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VCE UNITS 3 AND 4

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How to use this book

Chemistry 2 VCE Units 3 and 4 has the following features.

Each chapter opening page gives an overview of the key knowledge and outcomes addressed in the chapter.

Engaging quotes help focus, inspire and motivate.

Sample problems with worked solutions enhance understanding. These are often followed by revision questions.

studyON icons indicate where students can find more information and direct students to relevant animations and interactivities.

eLessons, interactivities and weblinks enhance understanding and bring concepts to life.

CHAPTER 5 Rates of reactions

Collisions cause change. Car accidents, tennis bowling, hitting a golf ball, hurricanes and striking a match; all of these collisions affect their surroundings. The more energy a collision has, the more dramatic are the changes produced. On a much smaller scale, collisions between atoms, molecules and ions are at the heart of all chemical reactions. The same ideas about energy and collisions causing change explain much about how chemical reactions occur.

Be less curious about people and more curious about ideas.
Marie Curie

Blasting is an important step in open-cut mining. It frees up the ore for collection and subsequent transport. The explosions that release the ore are chemical reactions designed to happen almost instantaneously, and they release huge volumes of gases and vast amounts of energy. The energy shatters the rock and it falls into smaller, more convenient pieces. Not all chemical reactions happen so quickly, however. Chemists can control the rates of reactions using knowledge of various factors.

YOU WILL EXAMINE:

- the concept of rate of a reaction
- the use of collision theory to explain reaction rates
- energy profile diagrams for exothermic and endothermic reactions and the concept of activation energy
- factors that affect the rate of a reaction
- how catalysts affect the rate of a reaction
- Maxwell-Boltzmann distribution curves and their use in explaining reaction rates.

How does a chemical reaction occur?

All chemical reactions involve the rearrangement of atoms that are already present. For such an arrangement to occur, existing (or old) bonds need to be broken and 'new' bonds allowed to form. This means that there is always an energy requirement before a chemical reaction can take place; this corresponds to breaking the 'old' bonds. This energy required to break these bonds is called the activation energy and comes from either or both:

- thermal energy (heating)
- the kinetic energy of colliding particles.

When new bonds form, energy is released as the particles involved organise themselves into stable arrangements that form the products. The total energy stored in a substance is called the *enthalpy*, or *heat content*, of the substance and is given the symbol *H*. It is not possible to measure *H* directly but the change in enthalpy (ΔH) can be measured when a substance undergoes a chemical reaction. Change in enthalpy was discussed in chapter 2. Energy changes can be conveniently summarised using the following energy profile diagrams.

Energy diagram for an exothermic reaction

Energy diagram for an endothermic reaction

From these diagrams we can note a number of points:

- The energy required to break the old bonds is called the activation energy.
- For an exothermic reaction, the activation energy is less than the energy released when new bonds form. Consequently, there is a net release of energy (usually as heat released to the surroundings).
- In an endothermic reaction, the activation energy is greater than the energy released when new bonds form. Consequently, there is a net input of energy (in most cases, heat is absorbed from the surroundings).
- In both cases, however, the activation energy represents a requirement for the progress of the chemical reaction. This must be overcome before a reaction proceeds.

Bond breaking > bond forming $+\Delta H$
Bond breaking < bond forming $-\Delta H$

Cracking

Cracking is a process that uses heat and pressure, and sometimes a catalysts to break larger hydrocarbon molecules into smaller molecules, including an alkene and hydrogen, or an alkane.

Sample problem 9.2

Write a semi-structural equation for each of the following.

(a) Ethene is produced from the cracking of propane.
(b) Carbon monoxide is produced by incomplete combustion of ethene in limited air.

Solution:

(a) $\text{CH}_3\text{CH}_2\text{CH}_3(\text{g}) \rightarrow \text{CH}_2=\text{CH}_2(\text{g}) + \text{CH}_3\text{CH}_3(\text{g})$
(b) $\text{CH}_2\text{CH}_2(\text{g}) + 2\text{O}_2 \rightarrow 2\text{CO}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

Revision questions

16. Write an equation for the complete combustion of octane, C_8H_{18} .
17. The alkenes burn in a similar way to alkanes. Write an equation for the complete combustion of propene.
18. How many possible products are there when ethane reacts with bromine? Write the name of each of these products.

Addition reactions of alkenes

Alkenes are more reactive than alkanes. They are unsaturated hydrocarbons and undergo addition reactions in which the $\text{C}=\text{C}$ bond is broken and new single bonds are formed. This is because the energy required to break the double bond is less than the energy released in the formation of two single bonds. For example, hydrogenation of ethene produces ethane and releases energy.

$$\text{H}_2\text{C}=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{H}_3\text{C}-\text{CH}_3(\text{g})$$

Substances that undergo addition reactions with alkenes include H_2 , Cl_2 , Br_2 , HCl , HBr and HI . Addition of H_2 requires the presence of a catalyst, such as finely divided Pt, Pd or Ni. The others react without the need for catalyst. The equations below are examples of addition reactions with alkenes. Note that the reactants Br_2 , HCl and H_2 in these reactions add across the double bond. Therefore, 1,2-dibromopropane is the only product.

$$\text{H}_2\text{C}=\text{CHCH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$$

propene bromine 1,2-dibromopropane

$$\text{H}_2\text{C}=\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{Cl}$$

ethene hydrogen chloroethane

$$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Pt}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$$

but-1-ene hydrogen butane

The reaction of an alkene with bromine is used as a test for unsaturation. When red-brown bromine water is shaken with an unsaturated hydrocarbon, the reaction mixture becomes colourless due to the formation of the dibromo derivative.

Ethene is used as a raw material in a fast method to produce the large amounts of ethanol needed for industrial use. Ethene is mixed with steam and passed over a phosphoric acid catalyst at 330°C . The reaction of the direct

ethanol can be produced by hydration of ethene or a substitution reaction of a haloalkane.

Model equation for the direct hydration of ethene to form ethanol

$$\text{H}_2\text{C}=\text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow{\text{H}^+/\text{H}_2\text{PO}_4^-} \text{CH}_3\text{CH}_2\text{OH}(\text{g})$$

ethene + steam $\rightarrow$ ethanol

Addition polymerisation

Another important reaction of some unsaturated hydrocarbons is polymerisation, a process in which many small molecules (monomers) are joined together to form a large molecule (polymer).

The monomer ethene, containing a double bond, undergoes addition polymerisation readily to form polyethene (also known as polyethylene or polythene). This product is one of the most commonly used synthetic polymers. Low-density (melting at lower temperatures) polyethene is used for making film, garbage bags and plastic wrappers and for making moulded articles such as squeeze bottles. High-density (containing linear rather than branched chains and melting at a higher temperature) polyethene is more rigid and is used for moulding items such as bread and drink crates.

monomer $\rightarrow$ polymer

Addition polymerisation of ethene to form polythene

This pie chart shows Australia's consumption of different types of polymers.

Polymer	Percentage
polyethene	46.3%
polypropylene	15.9%
PVC	14.5%
other	12.3%
polystyrene	5.4%
polyurethane	3.1%
ABS/SAN	1.4%
nylon	1.2%

Chapter review

Chapter summaries give a detailed overview of key knowledge.

Summary

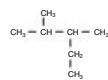
- Organic chemistry is the study of the compounds of carbon. This does not include the inorganic compounds of cyanides, carbonates and oxides of carbon.
- Carbon can form many different compounds due to its ability to create four covalent bonds with itself or other elements.
- In the methane molecule, a carbon atom can form covalent bonds with four other atoms. The resulting shape is tetrahedral, resulting in bond angles of 109.5° .
- Hydrocarbons are organic compounds consisting of carbon and hydrogen atoms only.
- A functional group is an atom or a group of atoms that confers a distinct set of chemical and physical characteristics on an organic compound.
- A homologous series is a group of organic chemical compounds that have a similar structure and whose structures differ only by the number of CH_2 units in the main carbon chain. They are compounds containing the same functional group and have similar properties.
- The alkanes, alkenes and alkynes are hydrocarbons and form homologous series with general formulas of $\text{C}_n\text{H}_{2n+2}$, C_nH_{2n} and $\text{C}_n\text{H}_{2n-2}$, respectively.
- Saturated hydrocarbons have only single C—C covalent bonds.
- Alkanes are saturated hydrocarbons. Alkenes and alkynes are unsaturated hydrocarbons with double and triple carbon bonds, respectively.
- Carbon compounds with the same molecular formula but different structural arrangements are called structural isomers.
- Rules for naming organic compounds:
 - Identify and name the longest unbranched carbon chain containing the principal functional group. (It is helpful to highlight this chain.)
 - If more than one functional group is present, the order of decreasing priority in determining the suffix is carboxylic acid > ester > aldehyde > ketone > alcohol > amine > alkene > alkane.
 - Number the carbon atoms in the longest unbranched chain, starting with the carbon atom nearest the functional group or branch (if an alkane).
 - Identify the branching group(s) of atoms, and state the number of the carbon atom to which it is attached. Branches are named using -yl.

For example, a branched group of $-\text{CH}_3$ would be named methyl, CH_3CH_2- would be ethyl, $\text{CH}_3\text{CH}_2\text{CH}_2-$ would be propyl and so on. These go before the name of the longest chain.

- For molecules with two or more branches of the same type, the branch type is named and a prefix (*di*, *tri*, *tetra* etc.) is used to indicate the number of branches.
- Branches are listed in alphabetical order, ignoring the prefix in the previous rule. Ethyl is written before methyl or dimethyl.
- Note: Adjacent numbers in a name are separated by a comma. Numbers are separated from words by a hyphen.
- Carbon compounds in the form of rings, such as benzene, belong to a group called aromatic compounds.
- Alcohols have the functional group $-\text{OH}$ (hydroxyl group) and are named using the suffix -ol.
- Aldehydes have the functional group $-\text{CHO}$ (aldehyde group) and are named using the suffix -al.
- Ketones have the functional group $-\text{CO}-$ (carbonyl group) and are named using the suffix -one.
- Carboxylic acids have the functional group $-\text{COOH}$ (carboxyl group) and are named using the suffix -oic.
- Primary amines have the functional group $-\text{NH}_2$ (amino group) and are named using the suffix -amine.
- Amides have the functional group $-\text{CONH}_2$ (amide group).
- Haloalkanes have the functional group $-\text{X}$ (where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) and are named using the prefix -fluoro-, -chloro-, -bromo or -iodo.

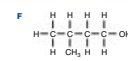
Multiple choice questions

1. The name of the organic compound shown is:



- A 2-methyl-3-ethylbutane
B 1,2-dimethylpentane
C 2,3-dimethylheptane
D 2,3-dimethylpentane.

2. Which of the following does not apply to alkanes?
A They have the general formula $\text{C}_n\text{H}_{2n+2}$.
B They contain C and H.
C Each has at least one C—C bond.
D They are saturated hydrocarbons.
3. Which of the following compounds is not regarded as an organic compound?
A C_2H_6
B H_2CO_3
C $\text{C}_2\text{H}_5\text{OH}$
D C_2H_4
4. Which of the following compounds is correctly classified as a tertiary alcohol?
A 3-methylbutan-1-ol
B 2-methylbutan-1-ol
C 3-methylbutan-2-ol
D 2-methylbutan-2-ol
5. Which of the following apply to alkenes?
A They are saturated hydrocarbons.
B They have the formula C_nH_{2n} .
C Each has a saturated covalent bond.
D They contain C, H and O.
6. The functional groups and suffixes for naming alcohols and carboxylic acids are respectively:
A OH, COOH, -oate, -ol
B COOH, OH, -ol, -oic
C OH, COOH, -ol, -oic
D OH, COOH, -ol, -oate.
7. Two structural isomers with the same molecular formula as butanol are:
A $\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\ | & | & | & | \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{OH} \end{array}$
B $\begin{array}{c} \text{H} & \text{H} & \text{CH}_3 & \text{H} \\ | & | & | & | \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{OH} \end{array}$
C $\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\ | & | & | & | \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{OH} \end{array}$
D $\begin{array}{c} \text{H} & \text{H} & \text{CH}_3 & \text{H} \\ | & | & | & | \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{OH} \end{array}$
E $\begin{array}{c} \text{H} & \text{CH}_3 & \text{CH}_3 \\ | & | & | \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\ | & | & | \\ \text{OH} & \text{H} & \text{H} \end{array}$



8. The systematic name of the compound $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ is:
A hexanoic acid
B heptanoic acid
C hexanol
D heptanol.

9. The structural arrangement of 2,2-dimethylbutan-1-ol is:
A $\begin{array}{c} \text{H} & \text{CH}_3 & \text{CH}_3 & \text{H} \\ | & | & | & | \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{OH} \\ | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$
B $\begin{array}{c} \text{H} & \text{H} & \text{CH}_3 & \text{H} \\ | & | & | & | \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{OH} \\ | & | & | & | \\ \text{H} & \text{H} & \text{CH}_3 & \text{H} \end{array}$
C $\begin{array}{c} \text{H} & \text{H} & \text{CH}_3 & \text{H} \\ | & | & | & | \\ \text{HO}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ | & | & | & | \\ \text{H} & \text{H} & \text{CH}_3 & \text{H} \end{array}$
D $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C} & -\text{C}-\text{OH} \\ | & | \\ \text{CH}_3 & \text{CH}_3 \end{array}$

10. Cycloalkanes have the same molecular formula as:
A alkanes
B alkenes
C alkenes
D benzene.
11. Which group of compounds does benzene belong to?
A alkanes
B alkenes
C alkenes
D aromatics
12. In the IUPAC nomenclature system, the name of which of the following would end in -al?
A an alcohol
B an aldehyde
C an alkane
D a ketone

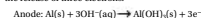
CHAPTER 8 Structures and nomenclature of organic compounds 237

Multiple choice and short answer review questions reinforce understanding and are divided by headings to make content easy to identify.

The studyON 'Sit VCAA exam' icon directs students to a large bank of VCAA exam questions at concept, topic and entire course levels. Students can also choose to undertake a full exam.

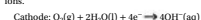
In the aluminium-air battery, a piece of aluminium is immersed in an electrolyte near a porous electrode. This porous electrode has air on one side and the electrolyte on the other. The electrolyte can be a common salt, NaCl solution, an alkali solution, such as potassium hydroxide, KOH, or sea water. Although the choice of electrolyte is quite flexible, only special alloys of aluminium can be used. With ordinary alloys, the aluminium immediately becomes coated with a protective oxide layer or simply dissolves as aluminium oxide, giving off hydrogen gas.

In this battery, the aluminium oxide reacts with hydroxide ions to form aluminium hydroxide, with the release of three electrons.

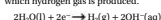


The OH^- ions are present either because the electrolyte is an alkali solution or because they are produced at the cathode.

At the porous cathode, the water in the electrolyte reacts with oxygen from the air and the electrons from the anode to produce hydroxide ions.



If the cathode is covered (for example, with water) so that oxygen cannot enter the cell, a slightly different reaction occurs in the cell in which hydrogen gas is produced.



- (a) Write the overall equation for the aluminium-air battery operating under optimal conditions.
(b) Write the overall equation if the cathode is covered with water.

Fuel cells

27. (a) What is a fuel cell?
(b) List the advantages of a fuel cell over a primary galvanic cell.
28. Fuel cells have been used in spacecraft for a number of years as a source of electrical energy. To obtain sufficient current, two gases, hydrogen and oxygen, are kept in cylinders under high pressure. The gases are passed over nickel electrodes. The product of these fuel cells is water,

which is used by the astronauts for drinking. Each hydrogen-oxygen fuel cell used in the Apollo spacecraft weighed approximately 100 kg.

- (a) What advantages do fuel cells have over internal combustion engines for use in spacecraft?
(b) What are the limitations of fuel cells, compared with the internal combustion engine?

29. Fuel cells have been developed to run on methane. Assuming that the electrolyte is acidic:
(a) write the half-equation for the oxidation reaction
(b) write the half-equation for the reduction reaction.

Draw a diagram of this cell, labelling the following.
(c) The methane and oxygen inlets
(d) The anode and cathode and their polarities
(e) The direction of electron flow
(f) The ion flow in the electrolyte

30. Obtaining hydrogen for use in fuel cells is not yet economically viable. But researchers have come up with a fuel cell that runs on octane, the main component of petrol. Previously, the reforming process caused a build-up of carbon on the electrodes in the fuel cell, reducing efficiency. A new system combines the reformer and the fuel cell and uses a more advanced catalyst.

(a) Write the equation for the combustion of octane, C_8H_{18} .

(b) This reaction is the same as the one that occurs in the fuel cell and produces the same amount of carbon dioxide. Explain what benefit there is in using a fuel cell to supply energy to power a vehicle.

- (c) Write the half-equations for the anode and cathode reactions in this fuel cell assuming an acidic electrolyte.
(d) Add the two half-equations from (c) to get the overall reaction. Compare your answer with (a). What do you notice?

31. Discuss the statement 'Electrochemical cells may help decrease our use of fossil fuels as an energy source'.

32. Describe how the method of producing electricity from an electrochemical cell differs from the method of producing electricity from:

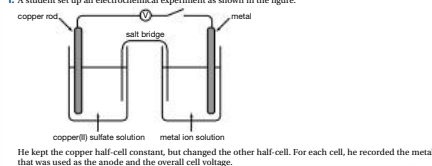
- (a) a hydro-electricity scheme
(b) a coal-fired power station.

Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

1. A student set up an electrochemical experiment as shown in the figure.

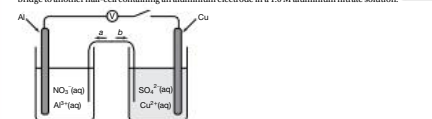


He kept the copper half-cell constant, but changed the other half-cell. For each cell, he recorded the metal that was used as the anode and the overall cell voltage.

Cell	Anode	Voltage (V)
copper-lead	lead	0.49
copper-silver	copper	0.31
copper-magnesium	magnesium	1.45
copper-iron	iron	0.57
copper-aluminium	aluminium	0.94
copper-copper	copper	0.00
copper-nickel	nickel	0.31

- (a) How did the student determine which of the metals in the cell acted as the anode?
(b) Why did the copper-copper cell produce no voltage?
(c) Determine the likely order of reactivity of the metals. Justify your placements.

2. A half-cell is constructed with a copper electrode in a 1.0 M copper(II) sulfate solution. It is connected by a salt bridge to another half-cell containing an aluminium electrode in a 1.0 M aluminium nitrate solution.



- (a) A voltmeter is connected into the external circuit. What would be the expected E° value for this cell?

