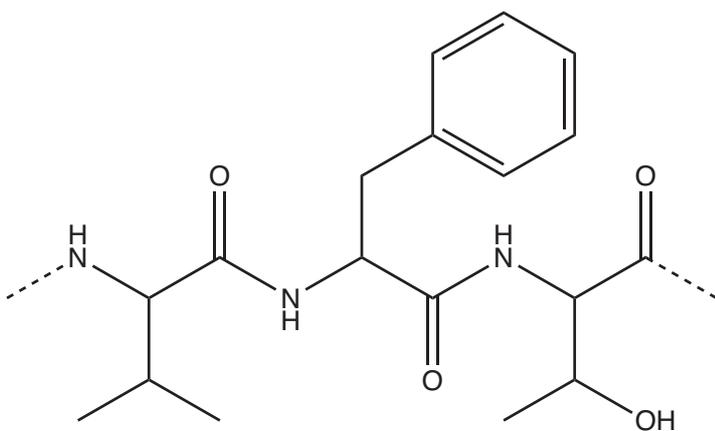
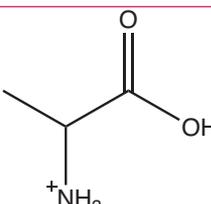
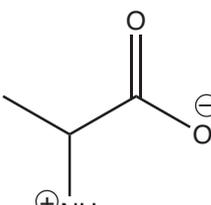
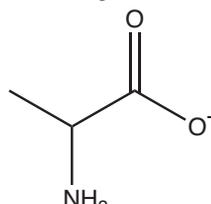
Question	Part	Author's response	Marks
31	(a)	carboxyl	1
	(b)	amino	1
	(c)	(i) 	2
	(c)	(ii) 	2
	(d)	Both molecules contain a polar amine and carboxyl group, capable of forming hydrogen bonds (N-H and O-H) and dipole-dipole bonds (C=O) with adjacent water molecules. Asparagine contains an amide on its side chain, in comparison to leucine which has only a hydrocarbon side chain. This additional polar functional group allows asparagine to form hydrogen bonds (N-H) and dipole-dipole bonds (C=O) with adjacent water molecules. This significant secondary bonding with water facilitates the molecule's solubility, in comparison to leucine.	1 1 1 1
32	(a)		2
	(b)	 Note: the amino acids are shown connected in the order alanine-glycine-serine, but any order is acceptable.	2
	(c)		2 2

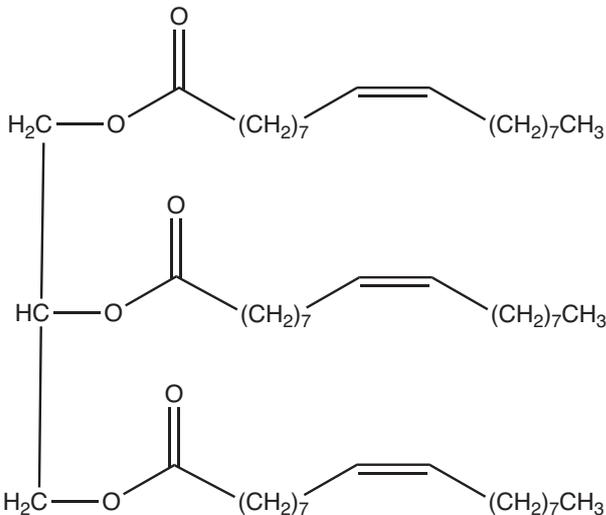
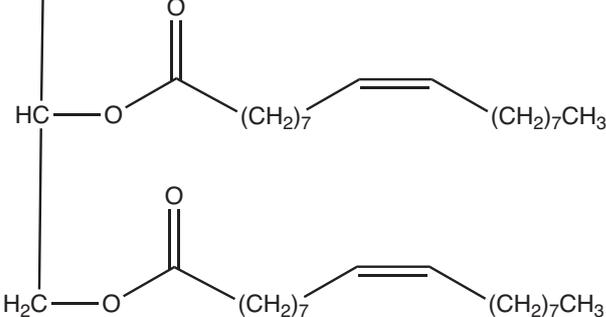
Question	Part	Author's response	Marks
	(a)	<p>Any one of:</p> 	1
33	(b)	<p>Any one of the following:</p> 	

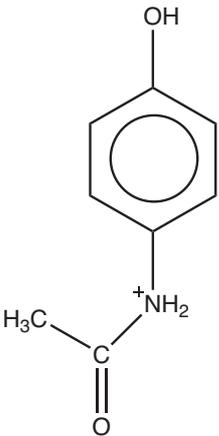
Summary test 3 solutions: Organic and biological chemistry

Question	Part	Author's response	Marks										
	(a)	$C_{10}H_{18}O$	2										
	(b)		2										
		i) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ ii) 1) Primary 2) Secondary iii)	2 1 1										
		<table border="1"> <thead> <tr> <th>Compound</th> <th>Organic product</th> </tr> </thead> <tbody> <tr> <td>$CH_3CH_2CH(OH)CH_3$</td> <td>$CH_3CH_2COCH_3$</td> </tr> <tr> <td>$CH_3CH_2COCH_3$</td> <td>NR</td> </tr> <tr> <td>$CH_3CH_2CH_2OH$</td> <td>CH_3CH_2CHO</td> </tr> <tr> <td>$CH_3CH_2CH_2CHO$</td> <td>$CH_3CH_2CH_2COOH$</td> </tr> </tbody> </table>	Compound	Organic product	$CH_3CH_2CH(OH)CH_3$	$CH_3CH_2COCH_3$	$CH_3CH_2COCH_3$	NR	$CH_3CH_2CH_2OH$	CH_3CH_2CHO	$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2COOH$	1 1 1 1
Compound	Organic product												
$CH_3CH_2CH(OH)CH_3$	$CH_3CH_2COCH_3$												
$CH_3CH_2COCH_3$	NR												
$CH_3CH_2CH_2OH$	CH_3CH_2CHO												
$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2COOH$												
	(iv)	A is an addition funnel or dropper funnel and B is a Liebig Condenser	1+1										
1	(c)	(v) 	1										
		(vi) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	2										
		(vii) Carboxyl	1										
	(d)	(i) 3-methylhexanal (ii) heptan-3-one 	2 2										

Question	Part	Author's response	Marks
2	(a)	Any two of: Carboxyl Ester Aromatic ring	1+1
	(b)	Compound A contains a carboxyl group.	1
		Addition of sodium carbonate to separate samples of A and B would induce an acid/carbonate reaction in the test tube containing compound A.	1
		Carbon dioxide would be observed in the form of effervescence indicating this reaction.	1
	(c)	Compound B contains a polar amide group.	1
The N-H group is capable of forming strong hydrogen bonds with adjacent polar water molecules, and the carbonyl group will form dipole-dipole interactions with water molecules. These interactions allow water molecules to surround and partially separate Compound B resulting in its partial solubility.		1 1	
(d)		2 2	
	(e)		2 2
3	(a)	$C_6H_{12}O_4$	2
	(b)	Example of a polyhydroxyaldehyde.	1
	(c)	(i) two compounds with the same molecular formula, but differing structural formulae.	1
		(ii) secondary	1
		(iii) Compound A contains an aldehyde (terminal carbonyl group). Compound B, does not.	1
Tollen's test will result in the formation of a silver mirror on the inside of the reaction vessel containing Compound A. This is due to the oxidation of the carbonyl group.		1 1	

Question	Part	Author's response	Marks
	(a)	Amino and carboxyl	2
	(b)	Threonine	1
	(c)	 <p>Note: The amino acids are shown connected in the order valine, phenylalanine, threonine, but any order is acceptable.</p>	2
4	(d)	<p>(i) </p> <p>(ii) </p> <p>(iii) </p>	2
	(e)	<p>(i) 1. hydrogen 2. hydrogen 3. dispersion 4. covalent</p> <p>(ii) Ionic and secondary bonding types are disrupted by changes to pH. An increase in pH (basic conditions) will change -NH_2 to -NH_3^+. Any change to functional groups will disrupt specific 3D shape. Shape determines function therefore the functionality of the protein will likely be impaired.</p>	1 1 1 1 1 1 1 1

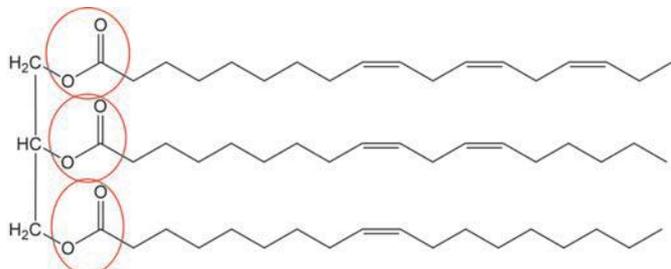
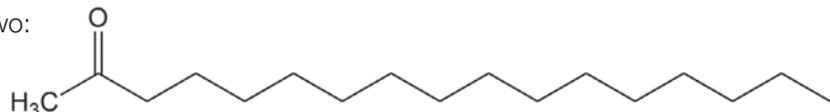
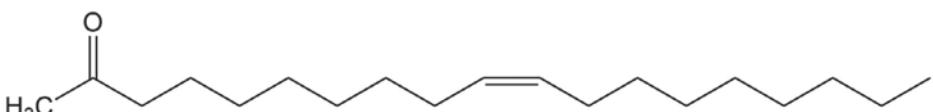
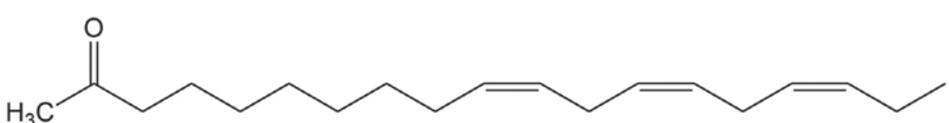
Question	Part	Author's response	Marks
	(a)	Propane-1,2,3-triol	2
	(i)		2
5	(b)		
	(ii)	Water	1
	(iii)	Plant	1
	(iv)	A: hydrogen, B: high pressure/temp, C: Nickel catalyst	3
	(i)	$n = \frac{m}{M}$ $n = \frac{0.1}{876.16}$ $n = 1.14 \times 10^{-4} \text{ mol}$	1
	(ii)	molar ratio of 1:5 (given the presence of 5 double bonds)	1
	(c)	$n = 1.14 \times 10^{-4} \text{ mol} \times 5$ $n = 5.71 \times 10^{-4} \text{ mol}$	1
	(iii)	$v = \frac{n}{c}$ $v = \frac{5.71 \times 10^{-4}}{0.01}$ $v = 0.0571 \text{ L}$ $v = 57.1 \text{ mL}$	1

Question	Part	Author's response	Marks
6	(a)	Hydroxyl, aromatic ring and amide.	1
	(b)	<p>(i)</p>  <p>(ii) The protonated form of acetaminophen contains a full positive charge. This results in the molecule being converted to its ionic form. The full positive charge on the nitrogen atom is able to form strong ion-dipole bonds with water. This allows water molecules to successfully surround and separate acetaminophen facilitating its solubility.</p>	2
	(c)	The evidence presented in the article regarding the non-treatment of fever to help fight the COVID-19 demonstrates collaboration between scientists from around the world. Daniel Davis from the University of Manchester and Mark Peters from the UCL Great Ormond Street Institute of Child Health in London both support that "by increasing your body temperature, you may be slowing down the ability of a virus to multiply".	1+1
	(c)	In addition to looking at treating COVID-19 without fever-reducing medicine, current medications are also being investigated regarding their efficacy and safety. UK's National Institute for Health and Care Excellence review of the evidence related to Ibuprofen's use in the treatment of COVID-19 is an example of communication and collaboration. The review and verification of results is important for science as a global enterprise.	1+1

Topic 4 solutions: Managing resources

Question	Part	Author's response	Marks
1	(a) (i)	$6\text{CO}_{2(g)} + 6\text{H}_2\text{O}_{(l)} \xrightarrow{\text{energy}} \text{C}_6\text{H}_{12}\text{O}_{6(s)} + 6\text{O}_{2(g)}$	2
	(ii)	Endothermic	1
		Photosynthesis requires the absorption of energy from sunlight.	1
	(b) (i)	Any one: Glucose is used during respiration.	1
		Glucose is used to form lipids (oils). Glucose, a monosaccharide, is being converted into more complex carbohydrates as biomass.	1
	(ii) (1)	Longer growth periods generate more lipids (oil) in the biomass, the raw material to produce biodiesel.	1
	(2)	Longer growth periods allow for greater opportunities for algae to remove carbon dioxide through photosynthesis.	1
		Carbon dioxide converted during growth offsets carbon dioxide produced during the combustion of biodiesel.	
		Carbon dioxide is a greenhouse gas which contributes to global warming.	1
	(c)	Any 6 of (at least one advantage and disadvantage for each fuel): Biodiesel – Advantages Sources for the raw materials to produce biodiesel are plentiful and can easily be grown. Renewable fuel source. Less net emission of carbon dioxide. Biodiesel – Disadvantages Competition for cropping land. Limited production and distribution infrastructure. Diesel – Advantages Well-established fuel including extraction, processing and infrastructure. Diesel – Disadvantages Non-renewable fuel source. Release of sulfur pollutants during combustion.	1 1 1 1 1 1 1 1



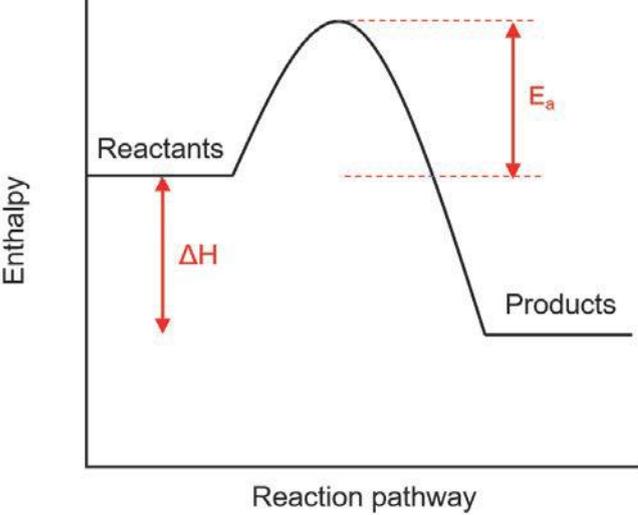
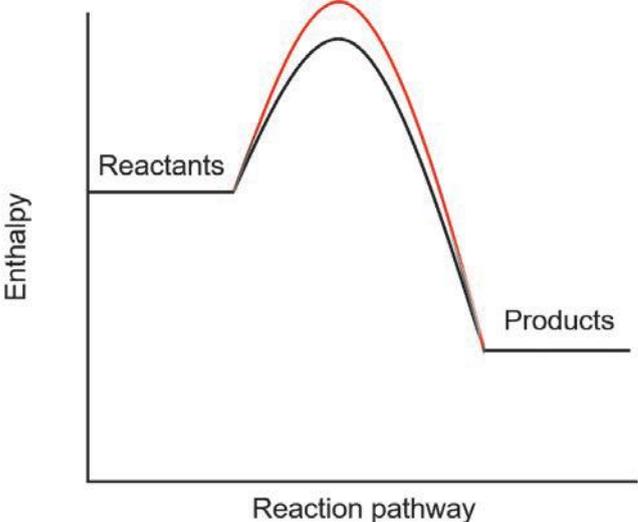
Question	Part	Author's Response	Marks
2	(a) (i)	Any two: Triglyceride (oil)	1
		Methanol Water Acid Sodium hydroxide.	1
	(ii)	Generation of atmospheric pollutants, oxides of nitrogen and sulfur, (which can lead to photochemical smog and acid rain) as well as carbon dioxide, (which can lead to global warming).	1
	(iii)	Rate of reaction is increased.	1
		A catalyst provides an alternative energy pathway with a lower activation energy.	1
		A greater proportion of reactant collisions are successful in reaching or exceeding the activation energy, resulting in more productive collisions per unit time.	1
	(b) (i)	propan(e)-1,2,3-triol	2
	(ii)	Glycerol contains three polar hydroxyl functional groups.	1
		This provides multiple opportunities for polar water molecules to form hydrogen bonds with glycerol.	1
		The glycerol molecule is relatively small and can be surrounded by water molecules during hydrogen bonding.	1
(iii)	Methanol has fewer opportunities for hydrogen bonding between molecules and has a smaller molecular mass, resulting in weaker dispersion forces.	1	
	Less energy is required to overcome these interactions, therefore resulting in a lower boiling point.	1	
(c) (i)		1	
(ii)	Coconut oil has a higher melting point.	1	
	The triglyceride shown in coconut oil is saturated, while the triglyceride shown in soybean oil is unsaturated (contains C=C).	1	
	This results in a more regular structure for molecules in coconut oil. Molecules can pack more closely in coconut oil compared to the irregular structure of molecules in soybean oil.	1	
	Stronger dispersion forces are experienced with closer interactions, requiring more energy to overcome.	1	
(iii)	Any two:	2	
		2	
		2	
			2