Acknowledgements

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UNIT 3

AREA OF STUDY 1

CHAPTER 1 Choosing fuels

CHAPTER 2 Energy calculations

CHAPTER 3 Converting chemical energy to electrical energy

AREA OF STUDY 2

CHAPTER 4 Electrolysis

CHAPTER 5 Rates of reactions

CHAPTER 6 Equilibrium systems

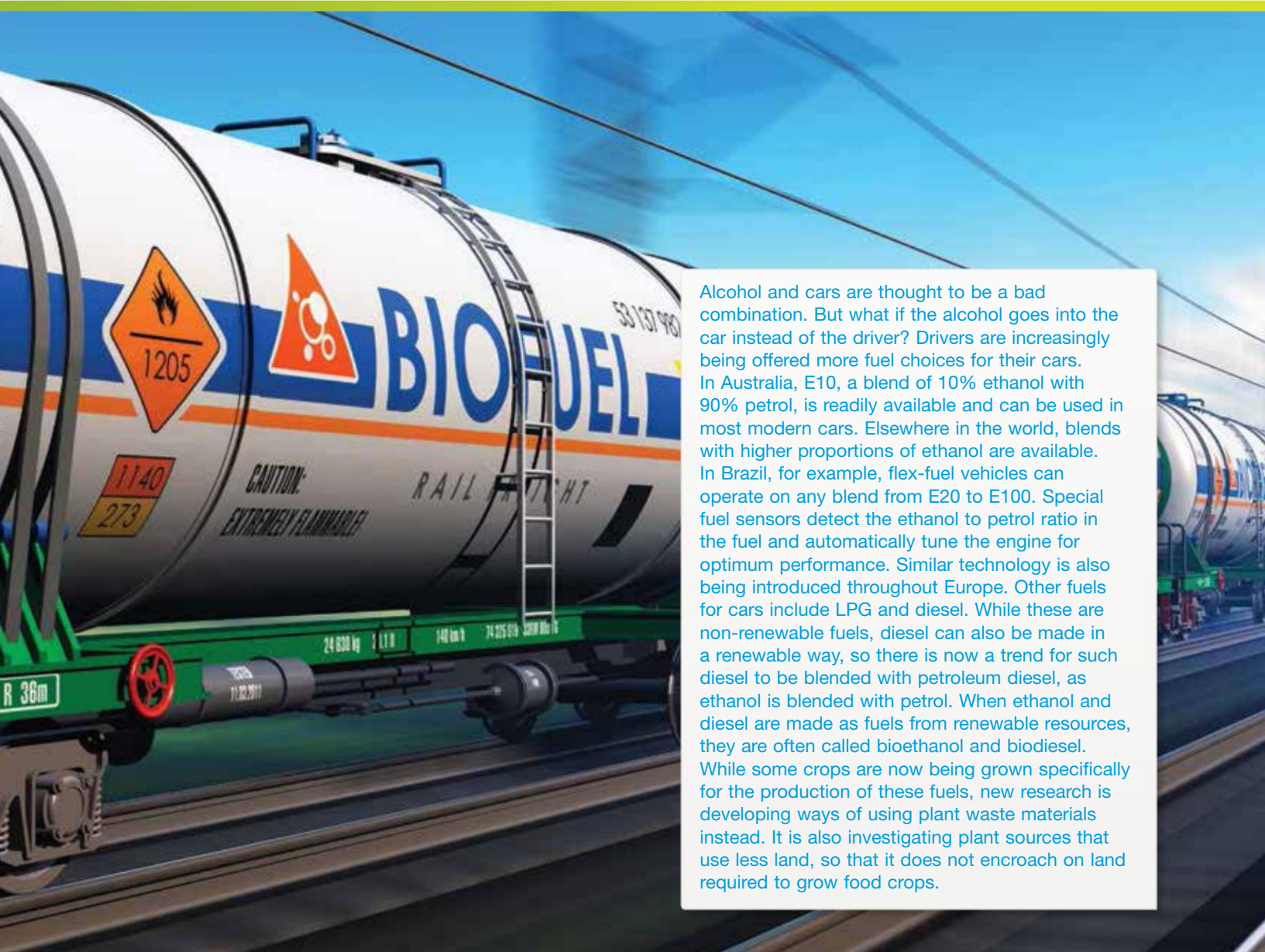


Choosing fuels

Fuels are burned to produce heat energy. The energy evolved from this combustion is used to heat our homes and for transport and industrial processes. It can also be converted into electrical energy, and, as such, can be conveniently transported over long distances and used to power many machines and appliances. The challenge to our society is to meet its increasing energy demands with a reliable supply of energy from clean, efficient and sustainable sources.

YOU WILL EXAMINE:

- the definition of a fuel
- how fuels and energy sources may be classified as renewable and non-renewable
- use of the joule as the SI unit for measuring energy
- energy transformation
- the concept of efficiency as it applies to energy transformations
- how fossil fuels and biofuels may be compared according to a range of criteria.



Alcohol and cars are thought to be a bad combination. But what if the alcohol goes into the car instead of the driver? Drivers are increasingly being offered more fuel choices for their cars. In Australia, E10, a blend of 10% ethanol with 90% petrol, is readily available and can be used in most modern cars. Elsewhere in the world, blends with higher proportions of ethanol are available. In Brazil, for example, flex-fuel vehicles can operate on any blend from E20 to E100. Special fuel sensors detect the ethanol to petrol ratio in the fuel and automatically tune the engine for optimum performance. Similar technology is also being introduced throughout Europe. Other fuels for cars include LPG and diesel. While these are non-renewable fuels, diesel can also be made in a renewable way, so there is now a trend for such diesel to be blended with petroleum diesel, as ethanol is blended with petrol. When ethanol and diesel are made as fuels from renewable resources, they are often called bioethanol and biodiesel. While some crops are now being grown specifically for the production of these fuels, new research is developing ways of using plant waste materials instead. It is also investigating plant sources that use less land, so that it does not encroach on land required to grow food crops.

Energy and fuels

What is energy?

Energy is the ability to do work.

We cannot see energy so it is difficult to define. Nevertheless, we can see the effects of energy; we can see things changing because of energy.

Energy is defined as the ability to do 'work'. Whenever something is being pushed or pulled, work is being done. When work is done, energy is used. The unit of energy is the joule; it has the symbol J. One joule is a relatively small amount of energy. It takes about 70 000 J (70 kJ) to boil the water to make a cup of coffee.

A fuel produces energy in a combustion reaction.

Most chemical reactions absorb or produce energy, generally in the form of heat. The study of heat changes in chemical reactions is called thermochemistry. An example of a reaction that produces heat energy is a combustion reaction.

Energy from common fuels

Fossil fuels are formed from the decayed remains of living matter that has been buried for millions of years.

A substance used for producing energy by combustion is called a **fuel**. Coal, petroleum and natural gas are also known as **fossil fuels** because they were formed from the decaying remains of plants and tiny marine animals that lived millions of years ago.

Use of explosives releases an enormous quantity of energy. An explosion is an uncontrolled chemical reaction that occurs suddenly and is highly exothermic.



Sample problem 1.1

The efficiencies of two fuels, propan-1-ol and butan-1-ol, were tested in a thermochemical experiment. The two fuels were ignited and the heat given out by each flame was measured by recording the change in temperature of a known amount of water heated by each flame. The results of this experiment are shown in table 1.1.

TABLE 1.1 Experimental results for the combustion of propan-1-ol and butan-1-ol

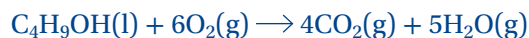
Alcohol	Mass of alcohol used in experiment (g)	Heat given out (kJ)
propan-1-ol, $\text{C}_3\text{H}_7\text{OH}$	3.75	126
butan-1-ol, $\text{C}_4\text{H}_9\text{OH}$	3.68	129

- Write balanced equations for each combustion reaction, given that the combustion products are carbon dioxide and water vapour.
- Calculate the energy produced by each fuel as kJ g^{-1} , and thereby determine the more efficient of the two fuels.
- Calculate the energy produced by each fuel as kJ mol^{-1} .

Solution: (a) Combustion of propan-1-ol:



Combustion of butan-1-ol:



- (b) Propan-1-ol produces $\frac{126}{3.75} = 33.6 \text{ kJ g}^{-1}$

and butan-1-ol produces $\frac{129}{3.68} = 35.1 \text{ kJ g}^{-1}$.

So, in terms of *energy per gram of fuel*, butan-1-ol is slightly more efficient than propan-1-ol.

- (c) Number of moles of propan-1-ol, $n(\text{propanol}) = \frac{3.75}{60.0} = 0.0625 \text{ mol}$.

Since 0.0625 mol produces 126 kJ of energy,

$$1 \text{ mol produces } \frac{126}{0.0625} = 2.02 \times 10^3 \text{ kJ of energy.}$$

Number of moles of butan-1-ol, $n(\text{butanol}) = \frac{3.68}{74.0} = 0.0497 \text{ mol}$.

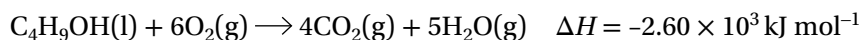
Since 0.0497 mol produces 129 kJ of energy,

$$1 \text{ mol produces } \frac{129}{0.0497} = 2.60 \times 10^3 \text{ kJ of energy.}$$

So, in terms of *energy per mole* of fuel, butan-1-ol is more efficient than propan-1-ol.

Thermochemical equations

The information in sample problem 1.1 may be neatly summarised by using **thermochemical equations**. These combine the normal chemical equation with ΔH notation (delta H) to specify the quantity of heat given out when the mole amounts as specified in the equation are burned. For example, the combustion of butan-1-ol in sample problem 1.1 may be summarised as:

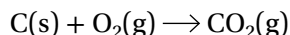


By convention, **exothermic** reactions (such as combustion reactions that give out heat) are assigned negative ΔH values.

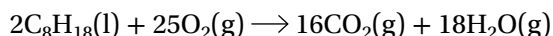
Thermochemical equations are discussed in detail in chapter 2.

Most of the energy obtained from the combustion of fossil fuels is derived from an exothermic reaction in which the carbon in the fuel is converted into carbon dioxide and the hydrogen in the fuel is converted into water.

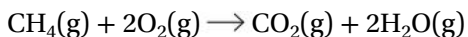
Coal is used for generation of electricity. The complete combustion of coal may be represented as:



Oil, from which petrol is obtained, is mainly used for transport. The complete combustion of octane, a major component of petrol, may be represented as:



Natural gas is used both for generation of electricity and directly for domestic and commercial cooking and heating. The complete combustion of methane, found in natural gas, may be represented as:



Revision question

1. The combustion of 3.15 g of methanol was found to yield 71.5 kJ of heat. Calculate the ΔH value for this reaction, and write the thermochemical equation.

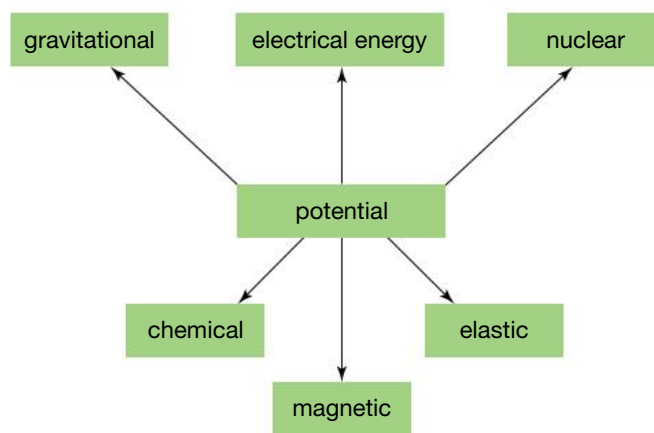
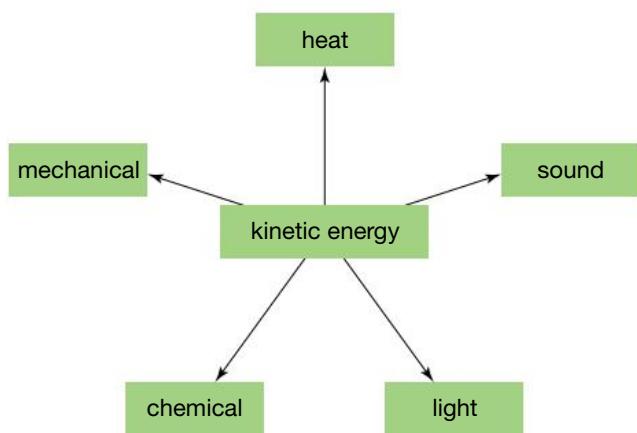
Different forms of energy

Energy may take a number of different forms. These include:

- mechanical energy
- thermal (heat) energy
- chemical energy
- light energy
- sound energy
- electrical energy
- gravitational energy
- nuclear energy.

The total energy of an object is the sum of its potential and kinetic energy.

However, all of these forms of energy may be classified as either *potential energy* (energy that is stored, ready to do work) or *kinetic energy* (energy associated with movement, in doing work).



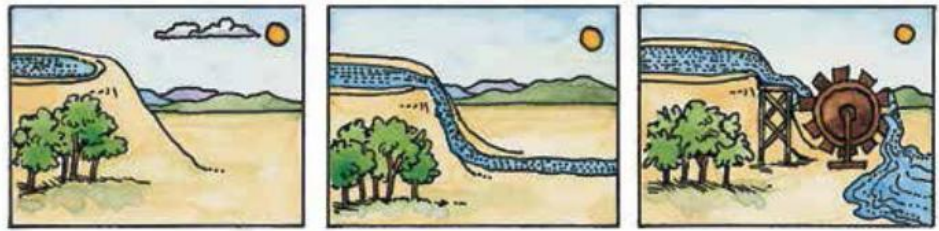
Types of potential and kinetic energy

The total energy of an object is the sum of its potential and kinetic energy. All objects, from the smallest atom to the largest space rocket, have potential and kinetic energy.

Energy conversions

Whatever form energy takes, it is governed by two general laws of thermodynamics.

The *first law* states that energy is neither created nor destroyed, but simply changes from one form into another. Whenever energy is converted from one form to another, the total quantity of energy remains the same. This is sometimes called the **Law of Conservation of Energy**.



(a) Water stored in a dam has potential energy.

(b) Water flows downhill and is converted to kinetic energy.

(c) The falling water turns the blades of a waterwheel so that kinetic energy is converted to mechanical energy.



(d) The waterwheel turns a generator to convert mechanical energy into electrical energy.



(e) Electrical energy may be converted into light energy, sound energy and heat energy in the home.

In any energy conversion, the total quantity of energy remains the same.

The *second law* states that, although the quantity of energy in the universe may stay the same, the quality or usability gets worse. This is because whenever energy is converted from one form to another, heat is also produced. This is low-temperature heat, which is difficult to use again. It simply warms up the Earth's atmosphere by a small amount. So, after each energy change, less usable energy remains.

Efficiency

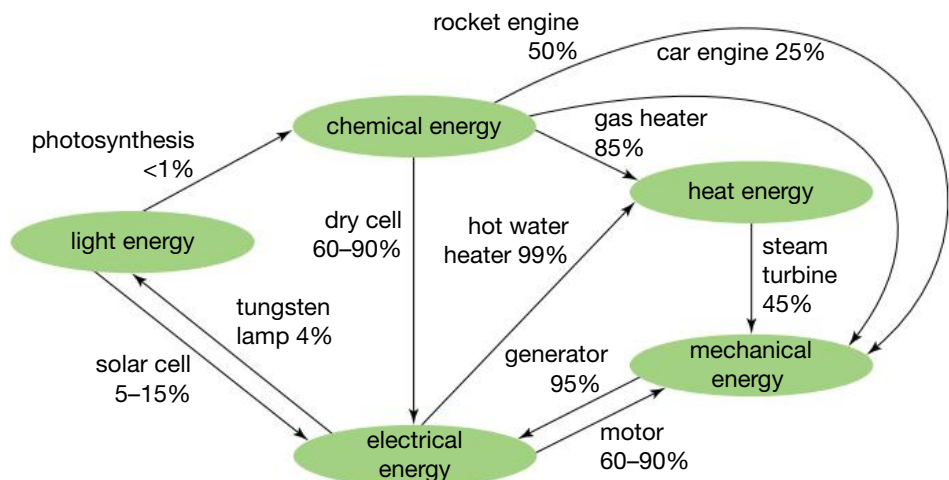
Efficiency is defined as a percentage according to the following formula.

$$\% \text{ efficiency} = \frac{\text{energy obtained in desired form}}{\text{energy available before conversion}} \times 100$$

The **efficiency** of energy conversion is a concept that follows from the second law. It takes the amount of usable energy obtained into account and is defined as a percentage according to the following formula.

$$\% \text{ efficiency} = \frac{\text{energy obtained in desired form}}{\text{energy available before conversion}} \times 100$$

The efficiency of changing one energy form into another varies.



Energy transformations are not 100% efficient. This is because, when energy conversions take place, heat is also produced. The second law of thermodynamics states that a high quality of energy is transformed to a lower quality of energy and some heat.

Sample problem 1.2

A compact fluorescent light bulb converts electrical energy into light energy. As part of a quality control test, it was found to convert 9.0 kJ of electrical energy into 1.8 kJ of light energy. Calculate its efficiency.

Solution:

$$\% \text{ efficiency} = \frac{\text{energy obtained in desired form}}{\text{energy available before conversion}} \times 100$$
$$\% \text{ efficiency} = \frac{1.8}{9.0} \times 100 = 20\%$$

Sample problem 1.3

The electricity from a coal-fired power station is used to power an electric motor. If the overall efficiency of the power station is 28%, and the efficiency of the motor in producing mechanical energy is 75%, calculate the overall efficiency for the conversion of chemical energy in coal to mechanical energy in this situation.

Solution: We can answer this by following the fate of 100 J of energy supplied originally by the coal. From the original input of 100 J, the power station produces 28 J of electricity. When this 28 J is fed into the electric motor, the mechanical energy produced can be calculated.

$$75\% = \frac{\text{mechanical energy produced}}{28} \times 100$$

$$\text{Mechanical energy produced} = \frac{75 \times 28}{100} = 21 \text{ J}$$

As 21 J of mechanical energy is produced from the original 100 J

$$\% \text{ efficiency} = \frac{21}{100} \times 100 = 21\%$$

Revision questions

Where necessary, use efficiency figures in the diagram at the bottom of the previous page to answer the following questions.

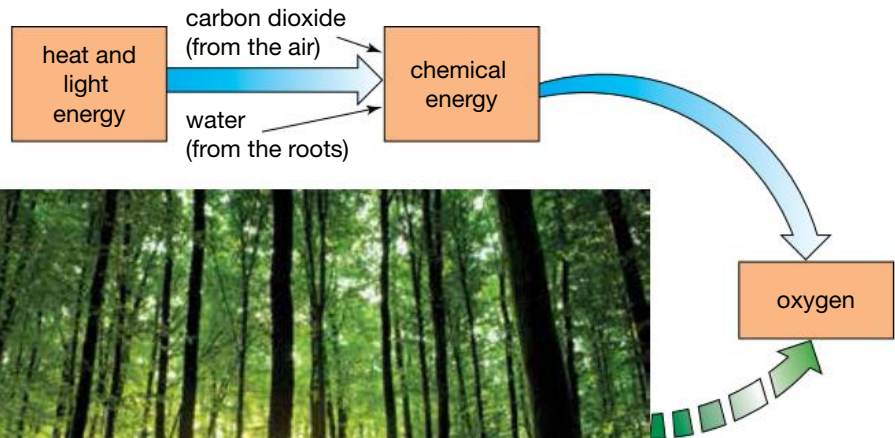
2. A device converts 350 J of mechanical energy into 120 J of output energy. Calculate the efficiency of this device.
3. Calculate the energy input required for a gas heater to produce 72 MJ.
4. Heat energy in steam is used to drive a steam turbine that, in turn, drives an electrical generator. Calculate the electrical energy produced from steam containing 400 000 kJ.

Energy converters

Energy converters enable one form of energy to be changed into another.

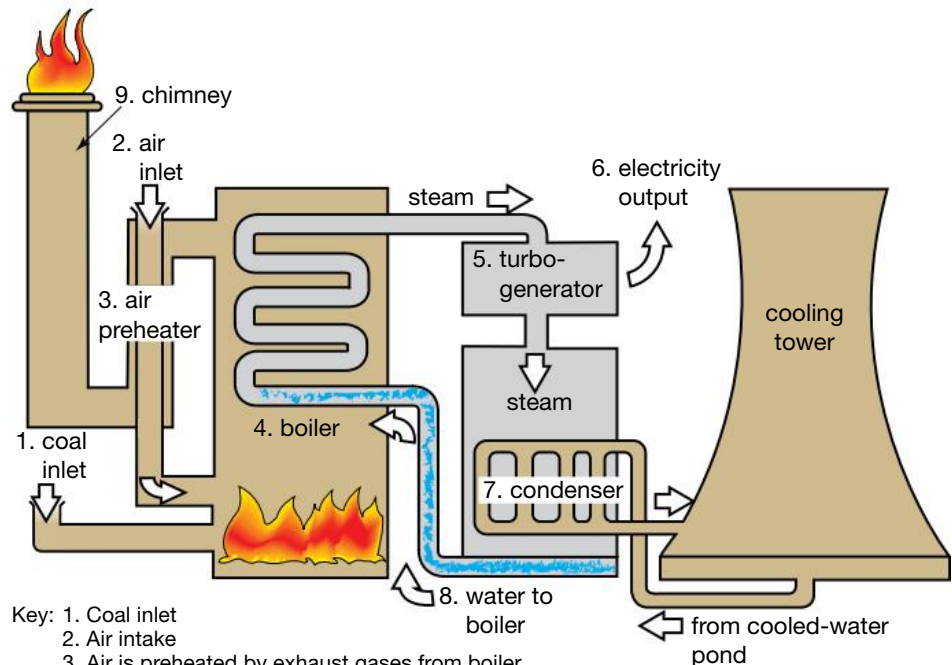
Plants

Plants take carbon dioxide from the air and water from the roots to effect the energy change in a process called photosynthesis. In addition to providing food for animals as a result of this process, they provide oxygen as a by-product of the reaction.