Question	Part	Author's Response	Marks
2	(iv)	Any one: Renewable source of triglyceride. Easily farmed in short growth periods.	1
	(v)	Any one: Cost and difficulty of processing. Access to technology.	1
3	(a) (i)	Hexadecane is a relatively large non-polar molecule.	1
		Dispersion forces are experienced between non-polar molecules.	1
		At room temperature (25°C), there is sufficient energy to overcome the forces holding the molecules in fixed positions in a solid, allowing them to flow as a liquid.	1
	(ii)	$C_{17}H_{34}O_2$	2
	(iii)	$C_{16}H_{34(l)} + 49/2 O_{2(g)} \rightarrow 16CO_{2(g)} + 17H_2O_{(l)} \quad \Delta H = -10701 \text{ kJ mol}^{-1}$	4
	(iv)	More	1
		Unlike methyl hexadecanoate, hexadecane does not contain an ester group with oxygen atoms present in the molecule. More molecules of oxygen are required to achieve the stoichiometric ratio.	1
	(v)	Concentration of oxygen in the air is relatively fixed.	1
		It is more difficult to achieve the stoichiometric ratio required for complete combustion with fuels containing a higher number of carbon atoms in the molecule.	1
	(b)	Carbon monoxide displaces oxygen from the blood, as haemoglobin forms carboxyhaemoglobin.	1
Carbon monoxide is delivered to the cells in the human body instead of oxygen.		1	
In low concentrations, carbon monoxide exposure leads to dizziness and fatigue. In high concentrations, exposure can lead to loss of consciousness and death.		1	
(c) (i)	Particle size of soot is large enough to be trapped in a particulate filter.	1	
(ii)	Climate change		
	Soot released locally in the atmosphere leads to greater absorption of solar radiation.	1	
	Black carbon in soot absorbs all wavelengths, resulting in warming in the lower atmosphere.	1	
	Soot landing on reflective bodies such as areas of ice and snow reduces reflectivity (albedo).	1	
	This results in less solar radiation being reflected from the Earth's surface, increasing warming.	1	
	Human health		
	As a fine particulate pollutant, soot enters the lungs and lodges in the alveoli. This leads to reduced respiratory function and increases the risk of respiratory and coronary disease.	1	
Compounds on the surface of carbon structures (polycyclic aromatic hydrocarbons) enter the bloodstream. PAH's are known carcinogens.	1		

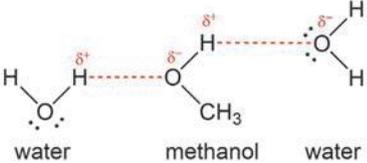
Question	Part	Author's Response	Marks	
4	(a) (i)	$m(\text{C}_{\text{complete combustion}}) = 5.00 \times 10^6 \text{ g}$ $= 5000 \text{ g}$ $n = \frac{m}{M}$ $n(\text{C}_{\text{complete}}) = \frac{5.00 \times 10^6}{12.01}$ $= 4.16 \times 10^5 \text{ mol}$ $Q = n \times \Delta H$ $Q(\text{C}_{\text{complete}}) = 4.16 \times 10^5 \times 393$ $= Q(\text{C}_{\text{complete}}) = 164 \text{ GJ kJ}$	2	
	(ii)	$m(\text{C}_{\text{complete combustion}}) = 5.00 \times 10^6 \times 0.8 (80\%) = 4.00 \times 10^6$ $m(\text{C}_{\text{incomplete combustion}}) = 5.00 \times 10^6 \times 0.2 (20\%) = 1.00 \times 10^6 \text{ g}$ $n = \frac{m}{M}$ $n(\text{C}_{\text{complete}}) = \frac{4.00 \times 10^6}{12.01}$ $= 3.33 \times 10^5 \text{ mol}$ $n(\text{C}_{\text{incomplete}}) = \frac{1.00 \times 10^6}{12.01}$ $= 8.33 \times 10^5 \text{ mol}$ $Q = n \times \Delta H$ $Q(\text{C}_{\text{incomplete}}) = 3.33 \times 10^5 \times 393$ $= 1.31 \times 10^8 \text{ kJ}$ $Q(\text{C}_{\text{complete}}) = 8.33 \times 10^5 \times \frac{232}{2}$ $= 9.66 \times 10^6 \text{ kJ}$ $Q(\text{C}_{\text{total}}) = 1.41 \times 10^8 \text{ kJ}$	2	
				1
		(b) (i)	CO (+2), CO ₂ (+4) Increase in oxidation number represents oxidation ∴ reducing agent (reducer/reductant).	2 1
(ii)		$m(\text{Fe}) = 959 \times 10^6 \times 10^6 \text{ g}$ $M(\text{Fe}) = 55.85 \text{ g mol}^{-1}$ $n(\text{Fe}) = \frac{m}{M}$ $n(\text{Fe}) = \frac{959 \times 10^6 \times 10^6}{55.85}$ $n(\text{Fe}) = 1.717 \times 10^{10} \text{ mol}$ <p>mole ratio $n(\text{Fe}) : n(\text{CO}_2) = 2 : 3$</p> $\frac{n(\text{CO}_2)}{n(\text{Fe})} = \frac{3}{2}$ $\therefore n(\text{CO}_2) = \frac{3 \times 1.717 \times 10^{10}}{2}$ $n(\text{CO}_2) = 2.576 \times 10^{13} \text{ mol}$ $M(\text{CO}_2) = 44.01 \text{ g mol}^{-1}$ $m(\text{CO}_2) = n \times M$ $m(\text{CO}_2) = 2.576 \times 10^{13} \times 44.01$ $m(\text{CO}_2) = 1.134 \times 10^{15} \text{ g}$ $m(\text{CO}_2) = 1.134 \times 10^{12} \text{ kg (3 sig. fig.)}$	2	
			2	

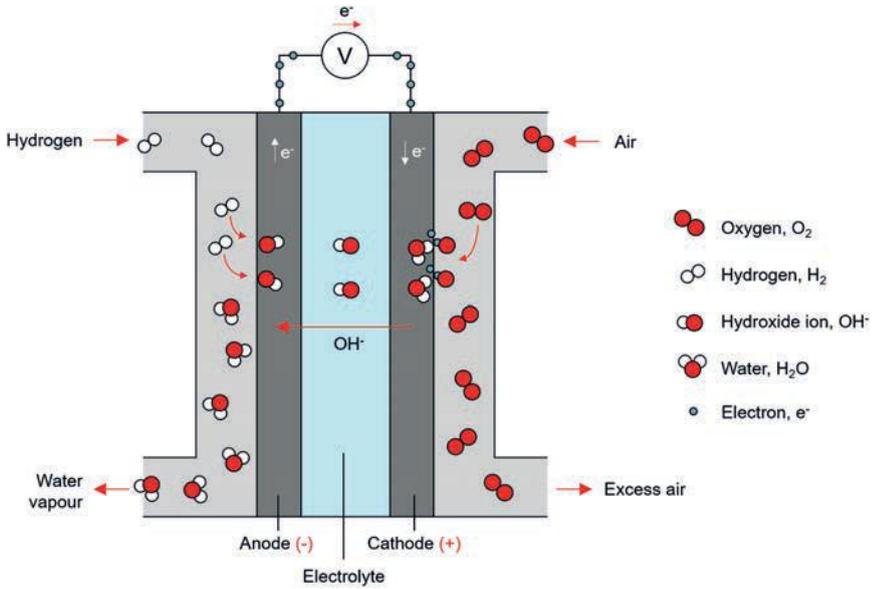
Question	Part	Author's Response	Marks
4	(c) (i)	After entering the lungs on the surface of carbon, PAHs (polycyclic aromatic hydrocarbons) can be absorbed into the bloodstream. PAHs are known carcinogens.	1 1
	(ii)	0.150 ppm = 0.150 mg in 1L = 0.150 × 8 mg = 1.20 mg	2
5	(a) (i)	$m(\text{CH}_3\text{OH}) = 5.00 \times 0.05 \text{ g}$ $M(\text{CH}_3\text{OH}) = 32.04 \text{ g mol}^{-1}$ $n(\text{CH}_3\text{OH}) = \frac{5.00 \times 0.05}{32.04} \text{ mol}$ $n(\text{CH}_3\text{OH}) = 7.803 \times 10^{-3} \text{ mol}$	2
		$m(\text{C}_2\text{H}_5\text{OH}) = 5 \times 0.95 \text{ g}$ $M(\text{C}_2\text{H}_5\text{OH}) = 46.07 \text{ g mol}^{-1}$ $n(\text{C}_2\text{H}_5\text{OH}) = \frac{5.00 \times 0.95}{46.07} \text{ mol}$ $n(\text{C}_2\text{H}_5\text{OH}) = 1.031 \times 10^{-1} \text{ mol}^{-1}$ $n_{(\text{Total})} = 7.803 \times 10^{-3} + 1.031 \times 10^{-1} \text{ mol}^{-1}$ $n_{(\text{Total})} = 0.1109 \text{ mol}$	2 1
	(ii)	$Q = n \times \Delta H$ $Q(\text{CH}_3\text{OH}) = 7.803 \times 10^{-3} \times 715.0$ $= 5.579 \text{ kJ}$ $Q(\text{C}_2\text{H}_5\text{OH}) = 1.031 \times 10^{-1} \times 1371$ $= 141.4 \text{ kJ}$ $Q_{(\text{Total})} = 146.9 \text{ kJ}$	2
		$Q = m \times c \times \Delta T \text{ (J)}$ $\Delta T = \frac{Q}{m \times c}$ $\Delta T = \frac{146.9 \times 10^3}{500 \times 4.18}$ $\Delta T = 70.30^\circ\text{C}$ $T_{\text{final}} = 21.0 + 70.3 = 91.3^\circ\text{C}$	2 2
(b)	Heat is lost to the cooking utensils and the surroundings. The combustion is incomplete.	1 1	

Question	Part	Author's Response	Marks
6	(a) (i)		2
	(ii)	$\text{C}_6\text{H}_{14(l)} + 19/2 \text{O}_{2(g)} \rightarrow 6\text{CO}_{2(g)} + 7\text{H}_2\text{O}_{(l)} \quad \Delta H = -4163 \text{ kJ mol}^{-1}$	4
	(1)	$\begin{aligned} \Delta m &= m_{\text{initial}} - m_{\text{final}} \\ &= 136.20 - 135.76 \\ &= 0.440 \text{ g} \end{aligned}$	1
		$\begin{aligned} M(\text{C}_8\text{H}_{18}) &= (8 \times 12.01) + (18 \times 1.008) \\ M(\text{C}_8\text{H}_{18}) &= 114.23 \text{ g mol}^{-1} \\ n &= \frac{m}{M} \\ &= \frac{0.44}{114.23} = 3.85 \times 10^{-3} \text{ mol} \end{aligned}$	2
	(b) (i)	$\begin{aligned} \Delta m &= m_{\text{initial}} - m_{\text{final}} \\ &= 134.70 - 134.27 \\ &= 0.430 \text{ g} \end{aligned}$	1
		$\begin{aligned} M(\text{C}_7\text{H}_{16}) &= (7 \times 12.01) + (16 \times 1.008) \\ M(\text{C}_7\text{H}_{16}) &= 100.21 \text{ g mol}^{-1} \\ n &= \frac{m}{M} \\ &= \frac{0.43}{100.21} = 4.29 \times 10^{-3} \text{ mol} \end{aligned}$	2
(2)	$\Delta H(\text{C}_8\text{H}_{18}) = \frac{m \times c \times \Delta T}{1000 \times n} \text{ (kJ mol}^{-1}\text{)}$	2	
	$\begin{aligned} \Delta H(\text{C}_8\text{H}_{18}) &= \frac{100 \times 4.18 \times 20}{1000 \times 3.852 \times 10^{-3}} \\ &= -2170 \text{ kJ mol}^{-1} \end{aligned}$	1	
	$\Delta H(\text{C}_7\text{H}_{16}) = \frac{m \times c \times \Delta T}{1000 \times n} \text{ (kJ mol}^{-1}\text{)}$	2	
	$\begin{aligned} \Delta H(\text{C}_7\text{H}_{16}) &= \frac{100 \times 4.18 \times 20}{1000 \times 4.291 \times 10^{-3}} \\ &= -1950 \text{ kJ mol}^{-1} \end{aligned}$	1	
(ii)	<p>Combustion occurs in pure oxygen.</p> <p>This leads to complete combustion of the fuels compared to incomplete combustion in air with a component of oxygen.</p>	2	
	<p>The bomb calorimeter is extremely well insulated.</p> <p>Very little thermal energy can escape; the majority enters the water surrounding the bomb and is measured as the temperature rises.</p>	2	
6	(c) (i)	Exothermic	1

Question	Part	Author's Response	Marks
	(ii)		2
	(iii)		1



Question	Part	Author's Response	Marks
7	(a) (i)	$\text{CH}_3\text{OH}_{(l)} + \frac{3}{2} \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \quad \Delta H = -715 \text{ kJ mol}^{-1}$	4
	(ii)	$\frac{\text{kJ}}{\text{mol}} \div \text{M} \frac{\text{kJ}}{\text{g}} \times \rho \frac{\text{kJ}}{\text{L}}$	2
		$= \frac{715}{32.04} = 22.32 \text{ kJ g}^{-1}$ $= \frac{715}{32.04} \times 792 = 17670 \text{ kJ L}^{-1}$	2
	(iii)	 <p>water methanol water</p>	1
		Methanol is a relatively small molecule containing a polar hydroxyl functional group.	1
		Polar water molecules have the ability to hydrogen bond to the hydroxyl group and surround the molecule.	1
	(b) (i)	$\frac{\text{kJ}}{\text{L}} \div \rho \frac{\text{kJ}}{\text{g}} \times \text{M} \frac{\text{kJ}}{\text{mol}}$ $= \frac{23\,475}{789} = 29.75 \text{ kJ g}^{-1}$ $= \frac{23\,475}{789} \times 46.07 = -1371 \text{ kJ mol}^{-1}$	2 2
(ii)	Per litre, ethanol and ethanol blends produce less energy when compared to petrol. This would mean a greater volume of fuel would have to be stored during transport or the vehicle would have to refuel more frequently.	1 1	
(iii)	Bioethanol blends contain ethanol derived from renewable sources such as plants. During their growth, the plants used for bioethanol production absorb and offset a proportion of the carbon dioxide produced by their combustion, contributing less to global warming.	1 1	

Question	Part	Author's Response	Marks
	(a) (i)	Chemical energy to electrical energy	2
	(ii)		2
8	(b) (i)	Oxidation Oxidation is represented by a loss of electrons or an increase in oxidation number (hydrogen increases from 0 to +1).	1
	(ii)	Anode	1
	(iii)	The water produced can be used by astronauts.	1
	(c)	Any four: (must include comparison) Components in the cell do not need to be regenerated if high-quality fuels are used. The cell can operate almost indefinitely, thus offering reliability. Many galvanic cells are single use. Waste products are removed from the cell during operation. Waste products sometimes form in the galvanic cell, thus reducing efficiency. Cell power output is consistent and does not decrease over the duration of use. Cell power is, in most traditional galvanic cells as reactants are depleted.	4
	(d) (i)	$\text{CO}_{2(g)} + 2\text{KOH}_{(aq)} \rightarrow \text{K}_2\text{CO}_{3(aq)} + \text{H}_2\text{O}_{(l)}$	2
	(ii)	The carbon dioxide produced is an acidic oxide.	1
		Acidic carbon dioxide undergoes a reaction with alkaline potassium hydroxide in the fuel cells and could effectively remove the excess carbon dioxide generated.	1
	(e) (i)	Galvanic cell	1
	(ii) Anode	1	
	(iii)	$\text{CO}_{(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{CO}_{2(g)} + 2\text{H}^+_{(aq)} + 2\text{e}^-$	2

Question	Part	Author's Response	Marks	
9	(a)	<p>Photovoltaic cells harness energy from the Sun. This energy is renewable.</p> <p>Power stations harness heat energy from the combustion of coal as a fossil fuel. Fossil fuels are non-renewable</p> <p>Photovoltaic cells do not produce pollutants during operation.</p> <p>Burning coal in power stations releases vast quantities of carbon dioxide and oxides of nitrogen and sulfur to the atmosphere as pollutants, leading to global warming, photochemical smog, and acid rain.</p>	4	
	(b) (i)		1	
	(ii)	$\text{Zn}_{(s)} \rightarrow \text{Zn}_{(aq)}^{2+} + 2e^{-}$	2	
	(iii)	Zinc is deposited as a solid electrode, rather than the cell containing only ions in solution.	1	
	(iv)	<p>Any four:</p> <p>The flow cell can remain depleted for extended periods of time. Residents can leave it depleted while away and recharge on returning to the premises.</p> <p>The flow cell provides a consistent power output. The cell can be used for extended periods without a decrease in performance.</p> <p>Virtually unlimited capacity as electrolytes are stored externally. They can be sized to suit the household requirements.</p> <p>The cells are rechargeable meaning that electrolytes can be used indefinitely. They are quickly charged through the addition of electrolyte.</p> <p>Components of the cell can be laid out in varying configurations, which can include burying the electrolyte tanks underground. This may suit the layout of the dwelling or industry.</p>	4	
	(v)	(1)	Electrical energy to chemical energy	2
		(2)	$2\text{Br}_{(aq)}^{-} + 2e^{-} \rightarrow \text{Br}_{2(g)}$	2
		(3)	Bromine could be released from the cell which is potentially toxic.	1