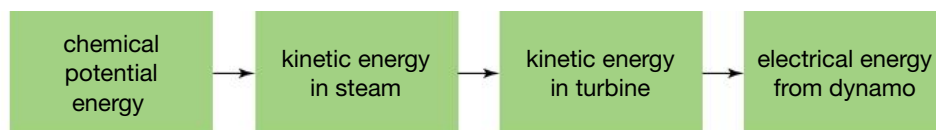
Plants act as energy converters. They change the heat and light energy from the Sun into chemical energy that is stored in the plant.

Power stations



- Key:
1. Coal inlet
 2. Air intake
 3. Air is preheated by exhaust gases from boiler.
 4. Water is converted to steam.
 5. Heat energy is converted to mechanical energy.
 6. Mechanical energy is converted to electrical energy.
 7. Hot water from condenser
 8. Steam from turbo-generator is cooled in condenser, then recycled to boiler.
 9. Waste products of combustion

When coal is burned, its stored chemical potential energy is converted into heat energy. This heat energy is used to convert water into steam, so heat energy is converted into kinetic energy. The steam flows past a turbine so the kinetic energy of the steam is converted into mechanical energy in the spinning turbine. The turbine is connected to a generator, which converts mechanical energy into electrical energy. Electrical energy may then be used in the home and in industry in a wide range of appliances.



Energy use in society

Global energy use

There is concern about the environmental effects of the use of fossil fuels.

About 80% of the world's energy requirements are provided by the fossil fuels coal, oil and gas. Australia has agreed to a pact with five other nations of the Asia-Pacific region (USA, Japan, South Korea, India and China) to collaboratively research more efficient and less polluting methods of generating power using fossil fuels.

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Unit 3

Classifying fuels

AOS 1

Summary screen and practice questions

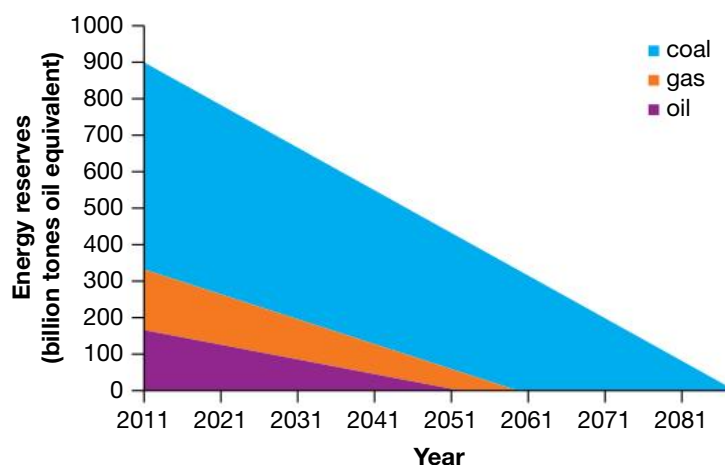
Topic 1

Concept 1

Renewable and non-renewable resources

About 95% of our energy requirements are provided by the fossil fuels coal, oil and gas. Australia has a diverse range of energy resources available, but the availability, abundance and relatively low cost of fossil fuels are the reasons that they are in high demand. About 75% of Australia's electricity generation is provided by black and brown coal, and 16% is supplied by natural gas. Access to these low-priced fuels is important for our manufacturing industry.

There is, however, extreme concern about the future use of fossil fuels. The combustion of fossil fuels releases gases that pose a threat to the environment. Carbon dioxide contributes to global warming, and sulfur dioxide contributes to acid rain. World reserves of fossil fuels are finite, and the fuels are being consumed at a much faster rate than they can be produced.



Projected depletion of world reserves of fossil fuels based on current usage

Non-renewable energy sources are those that are being used up faster than they can be produced. Renewable energy sources are those that can be produced at a faster rate than they are consumed.

Energy sources may be classified as non-renewable or renewable.

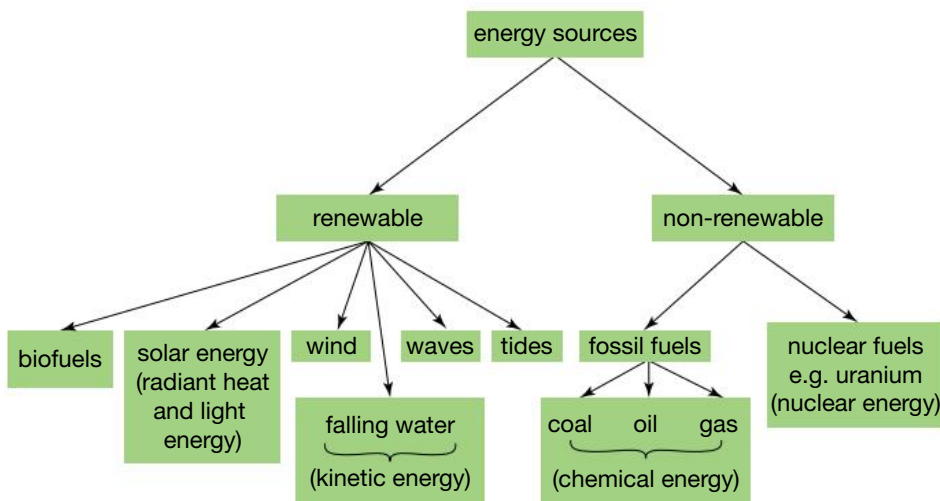
Non-renewable energy sources are those that are used up faster than they can be produced on Earth. Non-renewable energy sources include fossil fuels and nuclear energy sources. There is a limited supply of non-renewable energy sources on Earth.

Renewable energy sources are those that can be produced faster than they are used by society. Renewable energy includes solar energy, hydro-electricity, tidal power, wave power and geothermal energy. It also includes a group called biofuels. These are fuels that can be made from biological materials and include bioethanol, biodiesel and biogas.

Attention is increasingly being focused on the development of alternative renewable energy sources to provide our energy needs.



Uranium is a non-renewable energy source. Once its chemical energy has been converted to another form, it cannot be used again. In addition, only finite reserves of uranium exist — once it has been 'used up', it cannot be replaced. The rate of usage exceeds the rate of replacement for all non-renewable sources.



Renewable and non-renewable energy sources

Choosing energy sources

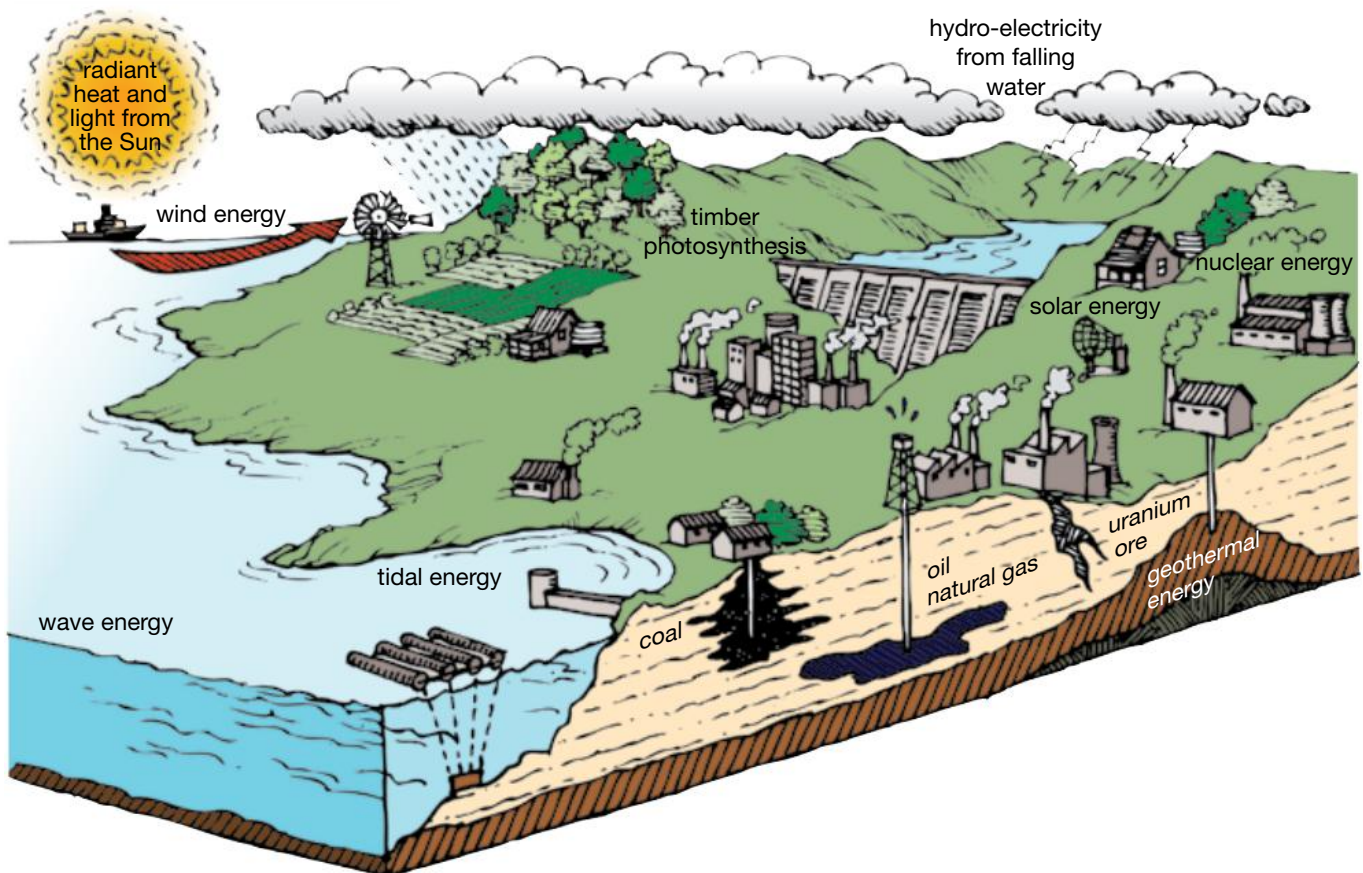
Although energy may be obtained from the direct combustion of fossil fuels, a more convenient form of energy is electricity. It can be carried from one place to another, it can be switched on and off, and it can be used as a source of energy for many different devices.

TABLE 1.2 Electricity production in Australia by energy source, 2014

Energy source	Production (GWh)
black coal	111 491
gas	51 053
brown coal	47 555
hydro-electricity	18 270
wind	7 328
oil	4 464
solar photovoltaic cells	3 817
bioenergy	3 151
geothermal	1

*Source: 2014 Australian Energy Update (Australian Government Bureau of Resources and Economics).

Sources of energy for society



Electricity is a secondary fuel because it is produced from other energy sources.

Electricity is sometimes described as a **secondary fuel**, since it is not a natural source of power; it is produced from other fuels or energy sources.

At present, most of Australia's electricity is generated by burning fuel at power stations. Fossil fuels could be made to last longer, and the environmental hazards of fossil fuel combustion could be decreased, if other ways of

generating electricity were used. One way is to use nuclear energy. Others involve wind, moving water, wave motion, falling water, tides and biomass reactions. Electricity may also be generated directly from chemical reactions, as in fuel cells, which are thought to be a possible energy source for the future. Photovoltaic (PV) cells are yet another method. Already these are becoming more and more popular as people install them on the roofs of their houses. PV cells convert solar energy into electrical energy. They can even feed excess electricity produced back into the grid.

Non-renewable fuels

Fossil fuels

Fossil fuels include coal, petroleum and natural gas.

As explained earlier, coal, petroleum and gas are called fossil fuels because they were formed from animals, trees and smaller plants that lived millions of years ago.

Coal was formed from the combined effects of pressure, temperature, moisture and bacterial decay on vegetable matter over several hundred million years. Decaying vegetation progressively became peat (very soft and mushy), lignite (crumbly brown coal), bituminous coal (hard black coal) and anthracite (very hard). Over this period, the moisture content dropped and the carbon content increased, so anthracite is the highest quality coal.



Electricity is known as a secondary fuel because it is produced from other sources of energy.

Petroleum and natural gas have their origin in marine life buried in the sediments of the oceans millions of years ago. Heat, pressure and the action of bacteria changed this residue into petroleum and natural gas.

Coal

Coal is the world's most plentiful fossil fuel. The main elements in coal are carbon (50–98%), hydrogen (3–13%), oxygen and very small amounts of nitrogen and sulfur. It also contains moisture and inorganic material that remains as ash when coal is burned. As coal was formed, it underwent changes in composition that made it a more efficient fuel.

study on

Unit 3

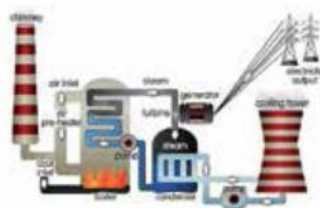
AOS 1

Topic 1

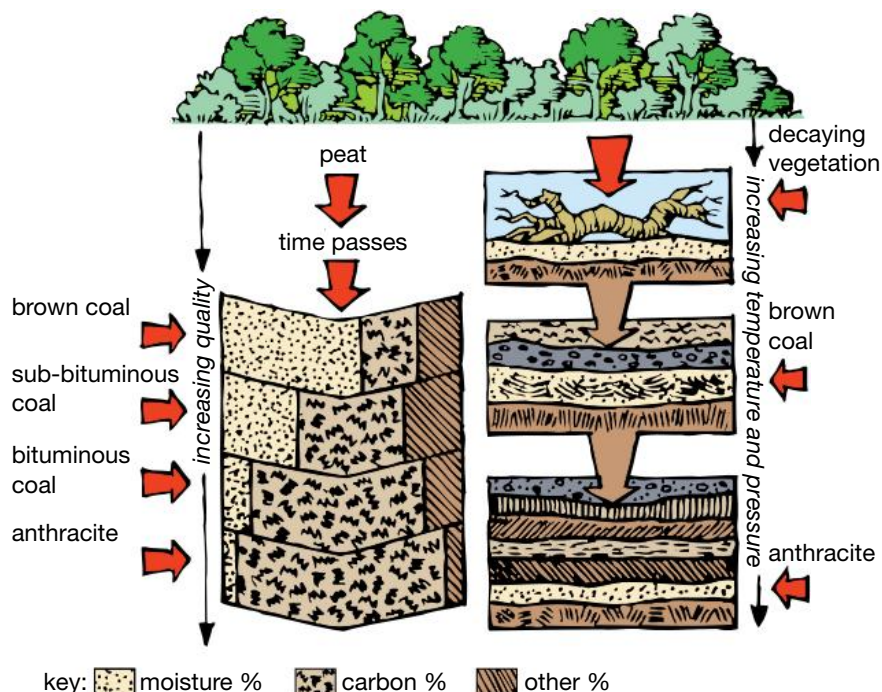
Concept 2



See more
Coal-fired
power station



Process of coal formation



Victoria generates most of its electricity from brown coal, which has about a quarter of the heat content of black coal. Brown coal can have up to 30% oxygen content, a relatively low carbon content (60–75% when dried), and a high moisture content (30–70%).

By a process called destructive distillation, coal can be converted into many useful products, such as briquettes for heating, coal gas, sulfur, ammonia, benzene, coal tar and coke. Coke is used in the reduction of Fe_2O_3 to iron.

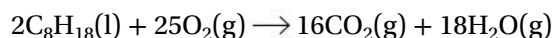
Traditionally, coal was burned in lumps, but ground coal powder is now used to improve the rate and efficiency of combustion.

In addition to electricity, coal may be converted into gas or liquid fuels. These can be transported and used more cheaply and conveniently than solid coal.

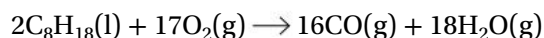
Petroleum

Petroleum (or crude oil) is a sticky, black substance composed of a combination of many different hydrocarbons. It must be *refined* before it can be used.

Octane, C_8H_{18} , is the major component of petrol and may burn in air to release energy according to the equation:



However, if the oxygen supply is limited, toxic carbon monoxide gas may be produced instead of carbon dioxide according to the equation:



Fuels obtained from petroleum include petrol, liquefied petroleum gas (LPG), diesel fuel, heating oil and kerosene. Petroleum is also the raw material for manufacture of a number of useful materials such as plastics, paints, synthetic fibres, medicines and pesticides.

LPG

Liquefied petroleum gas (LPG) is a hydrocarbon fuel that consists mainly of propane and butane. It is non-toxic, non-corrosive, lead-free and heavier

Petroleum, a mixture of hydrocarbons, is used to manufacture other fuels and many other chemicals.

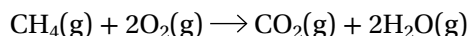
Natural gas, which is mainly methane, is a source of alkanes of low molecular mass.

than air. LPG is liquefied under pressure but when allowed to vaporise it expands to nearly 300 times its liquefied volume. This is why LPG can be stored as a compact liquid but burns as a dry, gaseous vapour. LPG is popular with many motorists, especially fleet-vehicle owners, because it is an economical energy source. Although LPG conversion costs for cars running on petrol are quite high, more people may make the conversion (or buy new cars designed to run on LPG) as petrol prices increase.

Natural gas

Natural gas is an important source of alkanes of low molecular mass. Victoria has large reserves of natural gas in the Gippsland basin. Typically, natural gas is composed of about 80% methane, 10% ethane, 4% propane and 2% butane. The remaining 4% consists of nitrogen and hydrocarbons of higher molecular mass. Natural gas also contains a small amount of helium and is one of its major sources.

Methane is the major constituent of natural gas and it burns with a hot, clean flame.



Since natural gas is lighter than air, it disperses in air. However, it is explosive in certain concentrations, so a safety measure incorporated by gas companies is to add an odour to natural gas so that leaks may be readily detected. Natural gas itself is odourless.

TABLE 1.3 Typical heat content values of some fossil fuels

Fossil fuel	Heat content	
	kJ g^{-1}	MJ/tonne
natural gas	54	54 000
petrol	48	48 000
diesel	45	45 000
black coal	34	34 000
brown coal	16	16 000

Coal seam gas

Coal miners have long been aware of the dangers of methane gas. Released from coal seams during underground mining operations, this gas has been responsible for many explosions and subsequent tragedies over the years. Methane gas, besides being found in association with petroleum deposits, is also a by-product of coal formation. It is often *adsorbed* onto the surface of coal deposits deep underground.