Question	Part	Author's Response	Marks	
10	(a) (i)	C=C, carbon–carbon double bond.	1	
	(ii)	Cationic	1	
	(iii)	(1)	$\text{Al}_2(\text{SO}_4)_3(\text{s}) \xrightarrow{\text{H}_2\text{O(l)}} 2\text{Al}^{3+}_{(\text{aq})} + 3\text{SO}_4^{2-}_{(\text{aq})}$	2
		(2)	Aluminium has a higher charge density (3+) compared to the surface of polyDADMAC (1+).	1
		(3)	It is a large molecule effective at physically trapping particles.	1
	(iv)		The positively charged surface of polyDADMAC effectively neutralises the negatively charged surface of clays.	1
			This destabilises the clay suspension leading to coagulation as micro-floc forms.	1
			Micro-floc aggregate, assisted by the polymer, entrapping the clay particles. The larger floc that form settle out from suspension.	1
	(b) (i)	Residual magnesium concentration is at a maximum when pH is low (pH = 4.5) and high (pH = 9). Residual magnesium concentration is at a minimum at a pH of 6.	2	
	(ii)		Value obtained from graph at pH 6, 0.01 mg L ⁻¹ = 0.01 mg in 1 L = 0.01 mg in 1000 mL = $\frac{0.01}{1000} \times 300$ mg in 300 mL = 3×10^{-3} mg = 3×10^{-6} g	1 2
(iii)		1.5 mg in 1 L = 3.0 mg in 2 L = 3.0 mg in 60 kg = $\frac{3.0}{60}$ mg in 1kg = 0.050 ppm	3	
(c)		The seeds are easily obtained and processed. There is no requirement for expensive and specialised equipment and infrastructure.	2	
		The polymers come from a natural source. The natural polymers are not toxic and are biodegradable when added to water.	2	



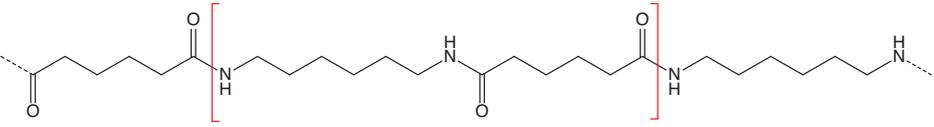
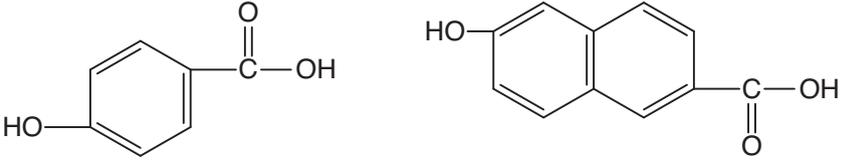
Question	Part	Author's Response	Marks	
11	(a)	Hard water	1	
	(b)	Pressure is applied on one side of a semipermeable membrane to overcome the osmotic pressure.	1	
		Water is forced to the side of the membrane with a lower concentration of dissolved salts, leaving the ions present on the other side of the membrane.	1	
	(c) (i)	The equation represents a chemical equilibrium.	1	
		Removal of carbon dioxide gas as the water is heated places a stress on the system at equilibrium.	1	
		The system responds to counteract the stress, according to Le Châtelier's principle, by shifting the position of equilibrium in the forward direction to replace carbon dioxide.	1	
		This results in the formation of calcium carbonate.	1	
	(ii)	$2\text{NH}_2\text{SO}_3\text{H}_{(aq)} + \text{CaCO}_{3(s)} \rightarrow \text{Ca}(\text{NH}_2\text{SO}_3)_{2(aq)} + \text{H}_2\text{O}_{(l)} + \text{CO}_{2(g)}$	2	
	(d) (i)	Zeolites have negatively charged surfaces.	1	
		Zeolites have exceptionally large surface area.	1	
	(ii)	(1)	An increased concentration of aqueous calcium ions places a stress on the system at equilibrium.	1
			The system responds to counteract the stress, according to Le Châtelier's principle, by shifting the position of equilibrium to favour the forward reaction.	1
		(2)	This results in the calcium ions exchanging onto the surface of the zeolite releasing aqueous sodium ions.	1
By increasing the aqueous concentration of sodium ions, through the addition of a concentrated sodium chloride solution to the zeolite.			1	
(e)	The colloidal particles are so fine that they pass through the filter and form a suspension.	1		

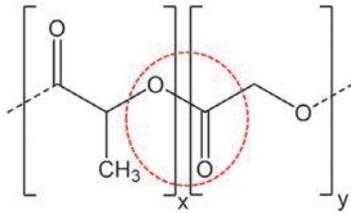
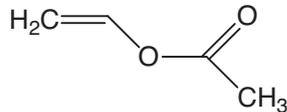
Question	Part	Author's Response	Marks	
12	(a) (i)	$\text{Cl}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HClO}_{(aq)} + \text{Cl}^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$	2	
	(ii)	(1) Oxidising agent (oxidant/oxidiser)	1	
		(2) Low pH	1	
	(iii)	Any one:		
		(1) It is not charged, and therefore can more easily enter the cell wall. It is a stronger oxidising agent.	1	
		(2) The three-dimensional protein (enzyme) structure determines the function of the protein. The three-dimensional structure of the enzyme is altered as it is degraded. The function of the protein is lost.	1 1 1	
	(b) (i)	Endothermic	1	
	(ii)		Cyanuric acid forms an equilibrium reaction with hypochlorite ions. Absorption of UV from sunlight decomposes hypochlorite ions.	1 1
		(1)	This places a stress on the system at equilibrium. According to Le Châtelier's principle, the equilibrium system counters the change. The position of equilibrium is shifted backwards, replacing hypochlorite ions.	1 1 1
		(2)	Cyanuric acid absorbs a component of UV radiation.	1
			This UV radiation is not being absorbed by hypochlorite ions, leading to their decomposition.	1
		(c) (i)	$3.0 \times 10^4 \text{ ng in 1 L}$ $= 3.0 \times 10^1 \text{ } \mu\text{g in 1 L}$ $= 30 \text{ ppb}$ $\therefore \text{Less than WHO limits.}$	1 1
(ii)	$\text{N} \equiv \text{C} - \text{Cl}$	2		
(iii)	(1)	Trigonal pyramidal	1	
	(2)	Trichloramine is a relatively small polar covalent molecule.	1	
		Secondary dipole-dipole forces are experienced between molecules. At room temperature, these secondary interactions can be overcome allowing the molecules to exist as a gas.	1 1	
(iv)	Less compounds of chlorine are available for disinfection.	1		
(d) (i)		Dissociated aluminium ions contain a positive charge (3+).	1	
		The positive charge is able to neutralise the charge on the surface of colloidal particles destabilising the suspension during coagulation.	1	
		Colloidal particles form micro-floc, which aggregate during flocculation. Larger floc settle out.	1	
(ii)	The water becomes clearer.	1		

Question	Part	Author's Response	Marks	
13	(a) (i)	Nutrients are continually being removed by plants during growth and harvesting.	1	
		Through intensive farming, these nutrients are being lost at a faster rate than they can naturally be replenished.	1	
	(ii)	The root systems of legumes contain nitrifying bacteria.	1	
		Nitrifying bacteria convert fixed nitrogen such as ammonia and ammonium ions into soluble nitrate ions available to plants.	1	
	(iii)	Plants are made of nitrogen-containing compounds such as proteins and nucleic acids.	1	
		On burial during green tilling, they decay aerobically, directly producing soluble nitrate ions in the soil. Or they decay aerobically, forming ammonia, which can then be converted to nitrates by nitrifying bacteria.	1	
			1	
	(b) (i)	(1) NH_4NO_3	2	
		(2) Nitrate and ammonium ions are soluble in soil solution.	1	
	(i)	(1) Eutrophication	1	
		(2) $6\text{CO}_{2(g)} + 6\text{H}_2\text{O}_{(l)} \xrightarrow{\text{energy}} \text{C}_6\text{H}_{12}\text{O}_{6(s)} + 6\text{O}_{2(g)}$	2	
		(3) The respiration and decomposition of algae uses more oxygen than photosynthesis produces.	1	
		(ii)	The thick mat of blue-green algae that forms during blooms covers the waterway and limits sunlight from penetrating the surface of the water.	1
			(4) Aquatic plants under the water are unable to photosynthesise to produce oxygen, and die and decay aerobically using up available oxygen. Algae also respire and decay using oxygen.	1
				Fewer aquatic species can be supported with lower concentrations of available oxygen.
		(iii)	Animal wastes and their decay products are nutrients.	1
	Their addition and decay in the waterway increases nutrient concentrations.		1	
	(c) (i)	Turbidity caused by the clay disperses sunlight, limiting its ability to reach aquatic plants.	1	
Plants are unable to photosynthesise limiting oxygen production.		1		
(ii)	(1) Negative surface charges of clays repel.	1		
	(2) Positively charged aluminium ions neutralise surface charge, destabilising clay suspensions.	1		
	(3) The quantity and associated cost of alum would be too great.	1		