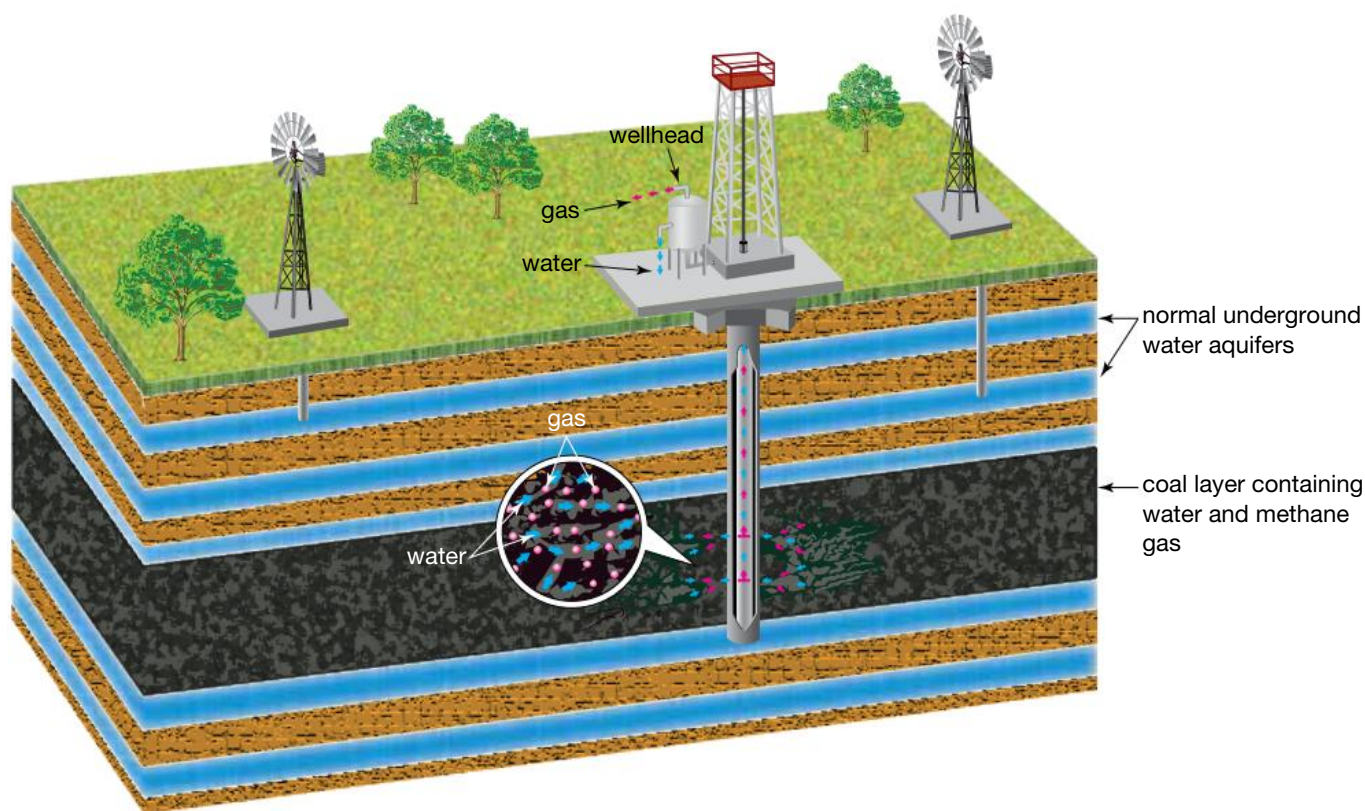
Coal seam gas (CSG), also called coal bed methane, is extracted by drilling deep wells into underground coal deposits. Such wells are typically 100 to 1500 metres deep and as such are below the level of aquifers used for bore water supplies in inland Australia. The coal seams are nearly always filled with water, which must be pumped to the surface to initiate gas production. This causes a reduction in pressure in the coal seam below and allows the methane to desorb from the coal. It is then brought to the surface along with more of the underground water through the drilled well.

Australia has large deposits of coal seam gas, which are now being extracted from the Bowen and Surat Basins in northern New South Wales and Queensland. The methane produced is relatively free from impurities, often containing only small amounts of ethane, nitrogen and carbon dioxide, and so requires

Coal seam gas is similar to natural gas. Its major constituent is methane.

only minimal processing. It is used in the same way as natural gas and also contributes to a growing LNG (liquefied natural gas) export industry.

Although the coal seam gas industry has shown enormous expansion since 1996, there are concerns from various groups concerning its environmental impact. These include farmers who worry that it may pollute aquifers that supply some of Australia's most economic farming land. Concerns have also been raised about some of the practices used to increase gas flow in wells using a process called 'fracking'.



Coal seam gas is produced from coal deposits that lie deep underground.

Revision questions

5. An examination of table 1.3 reveals that brown coal has a relatively low energy content. Why do you think brown coal is used on such an extensive scale to generate electricity in Victoria?
6. It is difficult to determine the total world reserves of fossil fuels. Estimates are constantly revised to take into account new discoveries, new information about known deposits and new techniques for extracting them. Conservation strategies will enable us to extend the 'life' of fossil fuels.
Discuss how each of the following factors affects the rate at which fossil fuels are used.
 - (a) Population growth rate
 - (b) Community awareness of the need for energy conservation
 - (c) Alternative technologies and fuel sources
 - (d) Fuel pricing policies, nationally and internationally
 - (e) Trade relations between nations
7. Fossil fuels took millions of years to form, yet they are likely to be used up within a few hundred years. Draw up a table with two columns.
 - (a) In the first column of the table, list the activities you do during a week that require energy from fossil fuels.

- (b) Assume that our supply of fossil fuels stops tomorrow. In the second column of the table, write down alternative ways in which your energy could be supplied for each of the activities you have listed.
- (c) How important are fossil fuels to your life?

Energy can be obtained from biomass (plant or animal matter) either in its unprocessed state or after converting it into gas or liquid fuels.

Bioethanol-blended fuel is more environmentally friendly than unblended petrol.

study on

Unit 3

Issues behind fuel choices

AOS 1

Summary screen

Topic 1

and practice

Concept 8

questions

Biodiesel is produced from vegetable oil or animal fats combined with an alcohol, usually methanol.

Biogas is produced from the bacterial breakdown of organic material in the absence of oxygen.

Biofuels

Biological matter obtained from plants or animal products that is used for cooking, heating, generation of electricity or automotive fuels is known as biomass. It can be used in its natural state or converted into a more easily handled gas or liquid form. In particular, bioethanol, biodiesel and biogas are in use in Australia as energy sources, although research into biofuels is ongoing.

Bioethanol is obtained by the fermentation of sugar from sources such as waste wheat starch and molasses, which is a by-product of sugar production. Up to about 10% anhydrous ethanol (E10) can be used as an additive to petrol without engine modification. Using ethanol-blended fuel has some advantages in that it reduces some pollutant emissions and is beneficial in reduction of greenhouse gases because production involves the use of a waste product. Environmentally, the presence of oxygen in the ethanol assists the complete combustion of the petrol. Emissions of CO and aromatic hydrocarbons are reduced. There are some disadvantages; for example, the cost of processing compared with petrol will need to be improved, and ethanol produces less energy per gram. Ethanol can contribute to the breakdown of some plastic and rubber parts in vehicles. In some countries there may be a dilemma concerning using land for food or fuel crops. Although burning ethanol puts back into the atmosphere carbon dioxide that was originally absorbed by photosynthesis, some carbon dioxide is released in the production of the ethanol.

Biodiesel fuels are alkyl esters manufactured from vegetable oil, such as canola, soyabean, sunflower, coconut and cotton seed, animal fats, such as beef tallow, sheep tallow and poultry oil, or used cooking oil. The oil or fat is combined with an alcohol in the presence of a catalyst. About 20% biodiesel (B20) can be blended with petroleum diesel as a transport fuel and so decreases our dependence on imported oil. Biodiesel is biodegradable, produces lower emissions of pollutants such as particulates and SO₂, and requires no engine modification even when used in unblended form. It has significant lubricant properties. On the negative side, it is economically unfavorable to produce and it emits more nitrogen oxides. The higher viscosity of biodiesel makes pure biodiesel (B100) unsuitable in colder climates. Planting of fuel crops requires large areas of land that could be used for food crops or may result in the destruction of natural habitats.

Biogas is sometimes called 'swamp gas' or 'marsh gas' and may contain up to 65% methane. It is a combustible fuel that is produced when animal waste or other organic material rots in the absence of oxygen, such as when rubbish has been buried underground, or in digestive processes of mammals that involve the breakdown of food by bacteria in the gut.

Biogas can be produced on a large scale and used as an energy source to generate electricity, light, heat, motion and fuels such as ethanol. The most common material used for biogas production is livestock manure. The manure is fed into an airtight 'digester' where it is allowed to ferment. The biogas produced is then collected and stored in a tank.

In addition to its use as a fuel in powering furnaces, heaters and engines, biogas can be used to generate electricity. Compressed biogas can also be used to fuel vehicles, and the residue from a biogas digester can be used as a fertiliser.

Biogas is a useful energy source.

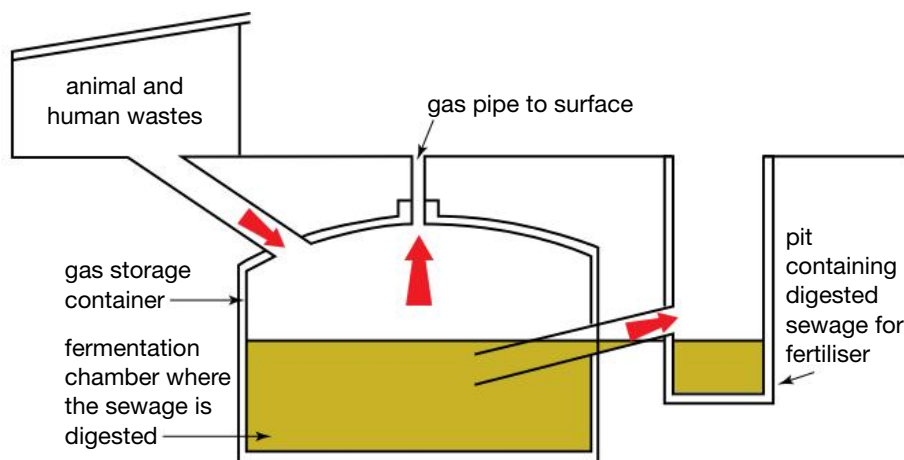


TABLE 1.4 Typical heat content of some renewable fuels

Renewable fuel	Heat content	
	kJ g^{-1}	MJ/tonne
Bioethanol	30	30 000
E10*	44	44 000
Biodiesel	42	42 000
Biogas	26	26 000

*a blend of normal petrol with 10% ethanol

Revision question

8. Using criteria such as molecular structure, combustion products, renewability, energy content and environmental issues, compare petrol with ethanol as a fuel for cars. Present your findings as a table.

Petrodiesel versus biodiesel — comparing fuels

After petrol, diesel is the most widely used transport fuel in the world. Traditionally used in larger scale engines such as those in boats, trucks, trains and buses, it is now becoming more and more popular as an alternative fuel for the smaller engines found in cars. Diesel engines, although heavier and initially more expensive, are more efficient than their petrol counterparts, have better fuel economy and tend to last longer. They produce less power than petrol engines of the same size but more torque. This makes them slower to accelerate but they are ideal for hauling heavier loads. Biodiesel can easily be substituted, either straight or blended with petrodiesel, as a fuel for diesel engines and requires little or no modification to the engine.

Producing petrodiesel

You may remember from Unit 1 that fuels such as petrol and diesel, as well as many other useful chemicals, are obtained from refining crude oil. One of the most important steps in this process is the first step — separation of crude oil into fractions based on boiling temperatures. As boiling temperature is related to molecular size, this represents a 'rough sorting out' according to the sizes of

study on

Unit 3

AOS 1

Topic 1

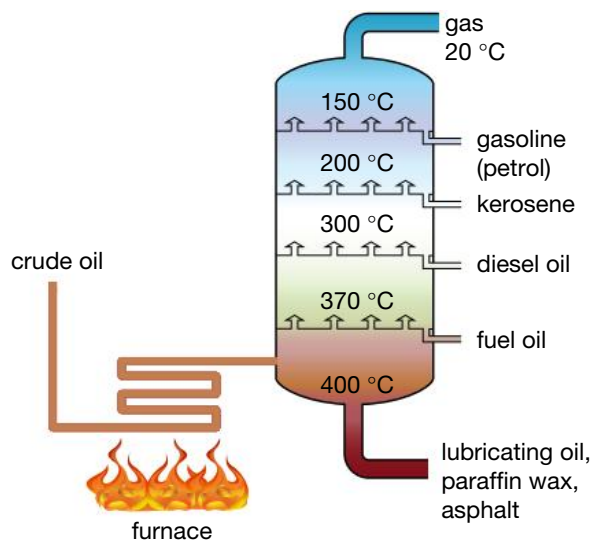
Concept 9

Comparing transport fuels

Summary screen and practice questions

Petrodiesel is produced from crude oil by fractional distillation. It is a non-renewable fuel.

the molecules that make up the crude oil. This process is known as fractional distillation (or fractionation). Petrodiesel contains alkanes with 12–24 carbon atoms per molecule.



Diesel fuel is one of many products obtained from fractional distillation of crude oil.

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Digital document

Experiment 1.1 Fractional distillation of an ethanol/water mixture

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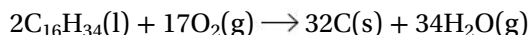
Fractional distillation is performed in tall towers that are cooler at the top than at the bottom. The crude oil is heated and then introduced to the base of the tower. At this point, many of its components vaporise. These vapours rise up the tower, being cooled as they do so. When they reach a point at which the tower's temperature equals their boiling temperature, condensation occurs. Specially designed trays containing bubble caps are placed inside the tower at strategic intervals. These are designed to allow the vapours to continue rising but stop condensed fractions from dripping back down to lower levels in the tower. The condensed fractions may then be removed from these trays to undergo further processing. The diagram at left shows a simplified outline of this process.

Combustion

As crude oil is mostly a mixture of alkanes, so too is the petrodiesel component obtained from it. Its combustion, therefore, follows the typical pattern of an alkane. In the presence of sufficient oxygen, carbon dioxide and water are produced. For example, hexadecane, $C_{16}H_{34}$, burns according to:



Other products of combustion include sulfur dioxide (from sulfur impurities), nitrogen oxides, carbon monoxide and particulate carbon (soot). The latter two are produced in situations where insufficient oxygen is present. Soot is often seen as 'black smoke' under conditions of heavy acceleration or when engines are poorly tuned. The following equation illustrates how less oxygen is required to make particulate soot.



In the past decade, however, considerable advances in both engine technology and fuel quality have led to a significant reduction in all of these emissions. Two such examples are: the introduction of ultra-low-sulfur diesel (ULSD), which not only lowers emissions of sulfur dioxide but also allows for more sophisticated pollution control measures in the engine itself; and the introduction of computer-controlled, self-cleansing exhaust filters designed to remove soot.



Sights such as this are becoming less frequent as modern engines and fuels reduce undesired emissions.

Other considerations

Besides the effects on the environment of exhaust emissions, other environmental considerations are associated with the use of petrodiesel (as there is with other petroleum-based fuels). The extraction of crude oil can cause significant degradation to the immediate environment, and its subsequent transportation, especially by sea, has resulted in a number of significant, environmentally damaging spills. The refining process can release hydrocarbons into the air. Vehicle exhaust emissions may also contain unburned hydrocarbons and, under the right conditions, which are often found in large cities, these can react to form photochemical smog. To this must also be added the emissions involved in the transport of both the crude oil and its petrodiesel product.

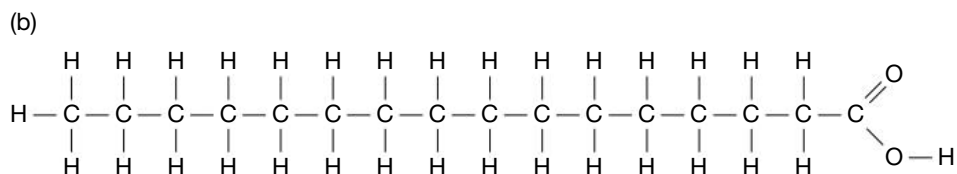
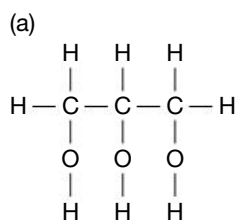
Biodiesel production

Biodiesel is a diesel alternative that can be made from plant oils and animal fats. Typical sources include canola, palm oil and animal tallow. It can also be made from used cooking oil, such as from restaurant fryers. The CSIRO has estimated that Australia could reduce its petrodiesel demand by 4-8% if all current sources of plant oil, tallow and waste cooking oil were used.

Oils and fats are naturally occurring esters formed between long-chain carboxylic acids (known as fatty acids) and a particular alcohol — glycerol.

TABLE 1.5 Formulas of some fatty acids

Name	Formula
palmitic	$C_{15}H_{31}COOH$
palmitoleic	$C_{15}H_{29}COOH$
stearic	$C_{17}H_{35}COOH$
oleic	$C_{17}H_{33}COOH$
linoleic	$C_{17}H_{31}COOH$
linolenic	$C_{17}H_{29}COOH$



Structures of (a) glycerol and (b) a typical fatty acid

Biodiesel is produced by reacting oils or fats (also called triglycerides) with an alcohol. Although a number of small alcohols can be used, the most common is methanol. Heat and either concentrated sodium or potassium hydroxide, which acts as a catalyst, are used in this process. It can be made on a small scale, using homemade equipment or with specially purchased kits, or on a much larger scale for commercial distribution. The chemical reaction involved turns one type of ester into another and is called **transesterification**. A typical transesterification is shown on the next page.

Revision questions

9. Name the fatty acid that the biofuel molecule was made from in the equation at the bottom of page 20.
10. Write the formula for biodiesel if it is produced from palmitic acid and methanol.
11. As is the case with petrodiesel, carbon monoxide may be produced if combustion occurs with insufficient oxygen.
 - (a) Write the equation for the combustion of the product in question 10 in plentiful oxygen.
 - (b) Write the equation for the combustion of the product from question 10 in limited oxygen.

Environmental issues

Biodiesel appears to be an excellent substitute for petrodiesel. It can be used in diesel engines with little or no modification. It also aids in engine lubrication and can clean engines of built-up deposits that result from the long-term use of petrodiesel. Emissions from a biodiesel-fuelled engine are similar to those from a petrodiesel one but are generally lower in quantity, the exception being nitrogen oxides, which may be slightly higher. As manufacturers strive to meet more stringent emission standards, it is anticipated that more petro- and biodiesel blends will be recommended.

Deforestation for palm oil plantations is endangering the habitat of the Sumatran orangutan.



Two additional environmental positives of biodiesel are that it is biodegradable, and it can be produced from a waste product, notably used cooking oil. In Australia, the main feedstocks are oil seeds such as canola, used cooking oil and tallow. However, as demand increases, new economical sources will need to be found. Elsewhere in the world, soybeans and sunflower seeds, as well as palm oil, are the main sources being used to meet this demand. However, there are some environmental concerns. There is the debate about land use — should crops be grown for food production or fuel production? In southeast Asia, massive deforestation is occurring to make way for palm oil plantations and is endangering the habitats of many species, the best known of which is the Sumatran orangutan.

Two possible ways of overcoming these issues are the use of algae and the use of seeds from jatropha trees. Research is being undertaken into the development of algae as an oil source. It is envisaged that such algae could grow in low-quality water bodies and maybe even the ocean. Seeds from the jatropha tree are being investigated due to their high oil content. Jatropha trees can be grown in marginal agricultural land and require minimal cultivation and irrigation. Additionally, they do not have to be replanted from season to season. Both of these possibilities would overcome the conflicting issues of whether to use land for food or fuel.

Technical issues

Two major technical issues facing the introduction of biodiesel are that it is hygroscopic and it can gel at low temperatures. To some extent, these also affect petrodiesel, but, due to multiple feedstocks, they have the potential to be a greater problem with biodiesel. If a substance is hygroscopic, it absorbs water vapour from the air. If biodiesel is poorly processed and contains partially converted mono- and diglycerides, this property is enhanced. If significant, this can affect engine life as it allows microbes to grow in the fuel. It also accelerates gelling and reduces the energy liberated upon combustion. Gelling at low temperatures is a major problem but is somewhat dependent on the

TABLE 1.6 Approximate yields of some biodiesel oil sources

Oil source	Yield (L/ha)
algae*	47 000–140 000
palm oil	5900
jatropha	1900
canola	1200
sunflower	950
safflower	800
soy	450

*estimate; depends on species

type of oil used in the original manufacture. Gelling increases viscosity of the fuel, reducing or even preventing its flow along fuel lines and through diesel injectors. A number of potential solutions to this problem are being investigated including blending it with petrodiesel, additives to lower the gel point, special fuel tanks that are heated as the car warms up and special reserve tanks containing petrodiesel for starting and warming up the engine.