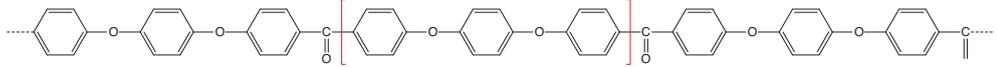
Question	Part	Author's Response	Marks
14	(a) (i)	Covalent network	1
	(ii)	s	1
	(iii)	$\%Be = \frac{M(3 \times Be)}{M(Be_3Al_2(SiO_3)_6)} \times 100$ $= \frac{27.036}{537.536} \times 100$ $= 5.030\%$	2
	(iv)	Balancing charge $\frac{2(3+) + 3(2+)}{6} = 2+ \therefore 2-$ or Oxidation numbers Si (+4) + O3(-2) = -2 $\therefore 2-$	2
	(v)	Magnetic materials would provide interference with radars and be attracted to the extremely strong magnetic fields in NMR.	1
	(b) (i)	$BaTiS_3O_9$	2
	(ii)	Benitoite is not an abundant mineral, offering a limited source of titanium.	1
	(c) (i)	Balancing charge $2(2+) + 3(3+) = 13+ \therefore 13-$ or Oxidation numbers Si 5(+4) + Al (+3) + O 18(-2) = -13 $\therefore 13-$	2
	(ii)	$\% \text{ replaced} = \frac{1}{6} = 16.67\%$	2
	(iii)	Overall charge decreases by one.	1
	(iv)	Aluminium ions are weakly bound on the surface of the silicate due to electrostatic forces, hence are easily removed.	1
		Aluminium substituted into the silicate structure is held by strong covalent bonds.	1
		It is able to maintain structural integrity at the high temperatures experienced in an exhaust system.	1

Question	Part	Author's Response	Marks	
15	(a) (i)	Soil porosity decreases from 0% to 25% clay content. From 25% to 100% clay content, soil porosity increases.	2	
	(ii)	Layers of clay in the soil are held together with cations. Clays provide soil structure, maintaining soil aeration between soil particles.	2	
	(b) (i)	$[\text{H}^+] = 10^{-\text{pH}}$ $[\text{H}^+] = 10^{-5.7}$ $[\text{H}^+] = 2.0 \times 10^{-6} \text{ mol L}^{-1}$	2	
	(ii)	$2\text{H}^+_{(\text{aq})} + \text{Ca}^{2+}_{(\text{clay})} \rightleftharpoons \text{Ca}^{2+}_{(\text{aq})} + 2\text{H}^+_{(\text{clay})}$ <p>Increasing the concentration of aqueous hydrogen ions places a stress on the system at equilibrium.</p>	1	
		<p>According to Le Châtelier's principle, the system counteracts the stress by shifting the position of equilibrium to favour the formation of products.</p>	1	
		<p>As a result, metal cations on the surface of the clay, such as calcium, are exchanged in to the soil solution while hydrogen ions are deposited on the clay surface.</p>	1	
	(iii)	<p>Cations of magnesium (Mg^{2+}) and calcium (Ca^{2+}) maintain flocculation in clays by binding the layers of clay within the soil.</p>	1	
		<p>Replacing these cations with hydrogen ions (H^+), through cation exchange, weakens the electrostatic attraction between layers of clay, resulting in their separation.</p>	1	
	(iv)	Aluminium ions released through cation exchange are toxic to plants and reduce growth.	1	
	(v)	(1)	$2\text{H}^+_{(\text{aq})} + \text{Ca}(\text{OH})_{2(\text{s})} \rightleftharpoons \text{Ca}^{2+}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})}$	2
		(2)	<p>It poses a risk to line markers and athletes.</p> <p>It can lead to the degradation of the soil in the sporting arena.</p>	1
	(c)	Water molecules can hydrogen bond to the hydroxyl groups present between layers of clay, causing the clay to swell. If the turf becomes too dry through the loss of water, the layers of clay contract and hydrogen bond to one another, leading to cracking.	2	
(d) (i)	<p>Increasing the concentration of aqueous sodium ions places a stress on the system at equilibrium.</p>	1		
	<p>According to Le Châtelier's principle the system counteracts the stress by shifting the position of equilibrium to favour the products.</p>	1		
	<p>As a result, metal cations on the surface of the clay, such as calcium, are exchanged into the soil solution, reducing their concentration on the surface of clays.</p>	1		
(ii)	<p>Replacing these cations with larger less positively charged sodium ions (Na^+), through cation exchange, weakens the electrostatic attraction between layers of clay, leading to soil dispersion.</p>	1		
	<p>Dispersion weakens aggregates in the soil, leading to structural collapse of the soil. Soil structure is lost.</p>	1		

Question	Part	Author's Response	Marks
16	(a) (i)	Proteins (polypeptides/polyamides)	1
		(1) Condensation	1
	(ii)	(2) 	1
	(1)	Secondary interactions are present between polymer chains: hydrogen bonding in nylon, and dipole–dipole interactions in Vectran®. Neither polymer has branching that is able to generate cross-links.	2
	(iii)	(2) 	4
	(iv)	Amide groups are formed as the monomers condense.	1
		These provide multiple opportunities for hydrogen bonding between the polymer chains.	1
		Hydrogen bonding is a stronger secondary interaction; to overcome this, a large amount of energy is required. This increases the strength of the fibres.	1
	(v)	(1) Addition	1
		Thermoplastic	1
		(2) The polymer chains are formed through the addition of a monomer containing one carbon–carbon double bond and no other functional groups. This does not allow the formation of cross-linking.	1
		(3) Weak dispersion forces are in operation between polymer chains. These can be overcome to allow the chains to move past one another.	1
(b)	With no cross-linking present, chains are able to slide past one another, allowing the polymer to stretch until it breaks.	1	
	Limited cross-linking in the polymer allows the chains to be shifted to the limits of the cross-links as forces are applied.	1	
	When the forces are removed, the polymer chains return to their original positions, generating an elastic material.	1	
(c) (i)	The branches can generate cross-linking between the carbon fullerenes. Increased cross-linking results in increased rigidity in the racquet.	2	
	(ii) Stiffer, more rigid racquets flex less and transfer more energy to the ball during play.	1	

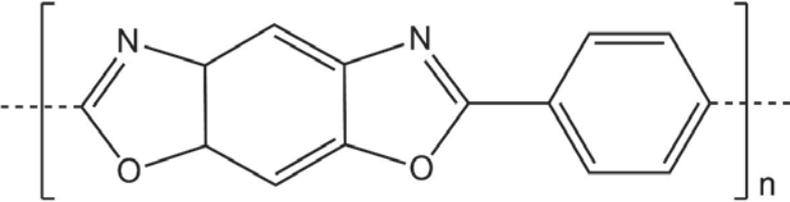
Question	Part	Author's Response	Marks
17	(a) (i)		1
	(ii)	Condensation	1
	(iii)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <chem>CC(O)C(=O)O</chem> lactic acid </div> <div style="text-align: center;"> <chem>OCC(=O)O</chem> glycolic acid </div> </div>	2 2
	(b) (i)	Hydrogen bonding	1
	(ii)	Ester groups undergo hydrolysis.	1
		This breaks down the long polymer chains into individual units that further decompose in the body.	1
		It allows for the slow release of the pharmaceutical (drug).	1
	(c)	Rate of degradation would be reduced.	1
		Fewer ester groups are present over the length of the polymer chain.	1
		There are fewer opportunities for hydrolysis to occur throughout the chain.	1
18	(a) (i)	Addition	1
	(ii)		2
	(b) (i)	Structural isomer	1
	(ii)	ethanal	2
	(c) (i)	methyl ethanoate	2
	(ii)	As the percentage of ester groups replaced is increased, the solubility in water increases.	1
		More ester groups are replaced with hydroxyl groups.	1
		Greater opportunity exists for hydrogen bonding to occur with polymer chains.	1
	(iii)	Any two (use and reason): Polymer sachets to hold dishwasher tablets:	1
		Caustic active ingredients are safe to handle and are released when the raised temperature in the dishwasher makes the polymer soluble. Dissolvable stitches: The ester groups would make the polymer degrade.	1

Question	Part	Author's Response	Marks	
19	(a)	$\%Cu = \frac{M(Cu)}{M(CuFeS_2)} \times 100$ $\%Cu = \frac{63.55}{183.52} \times 100$ $\%Cu = 34.63\%$	2	
	(b) (i)	Crushing and grinding exposes the mineral, increasing surface area.	1	
	(ii)	Froth flotation concentrates the mineral from the ore.	1	
	(iii)	(1)	Gangue (waste rock) is removed, so it does not have to be transported at a cost, and can be returned to the mine site.	2
		(2)	Fewer emissions of carbon dioxide and pollutants are released during the transportation of the concentrated ore which excludes the gangue.	1
	(c) (i)	$CuS_{(s)} + O_{2(g)} \rightarrow Cu_{(s)} + SO_{2(g)}$	2	
	(ii)	Copper is a metal of relatively low activity.	1	
		Chemical reduction with a reducing agent is sufficient to reduce copper ions to copper.	1	
	(d) (i)	Refining removes impurities from the blister copper.	1	
	(ii)	Impurities increase the resistance of electrical current in copper.	1	
	(iii)	Negative (-)	1	
	(e) (i)	$Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)}$	2	
	(ii)	Reduction of water.	1	
		Reduction is occurring in an aqueous electrolytic cell.	1	
		Once the copper is reduced, the water present in the cell is reduced in preference to calcium ions. Calcium is an active metal.	1	
	(f) (i)	(1) Oxidation	1	
(2) Any one: Limited yield. or Environmental issues associated with adding acid to the soil and water.		1		
(ii)	$Fe_{(s)} + Cu_{(aq)}^{2+} \rightarrow Fe_{(aq)}^{2+} + Cu_{(s)}$	1		
	Iron is a more active metal than copper. Iron displaces copper ions from solution.	1 1		