TABLE 1.7 Comparison of petrodiesel and biodiesel

Property	Petrodiesel	Biodiesel
sources	petroleum	- used cooking oil, tallow, oil seed crops such as canola, palm oil - oil from algae is possible - methanol production requires fossil fuels but production of methanol from glycerol (a by-product) currently under investigation
chemical structure	alkanes, both straight-chain and branched (typically containing 12–24 carbon atoms per molecule)	- esters from long-chain fatty acids (typically 15–20 carbon atoms per molecule) and methanol - other simple alcohols
combustion products	carbon dioxide, water, carbon monoxide, particulate carbon (soot), sulfur dioxide, nitrogen oxides	- same as petrodiesel but generally lower in quantity - may be increased emission of nitrogen oxides
viscosity	hygroscopic, but not generally an issue as seasonal blending allows for changes in outside temperature	hygroscopic and low outside temperatures; can lead to increased viscosity due to fuel gelling
environmental impact	- non-renewable - non-biodegradable - spills in transportation of both crude oil and refined products - combustion emissions in transportation chain	- renewable - biodegradable - issues with growing crops for food versus fuel - deforestation issues, especially in southeast Asia



Cattle and other livestock release significant amounts of methane into the atmosphere as a result of their digestive processes (mostly through belching).

Energy use and the environment

The effect of use of fossil fuels on the environment

Fossil fuels make up over 95% of the energy resources used in Australia today. There is great concern that their use has led to a number of environmental problems, particularly the enhanced greenhouse effect and acid rain.

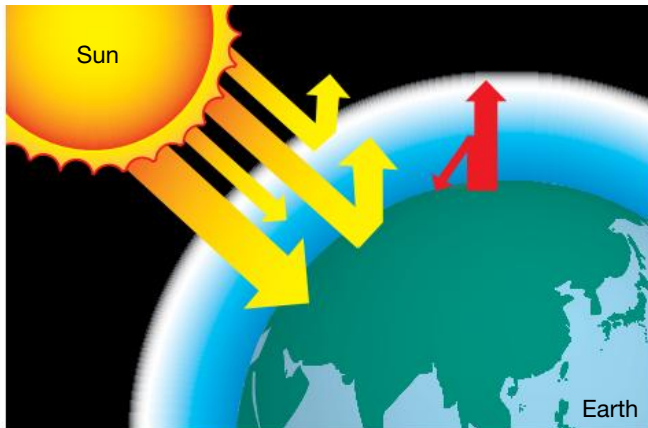
Greenhouse effect

Radiation from the Sun strikes the Earth and warms its surface. The warm surface then radiates heat energy back into space. Gases in the atmosphere known as **greenhouse gases**, including carbon dioxide, CO₂, methane, CH₄, nitrous oxide, N₂O and ozone, O₃, absorb some of this heat radiation, so the air warms up. The air may also radiate this energy back into space or down to Earth. This helps to keep the Earth at the appropriate temperature to support life and is called the **greenhouse effect**. Unfortunately, human activities

have led to an increase in the amount of greenhouse gases, so that more heat is absorbed, which has adversely affected weather and climate. This results in an **enhanced greenhouse effect**, causing **global warming**.

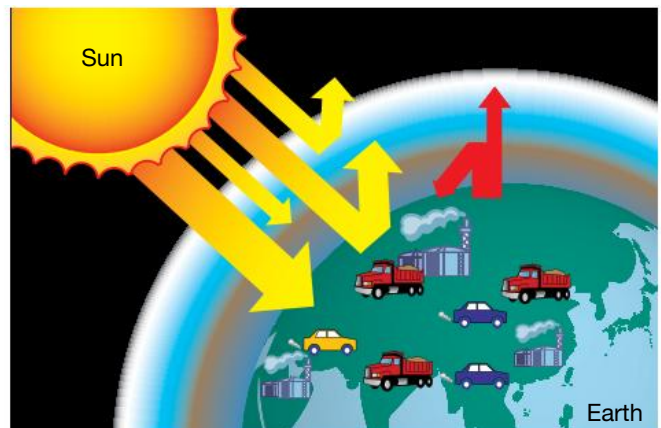
Some gases can absorb more energy than others. Such gases are known as greenhouse gases and contribute to global warming in the atmosphere. Carbon dioxide is the major greenhouse gas emitted by human activities in Australia and is generated during transportation, industrial processes, land use change and energy production.

Greenhouse effect



When light energy from the Sun reaches the Earth's surface, it is converted to heat energy, and this is radiated back into the atmosphere. Greenhouse gases absorb some of this heat energy, keeping the Earth's temperature relatively constant. Life on Earth depends on this heat.

Enhanced greenhouse effect



Excess production of greenhouse gases means that the atmosphere retains more heat energy. This increases the average temperature of the Earth, which will affect the Earth's climate.

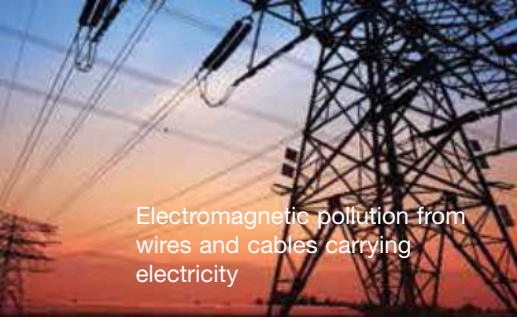
Carbon dioxide is essential to life as plants absorb it, enabling them to manufacture their own sugars through photosynthesis. The quantity of carbon dioxide on Earth has remained almost constant for many thousands of years but now we are producing more than can be converted back into oxygen and simple organic molecules. As the quantity of carbon dioxide increases, the amount of heat that is retained by the atmosphere increases, thereby contributing to the greenhouse effect.

When comparing the burning of fossil fuels with biofuels, at first glance it might appear that both contribute to the greenhouse effect as both produce carbon dioxide upon combustion. However, it must be remembered that, when a fossil fuel is burned, it is putting carbon into the atmosphere that has been locked away underground for many millions of years. The carbon in biofuels, however, has been obtained from the atmosphere much more recently via photosynthesis (and perhaps the subsequent eating of plant materials by animals). As such it is merely 'putting back what it recently took out'. Theoretically, this carbon dioxide will once again be removed when the next source crops for the biofuel are grown. This is described as being 'carbon neutral'.

Acid rain

Acid rain results from the reaction between rainwater and sulfur dioxide that is released into the atmosphere.

Many industrial processes burn coal, oil or some other fossil fuel. Many of these fuels contain sulfur in varying amounts. When sulfur is burned in air, it forms sulfur dioxide, SO_2 . This gas is often released into the air in vast quantities.



Electromagnetic pollution from wires and cables carrying electricity

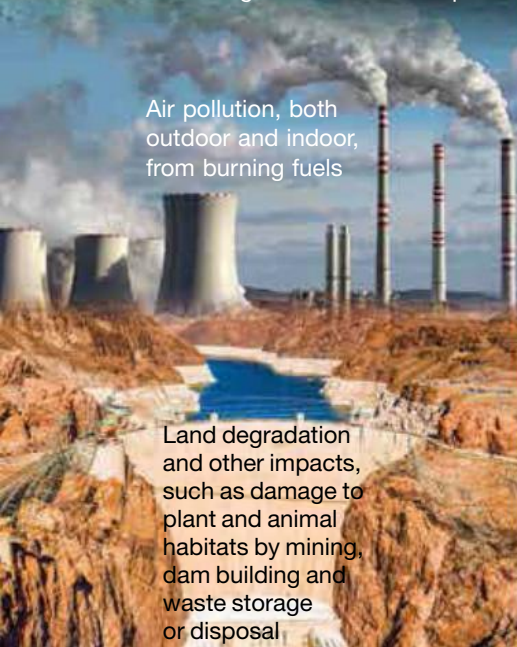


Radioactivity and fallout from the nuclear fuel cycle



Birds diving for fish become coated and die slowly as they ingest spilled oil while preening.

Water pollution from energy conversion processes, leakage from waste storage and accidental spills

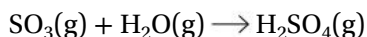
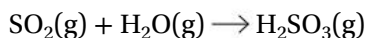


Air pollution, both outdoor and indoor, from burning fuels

Land degradation and other impacts, such as damage to plant and animal habitats by mining, dam building and waste storage or disposal

Sulfur dioxide is released in many natural processes as well. In particular, active volcanoes release a large amount of sulfur dioxide into the air. The atmosphere can cope with large quantities of sulfur dioxide if the gas is given time to disperse. When a large number of industries are all producing the gas over a small area, it cannot disperse in the air fast enough and becomes too concentrated to be safe.

Sulfur dioxide reacts with water to become sulfurous and sulfuric acid. So, when it rains, the rain is no longer a mild carbonic acid solution but contains enough sulfuric acid to make it dangerous to plant and animal life.



Other gases contribute to the acid rain problem and many of these are produced by industry.



In heavily industrialised countries, entire forests have been denuded by the effects of acid rain. Our energy use is responsible for more than half of the greenhouse emissions and widespread pollution of land, sea and air. These environmental impacts threaten our quality of life and, perhaps, existence.

Sustainable energy

A **sustainable energy** future means providing for the needs of today's society without compromising the ability of future generations to meet their own needs. Various responses have been proposed to meet society's increasing energy demands. These include:

- promoting energy conservation in the domestic, commercial and industrial sectors
- funding research into producing viable alternative energy sources
- decreasing our dependence on coal by using more renewable sources
- increasing the efficiency with which energy is produced from each resource
- developing technologies to reduce emissions when using fossil fuels.

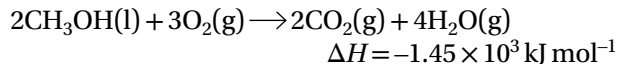
The availability of low-cost, clean and reliable energy will improve land, air and water quality, increase employment and promote health.

Major energy-related environmental issues

TABLE 1.8 Advantages and disadvantages of some common fuels

Energy source	Advantages	Disadvantages
natural gas	• high efficiency • some Australian sources • moderate cost	• non-renewability • pollution
oil	• ease of transportation • wide range of uses • some Australian sources	• non-renewability • limited world supplies • pollution
coal	• large Australian reserves • source of revenue via exports • easily mined	• non-renewability • contributes to air pollution, acid rain and global warming
biogas	• renewability • productive use of wastes	• energy inefficiency • low supplies
bioethanol and biodiesel	• renewability • less harmful emissions	• possible conflict in land use • low temperatures can be problematic for biodiesel

5. Methanol can be burned as a fuel and its heat output can be described by the following thermochemical equation.



The predicted heat output from the combustion of 3.20 g of methanol would be:

- A 72.5 J
B 7.25 kJ
C 72.5 kJ
D 7250 kJ.
6. The energy conversions that occur in a coal-fired power station may be best represented as:
A chemical energy to thermal energy to mechanical energy to electrical energy
B chemical energy to mechanical energy to thermal energy to electrical energy
C chemical energy to mechanical energy to electrical energy to thermal energy
D chemical energy to electrical energy to mechanical energy to thermal energy.
7. One of the criteria for the choice of fuels is the amount of heat released on combustion per gram of fuel. On this basis, which of the following would be the best fuel?

	Heat of combustion (kJ mol ⁻¹ of reactant)
A H ₂	238
B CO	284
C CH ₃ CH ₂ OH (ethanol)	1371
D C ₈ H ₁₈ (<i>n</i> -octane)	5447

8. A device converts 85 MJ of input energy into 50 MJ of useable output energy. The efficiency of this device is closest to:
A 50%
B 60%
C 64%
D 85%.
9. The overall efficiency of the photosynthetic process can be as low as 1%. This means that:
A photosynthesis is a very efficient process
B for every 200 J of solar energy received, 1 J of chemical energy is stored in the products
C photosynthesis requires other energy sources in addition to solar energy
D 99% of the solar energy received by plants is not used for photosynthesis.
10. Which of following lists shows fuels in order of increasing energy output, as measured in kJ g⁻¹?
A Brown coal, biogas, bioethanol, petrol
B Biogas, biodiesel, bioethanol, natural gas
C Brown coal, diesel, black coal, petrol
D Diesel, biodiesel, petrol, bioethanol

11. In which of the following situations might a biogas generator be built?
A As part of a sewage treatment works
B As part of a piggery
C As part of a dairy farm
D All the above
12. Worldwide, bioethanol is the most widely produced biofuel. It is often blended with petrol as a transport fuel, but it can be used pure in some situations. Which of the following statements is true?
A Bioethanol has a higher energy output than petrol.
B Many of the crops used to produce bioethanol are also food crops.
C Although bioethanol is a renewable fuel, it produces more harmful emissions.
D When blended with petrol, cars get better fuel consumption than with petrol alone.
13. A hygroscopic substance is a substance that:
A absorbs heat
B evolves heat
C evolves water
D absorbs water.
14. When petrodiesel is compared with biodiesel in terms of their chemical components, it can be said that:
A both consist of alkanes
B petrodiesel consists of alkanes whereas biodiesel consists of esters
C petrodiesel consists of esters whereas biodiesel consists of alkanes
D both consist of esters.
15. When biofuels are burned, the carbon dioxide produced:
A puts carbon atoms back into the atmosphere that were only recently removed
B puts carbon atoms back into the atmosphere that were removed millions of years ago
C puts oxygen atoms back into the atmosphere that were removed millions of years ago
D puts carbon atoms back into the atmosphere at a slower rate than when an equivalent amount of fossil fuel is burned.

Review questions

Energy and fuels

- (a) What is a fuel?
(b) Give four examples of fuels that you have used in the last week.
- What are the characteristics of a good fuel for:
(a) heating the home
(b) vehicle propulsion?
- Fuels, and energy sources in general, may be classified as either renewable or non-renewable.
(a) Define the terms 'renewable' and 'non-renewable' as they apply to this context.

- (b) Are all biofuels renewable? Explain.
- (c) Are renewable energy sources always biofuels? Explain.
- 4. Propane is often used as a fuel for camping stoves. In an experiment to determine its heat content, 2.70 g was found to evolve 135 kJ of heat energy when burned in a plentiful supply of oxygen.
 - (a) Write a balanced thermochemical equation describing this reaction.

Devices such as these often come with a warning to not operate them in enclosed spaces. In such situations, the supply of oxygen may be limited.

 - (b) Write a balanced equation for the combustion of propane in a limited supply of oxygen.
 - (c) How would the ΔH value for the equation in (b) compare with the one in (a)? Explain.
 - (d) Explain exactly why the operation of such a stove in an enclosed space is so dangerous.

Energy transformations

- 5. A fire is started at a campside fireplace by striking a match and lighting a piece of crumpled newspaper under a pile of dry twigs. Explain the energy transformations in this process.
- 6. Explain why the overall energy efficiency of a coal-fired power station that generates electricity is said to be only 30% efficient.
- 7. Describe the energy transformations occurring in each of the following situations.
 - (a) Bell ringing
 - (b) Battery lighting a torch
 - (c) Striking a match
 - (d) Inverting an egg timer
 - (e) Rubbing hands together on a cold day
 - (f) Pendulum swinging
 - (g) Thunder and lightning
 - (h) Starting a clockwork toy
- 8. A waste management/energy project near Ballarat uses organic waste from local piggeries to produce biogas (methane and carbon dioxide). The biogas is then converted to heat and electricity.
 - (a) Outline the energy changes in the conversion of organic waste to heat and electricity.
 - (b) Initial proposals for construction of the project were rejected by the local council. On what grounds could the council object to such a scheme?
 - (c) How could the success of such a scheme be gauged?
- 9. The Law of Conservation of Energy states that energy can neither be created nor destroyed. Explain how an energy conversion process that is only 85% efficient does not contravene this law.
- 10. (a) Outline the energy transformations that occur in a fossil-fuel thermal power station.
 - (b) Name two fossil fuels that are currently used in fossil-fuel power stations.
 - (c) Name one renewable fuel that is currently used in some thermal power stations.
- 11. A power station using brown coal as its fuel consumes 40 000 tonnes of coal per day. If it generates an average of 27.8 GWh of electricity per day, calculate its overall efficiency. (Heat energy evolved by 1.000 tonne brown coal = 6.7 GJ; 1 kWh = 3 600 kJ.)

Fuel choices

- 12. (a) What is a fossil fuel?
 - (b) Give at least three examples of fossil fuels.
- 13. 'Coal, gas and oil should be made more expensive to deter people from wasting them.' Discuss this statement, offering at least two arguments for and against the proposal.
- 14. (a) What is a biofuel?
 - (b) Give three examples of biofuels.
- 15. Search the internet and any other suitable resources to find the advantages and disadvantages of ethanol and petrol as transport fuels. Present your findings in the form of a table.
- 16. Repeat question 15 for petrodiesel and biodiesel.
- 17. Coal seam gas has become a significant energy source in Australia since the year 2000.
 - (a) Is coal seam gas a renewable or non-renewable energy source?
 - (b) Describe how coal seam gas is obtained.
 - (c) Which gas is the main component of coal seam gas?
 - (d) List two environmental concerns associated with the production of coal seam gas.

Energy use and the environment

- 18. Fossil fuels may be used to produce electricity.
 - (a) Explain how energy waste may occur in the conversion of fossil fuels to electricity.
 - (b) Explain how energy waste may occur in the use of electricity in the home.
- 19. (a) Assuming that each kilowatt hour of electricity produces about 1.44 kilograms of carbon dioxide, examine your family's electricity bills and determine how much carbon dioxide your family produces annually.
 - (b) Explain why the production of carbon dioxide may lead to environmental problems.
 - (c) Suggest three ways in which your family could decrease electricity use to contribute to the minimisation of carbon dioxide release into the atmosphere.

- 20.** In a fuel efficiency test, the percentage of petrol wasted due to incorrect handling techniques and altered car conditions was calculated for a particular car.

Altered variable	Percentage use
speeding	14
overloaded car	15
roof rack	10
soft tyres	5
poor tuning	28

The car has a fuel consumption of 15.0 km per litre of fuel. Assuming that the fuel costs 130 cents per litre, calculate how much money would be wasted on a 100 km trip, assuming that a driver exceeded the speed limit for a quarter of the journey and that the car was poorly tuned, overloaded and had soft tyres and a roof rack.

- 21.** Find out about the 'greenhouse effect' with respect to the use of different energy sources.
- 22.** You have been invited to debate the statement 'The world should stop using fossil fuels and replace their use with biofuels.'
- (a) Outline three environmental or societal issues you would argue if you were in favour of this statement.
 - (b) Outline three environmental or societal issues you would argue if you were against this statement.
- 23.** Fossil fuels and biofuels all undergo combustion to release carbon dioxide. Explain why the combustion of fossil fuels contributes to the enhanced greenhouse effect, whereas the combustion of biofuels does not.
- 24.**
- (a) Define the terms 'biodiesel' and 'petrodiesel'.
 - (b) State one disadvantage of using biodiesel in cold climates.
 - (c) Give one environmental advantage of increasing the usage of biodiesel.
 - (d) Give one environmental disadvantage that an increased usage of biodiesel may lead to.



Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

1. Methane gas is used as a fuel in many industrial and domestic situations. Sources of methane include biogas, natural gas and coal seam gas.

(a) Write an equation for the combustion of methane in excess oxygen. **1 mark**

(b) Methane may be classified as both a renewable and a non-renewable resource. Explain this using the information provided above. **2 marks**

In certain situations, the burning of methane may produce carbon monoxide gas.

(c) Under what conditions might this occur? **1 mark**

(d) Write an equation for the combustion of methane to produce carbon monoxide. **1 mark**

(e) Why is the production of carbon monoxide undesirable? **1 mark**

2. Biodiesel is a fuel that is steadily gaining popularity as an alternative to petrodiesel. It is produced by a process called transesterification. Another chemical is also produced.