Question	Part	Author's Response	Marks
20	(a) (i)	Condensation	1
	(ii)	Amide	1
	(iii)	Hydrogen bonding is an electrostatic attraction between the $\delta+$ hydrogen in the N–H dipole in one polymer molecule to the $\delta-$ oxygen in the C=O dipole in another polymer molecule.	2
	(iv)	Can be recycled.	1
		Hydrogen bonding is a secondary interaction between polymer chains that can be overcome on heating the polymer.	1
		The polymer will melt and soften and can be reshaped.	1
	(b) (i)	Contains an amide functional group that can be broken.	1
	(ii)	Fewer raw materials are required. Lowers costs, as wastes are converted to raw materials.	2
		Depolymerisation forms the original monomers.	1
		This makes the formation of new polymers simpler, as there are lower costs associated with processing of raw materials.	1
(iii)	Nylon is derived from petroleum, a non-renewable feedstock.	1	
	Less energy, pollution, and environmental damage are associated with the extraction and processing petroleum by recycling the raw material.	1	
21	(a) (i)	Lead paste, air (oxygen)	2
	(ii)	Increasing the oxygen concentration increases the frequency of collisions between reactant particles.	1
		A larger number of collisions of reactant particles reach and exceed the activation energy.	1
		More productive collisions occur per unit time, thus increasing the rate of reaction.	1
	(b) (i)	Lead is a metal of relatively low activity.	1
		Chemical reduction with a reducing agent is sufficient to reduce lead ions to lead.	1
	(ii)	Less energy intensive.	1
	(c)	Lower costs associated with obtaining the raw material.	2
Less mining, processing and use of a finite resource.			
22	(a) (i)		1
	(ii)	Dipole–dipole interactions	1
	(b) (i)	By creating a composite material, the properties of the reinforcement (carbon fibre) and matrix (polymer) are enhanced.	1
		The composite offers great strength as an implant in the spine. The composite is flexible in the spine.	1
		The resulting composite improves on the strength of the carbon fibre and the flexibility of the polymer.	1
	(ii)	The polymer may be a thermoplastic polymer that, when heated, will melt, allowing it to be separated from the reinforcement.	1
	(iii)	Any one:	1
The composite may be present in the body for many years and cannot be rejected.			
	(iii)	The composite must not release toxic compounds or compounds that interfere with the body.	
		The polymer cannot break down under the conditions experienced in the human body.	

Summary test 4 solutions: Managing resources

Question	Part	Author's response	Marks
	(a) (i)	$\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{CO}_2(\text{g})$	2
	(ii)	$\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \quad \Delta H = -1371 \text{ kJ mol}^{-1}$	4
	(iii)	$M(\text{C}_2\text{H}_5\text{OH}) = 46.068 \text{ g mol}^{-1}$ $\frac{\text{kJ}}{\text{mol}} \div \frac{\text{kJ}}{\text{g}}$ $= \frac{1371}{46.068}$ $= 29.76 \text{ kJ g}^{-1} \text{ (4 sig. fig.)}$	2
	(iv)	Racing teams want to extract the maximum energy from every litre of fuel. Racing teams want to complete as many laps as possible from each tank of fuel, to reduce the number of fuel stops.	1
	(v)	E85 is produced from a large component of bioethanol, which can be made from biomass (unlike petrol, which is derived from crude oil, a fossil fuel). Biomass is renewable, fossil fuels are non-renewable.	1 1
1	(b) (i)	$\Delta m = 1.8 \text{ g}$ $M(\text{CH}_3\text{OH}) = (2 \times 12.01) + (6 \times 1.008) + 16.00$ $M(\text{CH}_3\text{OH}) = 32.04 \text{ g mol}^{-1}$ $n = \frac{m}{M}$ $= \frac{1.8}{32.04} = 0.0561 \text{ mol}$ $\Delta H = \frac{m \times c \times \Delta T}{1000 \times n} \text{ (kJ mol}^{-1}\text{)}$ $\Delta H = \frac{100 \times 4.18 \times 30}{1000 \times 0.0561}$ $= -223.212 \text{ kJ mol}^{-1}$ $= -220 \text{ kJ mol}^{-1} \text{ (3 sig. fig.)}$	4
	(2)	Heat is lost to the surroundings. Incomplete combustion of the methanol.	1
	(ii)	More oxygen is available for every carbon atom in methanol, as it has a shorter carbon chain compared to octane.	1
	(iii)	<ul style="list-style-type: none"> Decomposition of nitrous oxide provides a higher concentration of oxygen in the air-fuel mixture. A higher concentration of oxygen increases the frequency of collisions. A larger number of productive collisions occur per unit time. 	3
	(iv)	(1) Condensation	1
		(2) Hydrogen bonding	1
	(c) (i)	4-	1
	(ii)	Magnesium is a more active metal than titanium Therefore magnesium metal can displace titanium ions to form solid titanium.	1 1

Question	Part	Author's response	Marks
1	(ii)	(1) 	1
		(2) Increased rigidity in the composite material.	1
		(3) As a composite, the properties of the individual materials are enhanced, such as increased strength or durability.	1
		(4) Heating the composite will not melt the thermoset polymer, it will char and decompose. This makes it extremely difficult to separate the matrix from the fibres, to allow recycling.	1
	(d)	<p>Any four of the following points (or alternatives). The science must be clearly identified, and explicit links made to society (people).</p> <p>Application and limitation</p> <p>The application of CFRP in materials innovation has increased due to its many advantages as a composite material. These include lower density and increased strength which allow industries to produce stronger, safer, and more efficient vehicles.</p> <p>The advantages of CFRP as a composite material also provide challenges for recycling, leading to issues of disposal and persistence in the environment. The nature of thermosetting polymers used for the matrix material means that they cannot be melted to separate the carbon fibre reinforcement. Extensive cross-linking hinders recycling.</p> <p>Existing chemical and mechanical methods applied for recycling result in potentially hazardous wastes and issues of disposal of the products formed. This may impact upon human health due to environmental exposure.</p> <p>The application of new methods by researchers has allowed cross links to be broken and the expensive carbon fibres separated intact while also retaining the polymer matrix for reuse.</p> <p>This ensures less raw materials are required for the future manufacture of CFRP and energy and resources associated with their production. This will reduce the demand on finite resources and impact less on the environment in terms energy production. This directly impacts upon human health from environmental exposure.</p> <p>Development</p> <p>As a composite material, CFRP provides challenges in recycling, leading to issues of disposal and persistence in the environment. The nature of thermosetting polymers used for the matrix material means that they cannot be melted to separate the carbon fibre reinforcement. Extensive cross-linking hinders recycling.</p> <p>The new method of recycling developed by researchers offers a way of recycling CFRP composites.</p> <p>Previous attempts using chemical or mechanical methods have been ineffective due to the formation of potentially hazardous wastes introducing issues for disposal. This may impact upon human health due to environmental exposure.</p> <p>The application of new methods by researchers has allowed cross-links to be broken and the expensive carbon fibres separated intact will also retaining the polymer matrix for reuse.</p> <p>This ensures less raw materials are required for the future production of CFRP and energy and resources associated with their production. This will reduce the demand on finite resources and impact less on the environment in terms energy production. This will reduce pollutants responsible for global warming which impact humans via climate change.</p>	4