(a) Define the term 'transesterification'. **1 mark**

(b) A sample of biodiesel is analysed and found to consist only of methyl stearate. With the aid of suitable molecular diagrams, show how this would have been made. You should make mention of any special reaction conditions required. **6 marks**

(c) Write the equation for the combustion of methyl stearate in excess oxygen. **3 marks**

(d) Name the other chemical produced by transesterification. **1 mark**

(e) To what class of organic compounds do the majority of molecules in petrodiesel belong? **1 mark**

(f) Give one advantage and one disadvantage associated with the use of biodiesel as a fuel. **2 marks**

2 Energy calculations

'Energy is neither created nor destroyed; it can only be converted from one form to another'; this is one of the famous laws of thermodynamics. Energy powers the way we live, but where does this energy come from? The most concentrated form of energy is held in the bonds of chemicals we live with every day. How can we determine the best choices for fuels to produce this energy? How can we make quantitative predictions that match energy requirements to fuel quantities?

YOU WILL EXAMINE:

- the meaning of enthalpy and the ΔH notation
- energy profile diagrams for exothermic and endothermic reactions
- thermochemical equations and subsequent calculations that can be made using them
- the calculation of the ΔH value for a reaction and from experimental data
- the kinetic molecular theory of gases
- the concept of gas pressure and common units used to measure it
- the absolute (or Kelvin) temperature scale
- Boyle's law and Charles' law
- standard conditions for measuring gas volumes and molar volume
- the universal gas equation
- mass-volume and volume-volume stoichiometry
- the calculation of greenhouse gas amounts associated with the production of energy from carbon-based fuels
- how ΔH values may be estimated from simple laboratory apparatus.



Many modern homes and buildings use 'burning log' fireplaces for their heating. Such fireplaces do not burn logs at all — they merely give the illusion that they are. In many cases, their heat output comes from fuels such as ethanol, natural gas and LPG. In designing such fireplaces, it is important to know the energy output of the chosen fuel so that combustion can produce the required amount of energy. It is also important to control the fuel to oxygen ratio so that unwanted and dangerous combustion products, such as carbon monoxide, are avoided.

Energy changes in chemical reactions

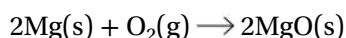
The energy changes that accompany chemical reactions are vital to us. To survive, we depend on the energy content of the food we eat. Our bodies can convert the energy of the chemical bonds in food into other kinds of energy. The quality of lifestyle we lead depends on harnessing energy from different chemical sources, including coal, oil, natural gas and renewable fuels. The study of the energy changes that accompany chemical reactions is called **thermochemistry** or **chemical thermodynamics**. In general, all chemical reactions involve energy changes. The chemical energy stored in a substance has the potential to be converted to heat (which will be discussed in this chapter) or electricity (see chapter 3).

A certain amount of chemical energy is stored within every atom, molecule or ion. This energy is the sum of the potential energy and kinetic energy of the substance and results from:

- the attractions and repulsions present between protons and electrons within the atom
- the attractions and, to some degree, repulsions present between atoms within a molecule
- the motion of the electrons
- the movement of the atoms.

The total energy stored in a substance is called the **enthalpy**, or **heat content**, of the substance and is given the symbol H . Unfortunately we cannot directly measure the heat content of a substance. What we can measure is the **change in enthalpy** when the substance undergoes a chemical reaction. Since, in virtually all chemical reactions, the energy of the reactants and products differ, such reactions usually involve some change in enthalpy, which is indicated by a temperature rise or fall. The change in enthalpy during a reaction is known as the **heat of reaction** and is denoted by ΔH .

Let us consider the following reaction:



Magnesium has a certain enthalpy. So too does the oxygen. The total enthalpy of the reactants — magnesium and oxygen — can be represented by the symbol H_r . The product, magnesium oxide, also has some enthalpy — call this H_p .

We can say that:

change in heat content = (heat content of products) – (heat content of reactants)

So, enthalpy change is equal to heat energy produced or absorbed.

$$\Delta H = H_p - H_r$$

The enthalpy change, or heat change, of a reaction depends on the amount of reactants used and the temperature of the initial reactants, compared with that of the final products. To remove these variables in enthalpy studies, the following conditions are assumed:

- the initial temperature of the reactants and final temperature of the products is the same, and is 25 °C
- 1 mole of the substance is involved
- solutions have a concentration of 1 M
- the heat absorbed or released is measured in kilojoules (kJ)
- the pressure is kept at 100.0 kPa.

These conditions are referred to as *standard laboratory conditions* (SLC).

Although the usual name for ΔH is heat of reaction (or change in enthalpy), there are some reactions for which specific names have been given.



A change in enthalpy occurs when magnesium burns.

Enthalpy is the heat content of a substance. It cannot be measured directly, but the change in enthalpy, known as the heat of reaction, ΔH , can be measured.

Enthalpy changes are stated at SLC; they refer to the energy needed to return the temperature to 25 °C and the pressure to 100.0 kPa.

- *Heat of solution* is the change in enthalpy when 1 mole of any substance dissolves in water.
- *Heat of neutralisation* is the change in enthalpy when an acid reacts with a base to form 1 mole of water.
- *Heat of vaporisation* is the change in enthalpy when 1 mole of liquid is converted to a gas.
- *Heat of combustion* is the enthalpy change when a substance burns in air, and is always exothermic.

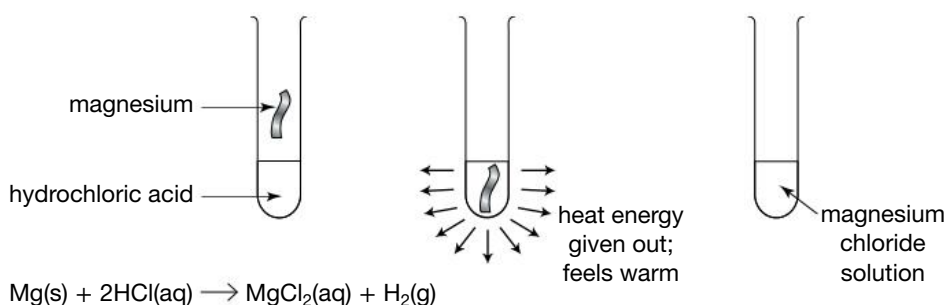


Exothermic and endothermic reactions

Chemical reactions accompanied by heat energy changes may be divided into two groups: exothermic reactions and endothermic reactions.

Exothermic reactions

Chemical reactions that release heat to the environment are called **exothermic** reactions.

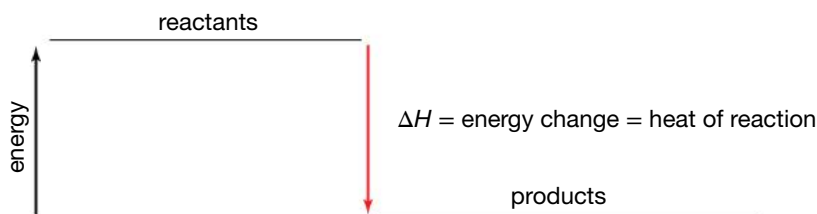


An exothermic reaction — magnesium ribbon dissolving in hydrochloric acid

Exothermic reactions release heat. The enthalpy change, ΔH , is negative.

When a strip of magnesium is placed in hydrochloric acid, heat is given out. This means that the enthalpy of the reactants, H_r , is greater than the enthalpy of the products, H_p . Therefore, the enthalpy change, $\Delta H = H_p - H_r$, is *negative*. The difference in energy between the reactants and the products is released into the environment, usually in the form of heat.

The energy change in a reaction can be drawn as an energy diagram or energy profile. Chemicals with more energy are drawn higher up and those with less energy lower down. The reactants are drawn on the left and the products are drawn on the right. The figure below is an energy diagram for an exothermic reaction.



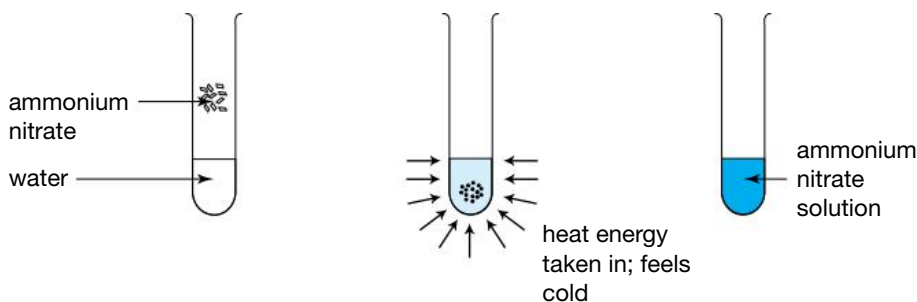
In an exothermic reaction, ΔH is always negative because the heat content of the reactants is greater than that of the products. The bonds in the products are more stable than the bonds in the reactants.

Endothermic reactions absorb heat. The enthalpy change, ΔH , is positive.

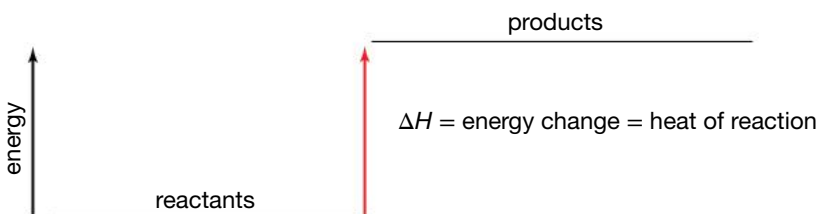
Endothermic reactions

Chemical reactions that absorb heat from the environment are called **endothermic** reactions.

An endothermic reaction — ammonium nitrate dissolving in water



When ammonium nitrate is dissolved in water, heat is absorbed from the environment; the test tube feels cold because the reaction takes in energy from the water and your hand. This means that the enthalpy of the products, H_p , is greater than the enthalpy of the reactants, H_r . Therefore, the enthalpy change, $\Delta H = H_p - H_r$ is *positive*. The difference in energy between the reactants and the products is absorbed from the environment. The figure below is an energy diagram for an endothermic reaction.



In an endothermic reaction, ΔH is always positive because the heat content of the reactants is less than that of the products. The bonds in the products are less stable than the bonds in the reactants.

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Experiment 2.1 Investigating heat changes in reactions

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Revision question

1. State whether the following are exothermic or endothermic processes.
 - (a) Water changing from liquid to gaseous state
 - (b) A reaction in which the total enthalpy of the products is greater than that of the reactants
 - (c) Burning kerosene in a blow torch
 - (d) Burning kerosene in a jet aircraft engine
 - (e) A chemical reaction that has a negative ΔH value
 - (f) A reaction in which the reactants are at a lower level on an energy profile diagram than the products

Thermochemical equations

A thermochemical equation is a balanced equation that includes the amount of heat produced or absorbed.

As we saw briefly in chapter 1, an equation that includes the amount of heat produced or absorbed by a reaction is a **thermochemical equation**. As with other chemical equations, charge and mass must balance. However, they must also include the enthalpy change.

In writing a thermochemical equation, the following points should be remembered:

- A positive or negative sign must be included with the ΔH value to indicate whether the reaction is either endothermic or exothermic. If an enthalpy

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Unit 3

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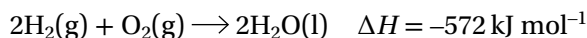
Topic 1

Concept 3

**Do more**
Combustion
equations

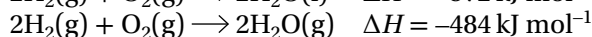
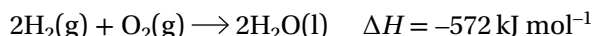
change is given as $\Delta H = 345 \text{ kJ mol}^{-1}$, the lack of sign does not mean that it is an endothermic reaction.

- Since enthalpy is measured in the units kJ mol^{-1} , the coefficients in the equation represent the amount in moles of each reacting substance. So, the reaction



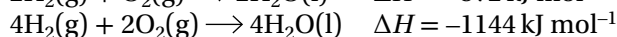
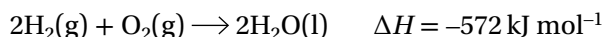
can be read as: when 2 moles of hydrogen react with 1 mole of oxygen, 2 moles of water form and 572 kJ of energy is produced. ΔH refers to the equation as it is written, even though the unit is expressed as kJ mol^{-1} .

- The physical state of matter must be shown, since changes of state require energy changes.



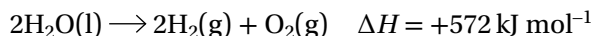
In one case, the product is a liquid. In the other case, the product is a gas. So, the condensation of 2 moles of water vapour to 2 moles of liquid water at 25°C produces 88 kJ of energy, which is the difference between the two enthalpies.

- If the coefficients are doubled, the ΔH value must be doubled.



The amount of energy produced by a chemical reaction is directly proportional to the amount of substance initially present. If, as in the above example, twice as much reactant is used, then twice as much energy can be produced.

- If a reaction is reversed, ΔH is equal to, but opposite in sign, to that of the forward reaction.



You will notice that the key point is that the enthalpy change in a reaction is proportional to the amount of substance that reacts. If these two quantities are measured in an experiment, it is possible to write the accompanying thermochemical equation. This was covered in chapter 1. Sample problem 2.1 provides another example of how this can be done.

Sample problem 2.1

In an experiment, it was found that the combustion of 0.240 g of methanol in excess oxygen yielded 5.42 kJ. Write the thermochemical equation for this reaction.

Solution: The equation for this reaction is:



To match this equation, it is necessary to calculate the heat evolved from 2 moles (64.0 g) of methanol. This can be done by scaling up the results from the experiment as follows.

$$\text{Heat evolved from 2 moles (64.0 g)} = \frac{64.0}{0.240} \times 5.42 = 1.45 \times 10^3 \text{ kJ}$$

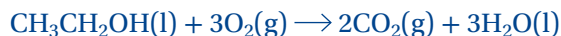
The thermochemical equation is therefore:

**Sample problem 2.2**

The molar heat of combustion of ethanol is tabulated as $-1364 \text{ kJ mol}^{-1}$.

- Write the thermochemical equation for the combustion of ethanol.
- If the density of ethanol is 0.790 g mL^{-1} , calculate the energy evolved in MJ when 1.00 L of ethanol is burned.

Solution: (a) The balanced chemical equation for the combustion of ethanol is:



The given heat value refers to 1 mole, as does the equation above.

The thermochemical equation is therefore:



(b) Since $\text{density} = \frac{\text{mass}}{\text{volume}}$

$$\begin{aligned}\text{mass of ethanol burned } (m) &= d(\text{ethanol}) \times V(\text{ethanol}) \\ &= 0.790 \times 1000 \\ &= 790 \text{ g}\end{aligned}$$

$$n(\text{ethanol}) = \frac{790}{46.0} = 17.17 \text{ mol}$$

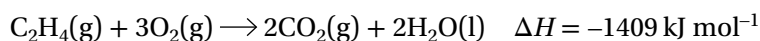
From the equation, 1 mole of ethanol evolves 1364 kJ.

By direct proportion, 17.17 moles produce x kJ.

$$\text{Therefore, } x = 17.17 \times \frac{1364}{1} = 23\,425 \text{ kJ} = 23.4 \text{ MJ.}$$

Sample problem 2.3

The combustion of ethene can be represented by the following thermochemical equation.



Calculate the mass of ethene required to produce 500 kJ of heat energy.

Solution: From the equation, 1 mole of C_2H_4 evolves 1409 kJ.

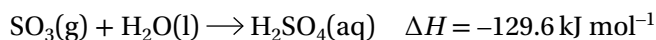
By ratio, x moles are required to evolve 500 kJ.

$$x = 500 \times \frac{1}{1409} = 0.355 \text{ mol}$$

$$\text{Therefore, } m(\text{C}_2\text{H}_4) = 0.355 \times 28.0 = 9.94 \text{ g.}$$

Sample problem 2.4

The air pollutant sulfur trioxide reacts with water in the atmosphere to produce sulfuric acid according to the equation:



Calculate the energy released, in kJ, when 0.500 kg $\text{SO}_3(\text{g})$ reacts with water.

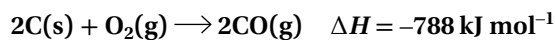
$$\text{Solution: } n(\text{SO}_3) = \frac{m}{M} = \frac{500}{80.1} = 6.24 \text{ mol}$$

From the equation, 1 mole of SO_3 releases 129.6 kJ.

So, 6.24 moles release $6.24 \times 129.6 = 809 \text{ kJ}$ of heat energy.

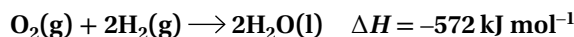
Revision questions

2. Calculate the energy released, in kJ, when 3.56 g of carbon undergoes combustion according to the thermochemical equation:

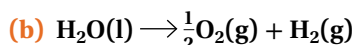
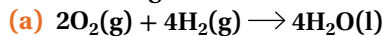


3. The use of hydrogen as a renewable and environmentally friendly fuel is currently the subject of much research. The main product of hydrogen

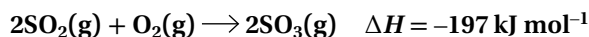
combustion is water. The production of liquid water from the reaction between gaseous hydrogen and gaseous oxygen can be represented by the following thermochemical equation.



Calculate how much energy, in kilojoules, would be released or absorbed by the following reactions.

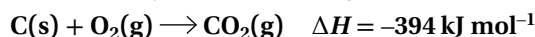


4. During the production of sulfuric acid by the Contact process, sulfur dioxide is converted to sulfur trioxide according to the equation:

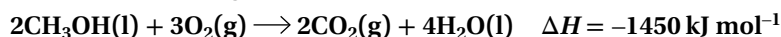


Calculate the heat energy released in the production of 1.00 tonne (10^6 g) of sulfur trioxide gas.

5. Calculate the energy released when 18.5 g of carbon undergoes combustion in a plentiful supply of air according to the equation:

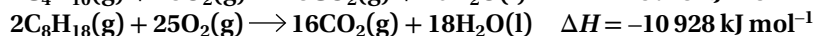
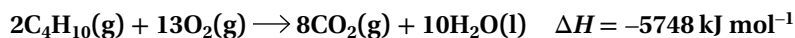


6. Methanol burns according to the equation:



Calculate the mass of methanol required to produce 1.000 MJ of energy.

7. Butane and octane are two hydrocarbons commonly used as fuels. The thermochemical equations for these two fuels are shown below.



(a) Calculate the heat evolved by the combustion of 100 g of butane.

(b) Use your answer to (a) to calculate the mass of octane required to produce the same amount of energy.

8. Explain why it is critical to show symbols of state in thermochemical equations.

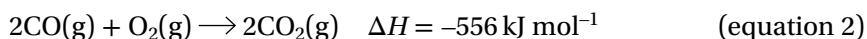
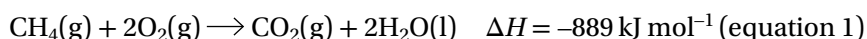
Calculating ΔH values from two or more related reactions

The ΔH value of a reaction can be calculated by manipulating and then adding together two or more related reactions and their associated ΔH values.

If the enthalpy change of a desired reaction is not known, it is possible to calculate it from a series of related reactions. The calculated value may then be used to make thermochemical predictions as shown previously. To do this, use some of the dot points mentioned on pages 34–35. The following sample problems show how this is done.

Sample problem 2.5

Calculate the enthalpy change for the incomplete combustion of methane in a limited oxygen supply, given the following two equations.



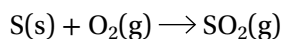
Solution: The required equation is $2\text{CH}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ (equation 3). Equations 1 and 2 need to be ‘manipulated’ so that, when added together, equation 3 is produced. This can be achieved by multiplying equation 1 by 2 and reversing equation 2.



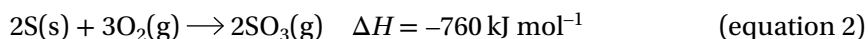
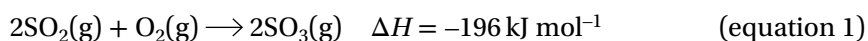
Adding together results in cancelling to produce the required equation. The ΔH values are also added, thus producing a value of $-1778 + 556 = -1222$. Therefore, $2\text{CH}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) + 4\text{H}_2\text{O}(\text{l}) \quad \Delta H = -1222 \text{ kJ mol}^{-1}$.