Question	Part	Author's response	Marks
2	(a) (i)	Any two:	
		<ul style="list-style-type: none"> Soot is a fine particulate that when it enters the lungs, decreases respiratory function. This can lead to acute bronchitis, aggravate asthma, and increases the risk of cardiovascular disease. Carcinogens are transported on the surface of soot particles that enter the bloodstream. 	1 1
		Any one: Depletion of a non-renewable resource.	
	(ii)	Emissions of oxides of nitrogen and sulfur may lead to the formation of acid rain or photochemical smog. Emissions of carbon dioxide contribute to global warming.	1
	(b) (i)	Chlorine is formed as gas that can be toxic.	1
	(ii)	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	2
	(iii)	Chemical reduction is not effective, as lithium is a highly active metal.	1
		A molten electrolytic cell is required. In an aqueous cell, water would be reduced in preference to lithium ions. Hydrogen gas would be produced instead of lithium.	1
	(c) (i)	Electrolytic	1
	(ii)	Electrode 1	1
		During recharging, cell reactions are reversed. The reaction at Electrode 1 would demonstrate a loss of electrons indicating oxidation. Oxidation occurs at the anode.	1
	(iii)	(1) Renewable energy source.	1
		(2) Wind turbines only generate electricity when conditions are favourable (windy, but not higher gusts). The battery can store electrical energy, for times when there is no electricity generation from the turbines.	1 1
(iv)	(1) Any one: <ul style="list-style-type: none"> The battery will have to be replaced at some stage and it will decrease in its capacity to store electricity. The battery may not be able to store electricity for extended periods of time. 	1	
	(2) Any one: <ul style="list-style-type: none"> Flow batteries can remain charged or uncharged for extended periods of time without loss of storage capacity. Flow batteries, performance does not degrade with charge/recharge cycles. Discharged electrolytes can easily be replaced with charged electrolytes. 	1	

Question	Part	Author's response	Marks
3	(a)	(i) Concentrated thermal energy from the Sun heats the sea water to boiling point.	1
		(i) Pure water turns to a gas as it boils off, then the gas is condensed and collected leaving the salts that were present in the seawater as a solid.	1
		(ii) The Sun provides a continuous renewable source of energy, unlike energy obtained from the combustion of fossil fuels to provide electricity to drive reverse osmosis.	1
	(b)	(iii) As a disinfectant to kill bacteria.	1
		(i) Nitrogen is present in the waste in compounds like urea. Nitrifying bacteria in the environment convert the nitrogen-containing compounds into nitrate ions. Nitrate ions are soluble, and therefore dissolve in soil solution when spread on the soil in fertiliser.	1 1
		(ii) Continually cropping and harvesting the crops removes essential nutrients from the soil. These nutrients need to be replaced through the addition of fertiliser.	1
	(iv)	(iii) Increased concentration of aqueous hydrogen ions present in the soil solution places a stress on the system at equilibrium. According to Le Châtelier's principle, to counteract the stress, the position of equilibrium is shifted in favour of the forward reaction. Cations such as aluminium on the surface of the clay are forced into soil solution as they are exchanged with aqueous hydrogen ions. A higher concentration of aqueous aluminium ions can lead to aluminium toxicity, as they are now available to be taken up by plant roots.	1 1 1
		(1) The electrostatic attraction to negatively charged surfaces on the layers of clay.	1
		(2) $\text{CaSO}_{4(s)} \xrightarrow{\text{H}_2\text{O}} \text{Ca}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)}$ or $\text{Ca}^{2+}_{(aq)} + 2\text{H}^+_{(\text{clay})} \rightleftharpoons 2\text{H}^+_{(aq)} + \text{Ca}^{2+}_{(\text{clay})}$ Dissociated aqueous calcium cations shift the position of equilibrium in the forward direction, exchanging with hydrogen ions on the surface of the clay.	1 1
		Calcium ions on the clay surface promote flocculation due to stronger electrostatic attraction holding layers of clay together and maintaining soil structure.	1

Appendices

Appendix 1: Molar Masses of the Elements

Name	Symbol	At. No.	At. Mass.	Name	Symbol	At. No.	At. Mass.
Actinium	Ac	89	227*	Mendelevium	Md	101	258*
Aluminum	Al	13	26.98	Mercury	Hg	80	200.6
Americium	Am	95	243*	Molybdenum	Mo	42	95.94
Antimony	Sb	51	121.8	Neodymium	Nd	60	144.2
Argon	Ar	18	39.95	Neon	Ne	10	20.18
Arsenic	As	33	74.92	Neptunium	Np	93	237.0
Astatine	At	85	210*	Nickel	Ni	28	58.71
Barium	Ba	56	137.3	Niobium	Nb	41	92.91
Berkelium	Bk	97	245*	Nitrogen	N	7	14.01
Beryllium	Be	4	9.012	Nobelium	No	102	255*
Bismuth	Bi	83	208.9	Osmium	Os	76	190.2
Bohrium**	Bh	107	272	Oxygen	O	8	16.00
Boron	B	5	10.81	Palladium	Pd	46	105.4
Bromine	Br	35	79.90	Phosphorus	P	15	30.97
Cadmium	Cd	48	112.4	Platinum	Pt	78	195.1
Calcium	Ca	20	40.08	Plutonium	Pu	94	244*
Californium	Cf	98	248*	Polonium	Po	84	209*
Carbon	C	6	12.01	Potassium	K	19	39.102
Cerium	Ce	58	140.1	Praseodymium	Pr	59	140.9
Cesium	Cs	55	132.9	Promethium	Pm	61	145*
Chlorine	Cl	17	35.45	Protactinium	Pa	91	231.0
Chromium	Cr	24	52.00	Radium	Ra	88	226.0
Cobalt	Co	27	58.93	Radon	Rn	86	222*
Copper	Cu	29	63.55	Rhenium	Re	75	186.2
Curium	Cm	96	245*	Rhodium	Rh	45	102.9
Damstadtium	Ds	110	271	Roentgenium	Rg	111	272
Dubnium	Db	105	262	Rubidium	Rb	37	85.47
Dysprosium	Dy	66	162.5	Rutherfordium	Rf	104	261
Einsteinium	Es	99	254*	Ruthenium	Ru	44	101.1
Erbium	Er	68	167.3	Samarium	Sm	62	150.4
Europium	Eu	63	152.0	Scandium	Sc	21	44.96
Fermium	Fm	100	254*	Seaborgium	Sg	106	271
Fluorine	F	9	19.0	Selenium	Se	34	78.96
Francium	Fr	87	223*	Silicon	Si	14	28.09
Gadolinium	Gd	64	157.3	Silver	Ag	47	107.9
Gallium	Ga	31	69.72	Sodium	Na	11	22.99
Germanium	Ge	32	72.59	Strontium	Sr	38	87.62
Gold	Au	79	197.0	Sulphur	S	16	32.064
Hafnium	Hf	72	178.5	Tantalum	Ta	73	180.9
Hassium	Hs	108	277	Technetium	Tc	43	99*
Helium	He	2	4.003	Tellurium	Te	52	127.6
Holmium	Ho	67	164.9	Terbium	Tb	65	158.9
Hydrogen	H	1	1.008	Thallium	Tl	81	204.4
Indium	In	49	114.8	Thorium	Th	90	232.0
Iodine	I	53	126.9	Thulium	Tm	69	168.9
Iridium	Ir	77	192.2	Tin	Sn	50	118.7
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.9
Lanthanum	La	57	138.9	Uranium	U	92	238.0
Lawrencium	Lw	103	260*	Vanadium	V	23	50.94
Lead	Pb	82	207.2	Xenon	Xe	54	131.3
Lithium	Li	3	6.941	Ytterbium	Yb	70	173.0
Lutetium	Lu	71	175.0	Yttrium	Y	39	88.91
Magnesium	Mg	12	24.31	Zinc	Zn	30	65.38
Manganese	Mn	25	54.94	Zirconium	Zr	40	91.22
Meitnerium	Mt	109	268				

* **Mass number of most stable isotope Source of Information:** Atomic weights of the elements 2005 (IUPAC Technical Report) (*Pure Appl. Chem.*, 2006, Vol. 78, No. 11, pp. 2051–2066)

Appendix 2: The Periodic Table of Elements

1	2	3	4	5	6	7	8	9	10
1 H hydrogen [1.007, 1.008]	2 He helium 4.003	3 Li lithium [6.938, 6.997]	4 Be beryllium 9.012	5 B boron [10.80, 10.83]	6 C carbon [12.00, 12.02]	7 N nitrogen [14.00, 14.01]	8 O oxygen [15.99, 16.00]	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium [24.30, 24.31]	13 Al aluminium 26.98	14 Si silicon [28.08, 28.09]	15 P phosphorus 30.97	16 S sulfur [32.05, 32.08]	17 Cl chlorine [35.44, 35.46]	18 Ar argon 39.95		
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4
55 Cs caesium 132.9	56 Ba barium 137.3	57-71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium
			111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine
			118 Og oganesson						
			119 Uue unbinilium	120 Uub unbinilium	121 Uut ununilium	122 Uuq ununilium	123 Uuq ununilium	124 Uuq ununilium	125 Uuq ununilium

57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0
89 Ac actinium 227.0	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

Lanthanide Series

Actinide Series

Appendix 3: SI prefixes, symbols and values

The following table, shows SI prefixes, their symbols and their values, and is useful when answering questions that involve the conversion of units:

SI Prefix	tera	giga	mega	kilo	centi	milli	micro	nano	pico
Symbol	T	G	M	k	c	m	μ	n	p
Value	10^{12}	10^9	10^6	10^3	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}