Sample problem 2.6

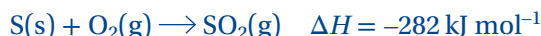
Fossil fuels such as coal and petroleum contain sulfur as an impurity. This produces sulfur oxides when they are burned. These are atmospheric pollutants. Develop the thermochemical equation for the reaction:



given the following equations.

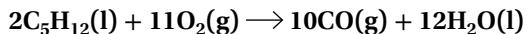


Solution: Equation 1 needs to be halved and reversed. Equation 2 needs to be halved. The ΔH values thus become $+98$ and -380 respectively. Adding the adjusted equations together produces the required thermochemical equation.

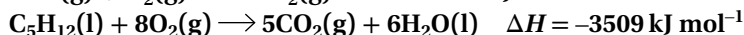
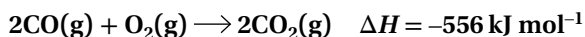


Revision questions

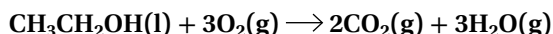
9. Calculate the ΔH value for the incomplete combustion of pentane, according to the equation:



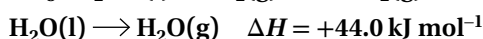
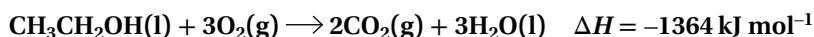
given the following equations.



10. Calculate ΔH for the reaction:



given the following equations.



Working with gases

When considering fuels as energy sources, it is often necessary to deal with gases. The products of combustion are nearly always gases, and some of the fuels themselves are gases. While it is possible to measure their masses, it is often more convenient and meaningful to measure their volumes.

Gases have properties and exhibit behaviours that are different from liquids and solids. Scientists use the **kinetic molecular theory of gases** to explain observed gas properties. This consists of five *postulates* (or points) that form a mental picture of how the particles in a gas would look and behave if we could observe them directly. These are applicable to gas samples under 'moderate conditions', which is usually taken to mean pressures that are not much greater than atmospheric pressure and temperatures considerably greater than those at which the gases liquefy.

The kinetic molecular theory states that matter is made up of continuously moving particles.

Hot air balloons use the properties of gases to achieve flight. A large fan is used to blow air into the balloon. Once inflated, the air is heated using a propane burner. The molecules move more rapidly, hitting each other in a random chaotic motion. As they move further apart, the density of the air decreases. The balloon rises because the air inside is warmer, and therefore lighter, than the surrounding air.



The five postulates that make up the kinetic molecular theory of gases can be summarised as follows.

1. Gases are made up of particles moving constantly and at random.
2. Gas particles are very far apart, and the volume of the particles is very small compared with the volume that the gas occupies.
3. The forces of attraction and repulsion between gas particles are practically zero.
4. Gas particles collide with each other and the walls of their container, exerting pressure. The collisions are perfectly elastic. This means that no kinetic energy is lost when they collide.
5. The higher the temperature, the faster the gas particles move, as they have increased kinetic energy.

Specifying the large-scale behaviour of gases

In any consideration of gas behaviour, the *pressure* each gas exerts, the *volume* that it occupies, its *temperature* and the *number of gas molecules* present in the sample must be determined.

Pressure is the force exerted by gas particles on the walls of a container.

Gas pressure

Particles exert a force by colliding with the walls of a container. Each tiny collision adds to all the others to make up the continuous force that we call **pressure**.

The surface of an inflatable airbed, such as the one shown here, exerts a force and tries to collapse. For the airbed to stay inflated, the particles inside the airbed must be able to exert a large enough force to balance the forces exerted by the surface and the external air pressure.



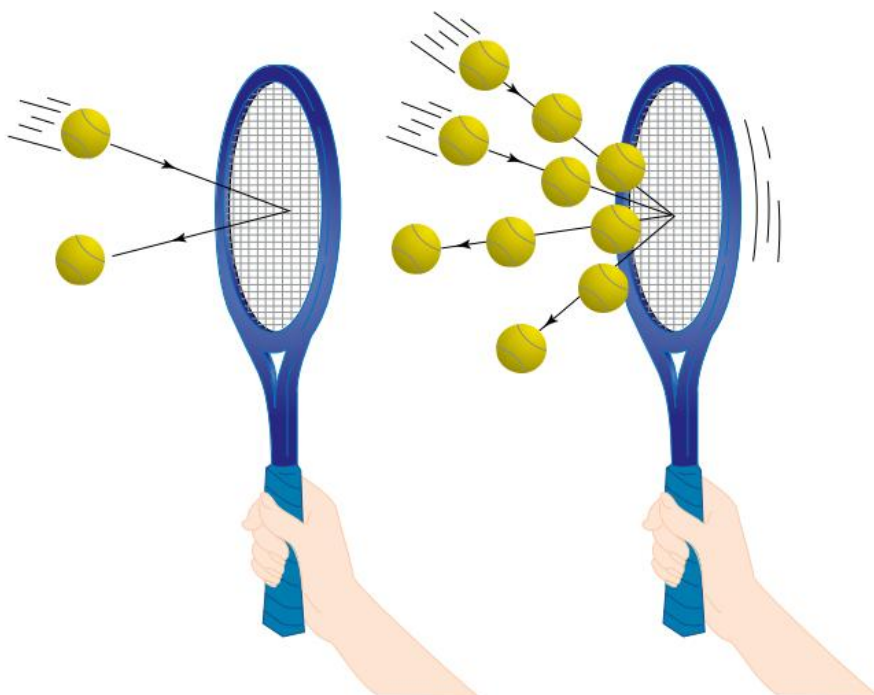
Pressure is force per unit area.

Pressure (P) is defined as *the force exerted per unit area*.

$$P = \frac{\text{force}}{\text{area}}$$

Pressure is measured using various units.

The SI unit of pressure is the **pascal (Pa)**, where 1 pascal is equivalent to a force of 1 newton exerted over an area of 1 square metre (N m^{-2}).



If a tennis racquet is struck by a tennis ball, a small force is felt. If a stream of balls is fired at the racquet, it is felt as a continuous pressure.

Units of pressure: $760 \text{ mmHg} = 1.00 \text{ atm} = 101.3 \text{ kPa}$

Atmospheric pressure

The pressure of the atmosphere is measured by a barometer. Atmospheric pressure at sea level is $101\,325 \text{ Pa}$. This is usually simplified to read 101.3 kPa (kilopascal). Two older units of pressure are *millimetres of mercury* and *atmospheres*. One millimetre of mercury (1 mmHg) is defined as the pressure needed to support a column of mercury 1 mm high. This unit developed from the early use of mercury barometers. One atmosphere (1 atm) is the pressure required to support 760 mm of mercury (760 mmHg) in a mercury barometer at 25°C . This is the average atmospheric pressure at sea level. So, 1 atm equals 760 mmHg .

$$760 \text{ mmHg} = 1.00 \text{ atm} = 1.013 \times 10^5 \text{ Pa} = 101.3 \text{ kPa}$$

In weather reports, *bars* and *hectopascals* are used to measure gas pressure.

$$1 \text{ bar} = 100\,000 \text{ Pa} = 100 \text{ kilopascal (kPa)}$$

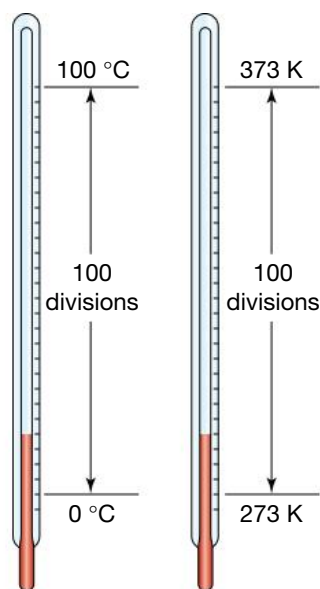
$$1 \text{ millibar (mb)} = \frac{1}{1000} \text{ bar} = 100 \text{ Pa} = 1 \text{ hectopascal (hPa)}$$

Units of temperature:
 $0^\circ\text{C} = 273 \text{ K}$

Temperature

The Celsius scale takes the freezing point of water as 0°C and the boiling point of water as 100°C . The space between these two fixed points is divided into 100 equal intervals, or degrees. Temperatures below the freezing point of water are assigned negative values, such as -10°C .

Another temperature scale is the **Kelvin**, or absolute, scale. On the Kelvin scale, the freezing point of water is 273 K and its boiling point is 373 K . Notice that a change of 1° on the Celsius scale is the same as that on the Kelvin scale. The zero point on the Kelvin scale, 0 K or **absolute zero**, is -273°C . The



These thermometers show a comparison of the Celsius and Kelvin temperature scales.

Units of volume:
 $1 \text{ m}^3 = 10^3 \text{ L} = 10^6 \text{ mL}$

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 Experiment 2.2 The relationship
 between pressure and volume
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relationship between the temperature on the Celsius scale and that on the Kelvin scale is given by the following equations.

$$K = ^\circ\text{C} + 273 \text{ or } ^\circ\text{C} = K - 273$$

For example, to convert 25°C to the absolute scale:

$$\begin{aligned} K &= 25 + 273 \\ &= 298 \end{aligned}$$

Note that temperatures given in K do not have a $^\circ$ sign.

Volume

The volume of a gas is commonly measured in cubic metres (m^3) or litres (L) or millilitres (mL).

$$1 \text{ m}^3 = 1000 \text{ L} = 1\,000\,000 \text{ mL}$$

or

$$1 \text{ m}^3 = 10^3 \text{ L} = 10^6 \text{ mL}$$

Revision question

11. Make the following conversions.

(a) 780 mmHg to atm	(e) 200°C to K	(i) 1600 mL to L
(b) 4.0 atm to Pa	(f) 500 K to $^\circ\text{C}$	(j) $3 \times 10^6 \text{ mL}$ to L
(c) 1000 mmHg to Pa	(g) 3.0 m^3 to L	(k) $5 \times 10^3 \text{ mL}$ to m^3
(d) 1250 mmHg to kPa	(h) 250 L to mL	(l) 600 mL to m^3

Laws to describe the behaviour of gases

The behaviour of gases has been studied for centuries. As a result, a number of laws have evolved to describe their behaviour mathematically. These laws are independent of the type of gas — it does not matter what the gas is (or even if the gas is a mixture such as air), these laws apply in exactly the same way to all gases. Two very useful such laws are Boyle's law and Charles' law.

Boyle's law for pressure–volume changes

Boyle's law is named after the English physicist and chemist who discovered the relationship between pressure and volume for a sample of gas. It states that, for a fixed amount of gas at constant temperature, pressure is inversely proportional to volume. Mathematically, this can be represented as:

$$P \propto \frac{1}{V}$$

from which it can be stated that $PV = \text{a constant value}$.

If $P_1V_1 = \text{a constant value}$ and $P_2V_2 = \text{a constant value}$, then:

$$P_1V_1 = P_2V_2$$

Revision questions

- 12. (a)** Set up a spreadsheet and enter the data from the table on the next page into the cells of the first two columns.
- (b)** In the third column of the spreadsheet, calculate pressure $\times$ volume. What pattern do you notice?

- (c) In the fourth column of your spreadsheet, convert each pressure measurement (P) into its reciprocal ($\frac{1}{P}$). For example, if P has a value of 120, $\left(\frac{1}{P}\right)$ would equal 8.33×10^{-3} .
13. (a) Use the data on your spreadsheet from question 12 to plot a graph of pressure versus volume. Put pressure on the horizontal (x) axis and volume on the vertical (y) axis.
- (b) Plot a second graph with the volume on the vertical axis and $\frac{1}{P}$ on the horizontal axis, and extrapolate the graph to the origin.
- (c) Compare and account for the two graphs.

Sample results showing the relationship between the pressure and volume of a gas

Pressure (kPa)	Volume (L)
120	0.261
145	0.218
162	0.193
180	0.171
200	0.159
216	0.145
240	0.130
258	0.120

Charles' law for temperature–volume changes

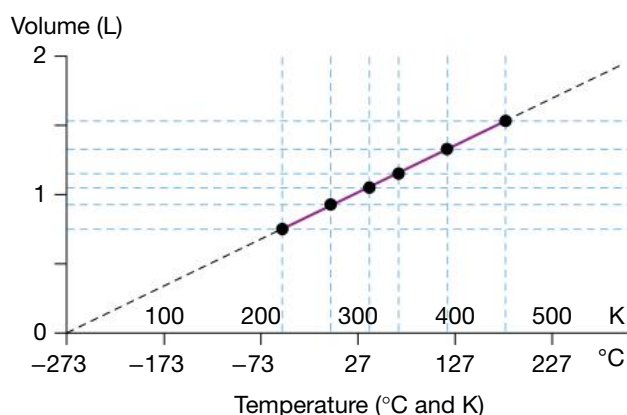
The relationship between temperature and volume was first identified by the French scientist Jacques Charles, after whom the law is named. While the expansion of all materials with increasing temperature is well known, Charles subjected constant amounts of various gases (at constant pressure) to changes in temperature, each time making accurate measurements of the resulting volume.

To understand this law better, consider a typical set of results as shown in table 2.1.

If these results are graphed as shown below, a pattern emerges.

TABLE 2.1 Sample results showing the relationship between the temperature and volume of a gas

Temperature (°C)	Volume (L)
-50	0.75
0	0.92
40	1.05
70	1.15
120	1.32
180	1.52



Representation of Charles' law showing the two temperature scales, Kelvin and degrees Celsius. The graph demonstrates that the volume of a gas varies in direct proportion to absolute temperature.

If the Celsius scale is used to measure temperature, a linear relationship is observed. However, this is not a directly proportional relationship as the graph does not pass through the origin. If, however, the Kelvin scale is used, it does. We can therefore state Charles' law as follows.

For a given amount of gas at constant pressure, volume is directly proportional to the absolute temperature.

Mathematically, this can be represented as, $V \propto T$, (where T is the absolute temperature), from which it can be stated that $\frac{V}{T}$ = a constant value.

If $\frac{V_1}{T_1}$ = a constant value and $\frac{V_2}{T_2}$ = a constant value, then:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

You will notice that the graph on the previous page implies a 'lowest possible temperature' — the temperature at which it intersects the x -axis. This temperature is -273.15°C or 0 K . It is referred to as 'absolute zero'.

The combined gas equation

Boyle's law and Charles' law may be combined to produce the gas equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This equation applies to a fixed amount of gas. It is particularly useful for making predictions when an amount of gas under a set of initial conditions (P_1 , V_1 and T_1) is changed to a second set of conditions (P_2 , V_2 and T_2). If any two of the new set of conditions are known, the third can easily be calculated.

Sample problem 2.7

A sample of air at 10°C and 1.1 atm has a volume of 2.2 L . If the pressure is changed to 1.0 atm and the temperature increases to 15°C , what volume will it occupy?

Solution: STEP 1

List the known information:

$$\begin{aligned} P_1 &= 1.1\text{ atm} \\ V_1 &= 2.2\text{ L} \\ T_1 &= 10 + 273 = 283\text{ K} \end{aligned}$$

$$\begin{aligned} P_2 &= 1.0\text{ atm} \\ V_2 &= ?\text{ L} \\ T_2 &= 15 + 273 = 288\text{ K} \end{aligned}$$

STEP 2

Transpose the general gas equation and substitute the values above.

$$\begin{aligned} \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ V_2 &= \frac{P_1 V_1 T_2}{P_2 T_1} \\ &= \frac{1.1 \times 2.2 \times 288}{1.0 \times 283} \\ &= 2.5\text{ L} \end{aligned}$$

The new volume is, therefore, 2.5 L .

Note that units for pressure and volume must be the same on each side. Temperature must be in kelvin.

Standard conditions for measuring gases

Boyle's law and Charles' law tell us that the volume of a gas sample is sensitive to both temperature and pressure. This makes the comparison of gas volumes very tricky. In order to make these comparisons easier, scientists have established sets of standard conditions. These are accepted worldwide and enable gas volumes to be compared meaningfully without temperature or pressure having unwanted effects.

There are two commonly used such sets of standard conditions.

1. **Standard temperature and pressure (STP)**. Standard temperature is 0°C or 273 K , and standard pressure is 100.0 kPa .
2. **Standard laboratory conditions (SLC)**. Since most experiments are carried out in the laboratory, normal room temperature is substituted for the STP condition. Standard laboratory conditions are a temperature of 25°C (298 K) and a pressure of 100.0 kPa .

This book will generally refer to SLC only, as STP is not part of the VCE Chemistry study design.

STP and SLC are standard sets of conditions for comparing gases.

The molar gas volume is the volume of 1 mole of any gas at a stated temperature and pressure.

$$V_{\text{M}}(\text{STP}) = 22.7\text{ L}$$

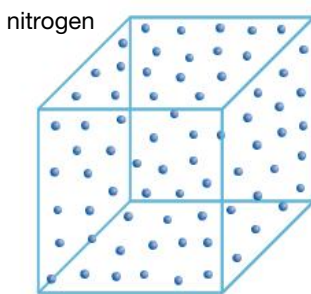
$$V_{\text{M}}(\text{SLC}) = 24.8\text{ L}$$

Molar gas volume and Avogadro's hypothesis

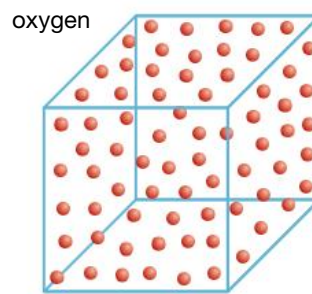
Avogadro put forward the hypothesis that 'equal volumes of all gases measured at the same temperature and pressure contain the same number of particles'.

This means that, if two gases have the same temperature, pressure and volume, they must contain the same number of moles.

It has been found experimentally that 1 mole of any gas at SLC occupies a volume of 24.8 L . This volume is called the **molar gas volume**.



$V = 24.8\text{ L}$
 $T = 298\text{ K}$
 $P = 100.0\text{ kPa}$
 $6.02 \times 10^{23}\text{ molecules}$



$V = 24.8\text{ L}$
 $T = 298\text{ K}$
 $P = 100.0\text{ kPa}$
 $6.02 \times 10^{23}\text{ molecules}$

The standard molar gas volume. Under the same conditions of temperature and pressure, the volume of a gas depends only on the number of molecules it contains, and not on what the particles are. The volume occupied by 28.0 g of nitrogen gas (1 mol or 6.02×10^{23} molecules) at SLC is 24.8 L . The volume occupied by 1 mole of any gas at the same temperature and pressure is 24.8 L . (Note: In these diagrams, the number of particles shown is only a fraction of those actually present, since this number is too great to be represented here.)

The molar volume of a gas at SLC is 24.8 L. This means that 1 mole of any gas occupies 24.8 L at 25 °C and 100.0 kPa. The molar volume of a gas varies with temperature and pressure but, at any given temperature and pressure, it is the same for all gases. There is a direct relationship between the number of moles of a gas and its molar volume. This is illustrated by the formula

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

where n is the number of moles of gas, V is the actual volume and V_m is the molar volume of the gas. Therefore, at SLC:

$$n_{\text{SLC}} = \frac{V}{24.8}$$

where V is measured in L.

Sample problem 2.8

How many moles of chlorine gas are present in 48.0 L of the gas at SLC?

Solution:

$$n = \frac{V}{24.8}$$

$$n = \frac{48.0}{24.8} = 1.94 \text{ mol of Cl}_2 \text{ gas}$$

Sample problem 2.9

Find the mass of 1556.5 mL of H₂ gas that was collected at SLC.

Solution:



Why are these bubbles floating upwards? These soap bubbles are filled with hydrogen gas, which is lighter than the same volume of bubbles filled with air. A mole of hydrogen gas would occupy the same volume as a mole of oxygen molecules, but the hydrogen would not weigh as much as the oxygen.

STEP 1

Convert the volume to litres.

$$1556.5 \text{ mL} = 1.5565 \text{ L}$$

STEP 2

Determine the number of moles of H₂ gas

$$\text{using } n = \frac{V}{24.8}$$

$$n = \frac{1.5565}{24.8} \\ = 0.0628 \text{ mol}$$

STEP 3

Determine the mass (m) of 0.0628 moles of H₂ gas using $n(\text{H}_2) = \frac{m}{M}$

$$0.0628 = \frac{m}{2.0}$$

The mass of H₂ gas collected was 0.13 g.

Sample problem 2.10

- 5345 mL of a gas was collected at SLC and weighed. Its mass was 9.50 g. Find the molar mass of the gas.
- Given that the gas is one of the main constituents of air, identify the gas.

Solution:

(a) **STEP 1**

Convert the volume to litres.

$$5345 \text{ mL} = 5.345 \text{ L}$$

STEP 2

Determine the number of moles of the gas.

$$\begin{aligned}n &= \frac{V}{24.8} \\&= \frac{5.345}{24.8} \\&= 0.216 \text{ mol}\end{aligned}$$

STEP 3

Determine the molar mass (M) of 0.216 mole of the gas.

$$\begin{aligned}n &= \frac{m}{M} \\0.216 &= \frac{9.50}{M} \\M &= \frac{9.50}{0.216} \\&= 44.0\end{aligned}$$

The molar mass of the gas is 44.0 g mol^{-1} .

- (b) The main constituents of air are nitrogen ($M = 28.0$), oxygen ($M = 32.0$), argon ($M = 40.0$) and carbon dioxide. The gas must therefore be carbon dioxide as the M of $\text{CO}_2 = 12 + (2 \times 16) = 44.0 \text{ g mol}^{-1}$.

Revision questions

14. Calculate the numbers of moles of the following gases at SLC.
 - (a) 15 L of oxygen, O_2
 - (b) 25 L of chlorine, Cl_2
15. Calculate the volumes of the following gases at SLC.
 - (a) 1.3 mol hydrogen, H_2
 - (b) 3.6 g of methane, CH_4
 - (c) 0.35 g of argon, Ar
16. Calculate the masses of the following gas samples. All volumes are measured at SLC.
 - (a) 16.5 L of neon, Ne
 - (b) 1050 mL of sulfur dioxide, SO_2
17. What is the mass (in kg) of 850 L of carbon monoxide gas measured at SLC?
18. A 0.953 L quantity of a gas measured at SLC has a mass of 3.20 g. What is the molar mass of the gas? What is the gas?

The universal gas equation

$$PV = nRT$$

is used to calculate the amount of a gas at a given volume and temperature.

It is important that the correct units are used in the universal gas equation.

The universal gas equation

When Boyle's law and Charles' law are combined with Avogadro's hypothesis, the following equation is obtained.

$$PV = nRT$$

This equation is known as the **general gas equation** or the **universal gas equation**.

When using the universal gas equation, the following units must be used for the **universal gas constant** $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

- *Pressure* is measured in kilopascals.
- *Volume* is measured in litres.
- *Temperatures* is measured in kelvin.
- The *quantity* of gas is measured in moles

- The *number of moles* can be expressed as:

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

where m represents the mass of the substance (in grams) and M represents the molar mass of the substance.

So, the universal gas equation can be rewritten as:

$$PV = \frac{mRT}{M}$$

Sample problem 2.11

Find the volume of 6.30 mol of carbon dioxide gas at 23.0 °C and 550 kPa pressure. ($R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

Solution: STEP 1

Assign the variables.

$$P = 550 \text{ kPa}$$

$$V = ? \text{ L}$$

$$n = 6.30 \text{ mol}$$

$$T = 23 + 273 = 296 \text{ K}$$

$$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

STEP 2

Use the universal gas equation to calculate V .

$$PV = nRT$$

$$\begin{aligned} \therefore V &= \frac{nRT}{P} \\ &= \frac{6.30 \times 8.31 \times 296}{550} \\ &= 28.2 \text{ L} \end{aligned}$$

study on

Unit 3

AOS 1

Topic 1

Concept 4



Do more
The mole

Revision questions

- Calculate the volume of gas, in litres, occupied by the following.
 - 3.5 mol of O_2 at 100 kPa and 50 °C
 - 12.8 mol of CH_4 at 10 atm and 60 °C
 - 6.5 g of Ar at 50 kPa and 100 °C
 - 0.56 g of CO_2 at 50 atm and 20 °C
 - 1.3×10^{-3} g He at 60 kPa and -50 °C
 - 1.5×10^{21} molecules of Ne at 40 kPa and 200 °C
- Calculate the volume occupied by 42.0 g of nitrogen gas at a pressure of 200 kPa and a temperature of 77 °C.
- A 5.00 L balloon contains 0.200 mol of air at 120 kPa pressure. What is the temperature of air in the balloon?
- If 55 mol of H_2 gas is placed in a 10 L flask at 7 °C, what would be the pressure in the flask?

Mass–volume stoichiometry

Many chemical reactions involve gases. For example, barbecues, furnaces and engines, such as the internal combustion engine, burn fuel and produce carbon dioxide and water vapour. In order to ensure that the reactions are

Quantities of gases can be calculated using the four stoichiometric steps.

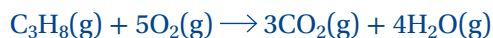
efficient and as complete as possible, calculations of volumes or masses of the gases or fuels required are essential.

Sample problem 2.12

In a gas barbecue, propane is burned in oxygen to form carbon dioxide and water vapour. If 22.0 g of CO_2 is collected and weighed, find the volume of propane at 200°C and $1.013 \times 10^5 \text{ Pa}$.

Solution: STEP 1

Write the equation and given information.



$$P = 1.013 \times 10^5 \text{ Pa} \quad m(\text{CO}_2) = 22.0 \text{ g}$$

$$T = 200 + 273 = 473 \text{ K}$$

$$V = ? \text{ L}$$

STEP 2

Calculate the number of moles of the known quantity of substance.

$$n(\text{CO}_2) = \frac{22.0}{44.0} = 0.500 \text{ mol}$$

STEP 3

Use the equation to find the molar ratio of unknown to known quantities, and calculate the number of moles of the required substance. Since 3 moles of CO_2 are produced from 1 mole of C_3H_8

$$\begin{aligned} n(\text{C}_3\text{H}_8) &= \frac{n(\text{CO}_2)}{3} \\ &= \frac{0.500}{3} \\ &= 0.167 \text{ mol} \end{aligned}$$

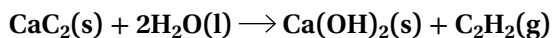
STEP 4

Find the volume of the propane using $PV = nRT$, where $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ and $P = 101\,325 \text{ Pa} = 101.325 \text{ kPa}$. Then,

$$\begin{aligned} V(\text{C}_3\text{H}_8) &= \frac{nRT}{P} = \frac{0.167 \times 8.31 \times 473}{101.3} \\ V(\text{C}_3\text{H}_8) &= 6.47 \text{ L} \end{aligned}$$

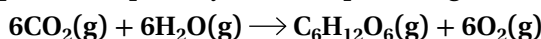
Revision questions

23. Ethyne, C_2H_2 , is also called acetylene and is used as a welding gas. It is produced from calcium carbide as shown by the ethyne reaction.



What volume of ethyne measured at 25°C and 745 mmHg would be produced from 5.00 g of H_2O ?

24. The equation for photosynthesis to produce glucose is as follows.



What volume of carbon dioxide, measured at 28°C and 1.3 atm pressure, is needed to produce 1.5 g of glucose?

Sample problem 2.13

Calculate the mass of hexane that is required to produce 100 L of carbon dioxide gas at SLC.

Solution: STEP 1

Write the equation and identify the given information.



$$m = ? \text{ g} \quad V = 100 \text{ L} \quad \text{Conditions are SLC.}$$

STEP 2

Calculate the number of moles of the known substance — in this case, CO_2 gas. Normally the universal gas equation would be used but, because it is at SLC, we know the molar volume and can therefore use the formula

$$n = \frac{V}{V_{\text{m}}}$$

$$\text{Therefore, } n(\text{CO}_2) = \frac{100}{24.8} = 4.03 \text{ mol.}$$

STEP 3

Using the mole ratios from the equation, the number of moles of hexane can be calculated.

$$n(\text{C}_6\text{H}_{14}) = \frac{2}{12} \times n(\text{CO}_2)$$

$$\text{Therefore, } n(\text{C}_6\text{H}_{14}) = \frac{2}{12} \times 4.03 = 0.672 \text{ mol.}$$

STEP 4

The mass of hexane can now be calculated.

$$m(\text{C}_6\text{H}_{14}) = n(\text{C}_6\text{H}_{14}) \times M(\text{C}_6\text{H}_{14}) = 0.672 \times 86.0 = 57.8 \text{ g}$$

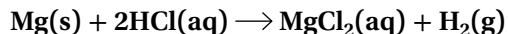
Revision questions

25. Oxygen gas can be prepared in the laboratory by the decomposition of potassium nitrate according to the equation:



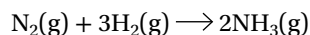
When 14.5 L of O_2 is formed at 1.00 atm and 25.0°C , what mass of KNO_2 is also formed?

26. Magnesium reacts with hydrochloric acid according to the equation:



What mass of magnesium, when reacted with excess hydrochloric acid, would produce 5.0 L of hydrogen gas, measured at 26.0°C and 1.2 kPa pressure?

If gases are at the same pressure and temperature, their molar ratios are equal to their volume ratios.



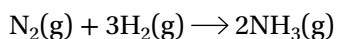
$$1 \text{ mol} \quad 3 \text{ mol} \quad \rightarrow 2 \text{ mol}$$

$$1 \text{ vol} \quad 3 \text{ vol} \quad \rightarrow 2 \text{ vol}$$

$$10 \text{ vol} \quad 30 \text{ vol} \quad \rightarrow 20 \text{ vol}$$

Volume–volume stoichiometry

Consider the reaction between nitrogen and hydrogen gas.

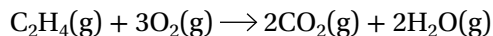


According to this equation, 1 mole of N_2 reacts with 3 moles of H_2 to produce 2 moles of ammonia.

Considering Avogadro's hypothesis, if the gases are at the same pressure and temperature, their *molar* ratios are equal to their *volume* ratios. We therefore use volumes instead of moles and can say that 10 mL of N_2 reacts with 30 mL of H_2 to form 20 mL of ammonia.

Sample problem 2.14

If 100 m³ of ethene is burned according to



calculate the volume of:

(a) carbon dioxide produced

(b) oxygen consumed.

(Assume all gas volumes are measured at the same temperature and pressure.)

Solution: Because all gas volumes are measured at the same temperature and pressure, the equation may be interpreted in terms of volume ratios.

(a) $V(\text{CO}_2) = 2 \times V(\text{C}_2\text{H}_4)$

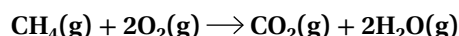
Therefore, $V(\text{CO}_2) = 2 \times 100 = 200 \text{ m}^3$.

(b) $V(\text{O}_2) = 3 \times V(\text{C}_2\text{H}_4)$

Therefore, $V(\text{O}_2) = 3 \times 100 = 300 \text{ m}^3$.

Revision questions

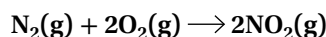
27. Methane gas burns in air at room temperature and pressure, according to the equation:



If 25 mL of methane is burned at room temperature and pressure, find the volumes of the following reactants and products:

(a) oxygen (b) carbon dioxide (c) water.

28. At high temperatures, such as those in a car engine during operation, atmospheric nitrogen burns to produce the pollutant nitrogen dioxide, according to the equation:



(a) If 20 mL of nitrogen is oxidised, calculate the volume of oxygen needed to produce the pollutant. Assume that temperature and pressure remain constant.

(b) What is the initial volume of reactants in this combustion reaction?

(c) What is the final volume of products in the reaction?

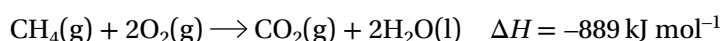
(d) Is there an overall increase or decrease in the volume of gases on completion of the reaction?

Applying volume stoichiometry to thermochemistry

Just as the principles of mass–mass stoichiometry can be extended to include gas volumes, the thermochemical calculations introduced earlier in this chapter can also be extended to include gas volumes. This is very useful because it is often more convenient to measure a gas's volume than its mass. If pressure and temperature are measured as well, the universal gas equation, $pV = nRT$, provides a formula to change between volumes and moles.

Sample problem 2.15

Calculate the heat energy released when 375 mL of methane at 21 °C and 767 mmHg pressure is burned according to:



Solution: STEP 1

The universal gas equation, $PV = nRT$, can be used in thermochemical calculations to link energy amounts to volumes of gases involved.

Calculate the number of moles of methane used. To do this, the information in the question needs to be changed to the appropriate units to enable the universal gas equation to be used.

$$\text{Temperature: } 21\text{ }^{\circ}\text{C} = 21 + 273 = 294\text{ K}$$

$$\text{Volume: } 375\text{ mL} = 0.375\text{ L}$$

$$\text{Pressure: } 767\text{ mmHg} = \frac{767}{760} \times 101.3 = 102.2\text{ kPa}$$

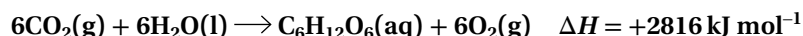
$$\text{Therefore, } n(\text{CH}_4) = \frac{PV}{RT} = \frac{102.2 \times 0.375}{8.31 \times 294} = 0.0157\text{ mol.}$$

STEP 2

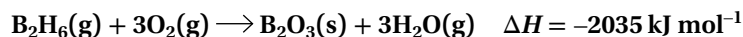
$$\text{Heat evolved} = 889 \times \frac{0.0157}{1} = 14.0\text{ kJ}$$

Revision questions

29. Calculate the energy required to convert 2.50 L of carbon dioxide, at SLC, to glucose according to the equation:



30. Calculate the energy released when 200 mL of diborane, B_2H_6 , is burned at $150\text{ }^{\circ}\text{C}$ and 1.50 atmospheres according to the following equation.



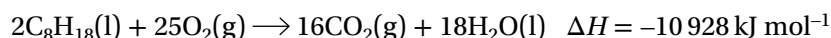
Fuels and greenhouse gases

The principles of stoichiometry and thermochemistry can be combined to quantify the effect that energy production, especially through the combustion of fossil fuels, has on the environment. As we saw in chapter 1, gases such as carbon dioxide, methane, nitrous oxide and ozone contribute to the enhanced greenhouse effect. Of these, carbon dioxide is produced in the greatest amounts due to the use of fossil fuels as energy sources. The increasing level of these gases has led to international treaties such as the Kyoto Protocol. These obligate signatory countries to reduce their greenhouse gas emissions in an attempt to limit future global warming.

In order to meet targets for reduction, countries need to estimate their energy requirements, both current and future, and compare the energy sources available for the required energy production. A useful unit in such comparisons is the amount of greenhouse gas produced (usually carbon dioxide) per megajoule of energy released. Typical units are g MJ^{-1} and L MJ^{-1} .

Sample problem 2.16

If it is assumed that petrol is entirely octane, and that it burns according to



calculate the:

- mass of carbon dioxide produced per MJ of energy evolved
- volume of carbon dioxide produced at 100 kPa and $20\text{ }^{\circ}\text{C}$ per MJ of energy evolved.

Solution: (a) **STEP 1**

Calculate the mass of octane required to evolve 1 MJ of heat energy. From the equation, 2 moles of octane evolves 10.928 MJ.

$$M(\text{C}_8\text{H}_{18}) = 114.0 \text{ g mol}^{-1}$$

Therefore, $2 \times 114.0 \text{ g}$ evolves 10.928 MJ.

$$\text{Therefore, 1 MJ requires } \frac{2 \times 114.0}{10.928} = 20.9 \text{ g.}$$

STEP 2

Calculate the mass of CO_2 produced from this amount of octane.

$$n(\text{C}_8\text{H}_{18}) = \frac{m}{M} = \frac{20.9}{114.0} = 0.183 \text{ mol}$$

$$\text{From the equation, } n(\text{CO}_2) = \frac{16}{2} \times 0.183 = 1.464 \text{ mol.}$$

$$\text{Therefore, } m(\text{CO}_2) = 1.464 \times 44.0 = 64.4 \text{ g.}$$

It can therefore be stated that, if petrol is assumed to be pure octane, it produces 64.4 g of carbon dioxide per megajoule of energy released (64.4 g MJ^{-1}).

(b) $PV = nRT$

$$n = 1.464 \text{ mol}$$

$$T = 273 + 20 = 293 \text{ K}$$

$$P = 100 \text{ kPa}$$

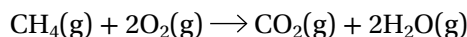
$$\text{Therefore, } V = \frac{nRT}{P} = \frac{1.464 \times 8.31 \times 293}{100} = 35.6 \text{ L.}$$

Therefore, 35.6 L of CO_2 is produced per megajoule of energy released (35.6 L MJ^{-1}) at the stated conditions of temperature and pressure.

When comparing the effect of fuels on the environment, it is often useful to consider the carbon dioxide emissions produced per unit of energy. Two common units for making such comparisons are g MJ^{-1} and L MJ^{-1} .

Sample problem 2.17

Methane is produced by a number of natural processes and, in many of these situations, it can easily enter the atmosphere. Methane is a more potent greenhouse gas than carbon dioxide as it is better at absorbing heat. However, it can also be used as a fuel. The equation for burning methane is:



If methane is captured and then used as a fuel, calculate the net change in greenhouse gas volume that would occur. Assume that all volumes are measured at the same temperature and pressure.

Solution: As temperature and pressure is constant, we can write:

$$V(\text{CH}_4) \text{ consumed} = V(\text{CO}_2) \text{ produced}$$

Therefore, there is no net change.

You might think that a process such as capturing and then burning methane would produce no net environmental benefit. However, when it is remembered that methane is a more potent greenhouse gas than carbon dioxide, it can be seen that there is an environmental benefit gained from burning the methane, rather than just letting it escape into the atmosphere. Of course, if carbon dioxide could also be captured and prevented from entering the atmosphere, the environmental benefit would be even greater.

Carbon dioxide is the most significant greenhouse gas due to the large volumes in which it is produced. For this reason, other greenhouse gas emissions are often

measured in 'carbon dioxide equivalent'. That is, all these other gases are converted to the volume of carbon dioxide that would produce the same effect.

Revision question

31. (a) Calculate the net change in mass of greenhouse gas produced by the combustion of 128 g of methane.
(b) Express your answer as a percentage increase or decrease.
(c) Comment on how the units used (mass or volume) may influence the conclusions drawn from calculations such as in this question and in sample problem 2.17.

When electricity generation is considered, the calculations must take into account the efficiency of the generation process. For example, to produce 1 MJ of electrical energy, enough fuel would need to be burned to produce 3.33 MJ of heat energy, assuming that the process is 30% efficient. The mass of carbon dioxide produced in supplying 3.33 MJ would then need to be calculated.

Both transport and the generation of electricity consume large amounts of fossil fuels and, in the process, add large amounts of carbon dioxide to the atmosphere. As nations work to reduce their greenhouse gas emissions, alternative fuels need to be considered. When considering fuels, the amount of carbon dioxide emitted per unit of energy produced is a useful comparison.



Sample problem 2.18

Calculate the carbon dioxide emissions, in kg MJ⁻¹, from a power station that has an overall efficiency of 33.0% and burns black coal with a carbon content of 81.5%. (Heat evolved from black coal = 34.0 kJ g⁻¹)

Solution: At 33.0% efficiency, the energy input required to produce 1 MJ of electrical energy output is:

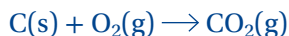
$$\text{Efficiency} = \frac{\text{output energy}}{\text{input energy}} \times 100$$

$$\text{Therefore, input energy} = \frac{1 \times 100}{33} = 3.03 \text{ MJ.}$$

$$\text{Mass of black coal required to produce 3.03 MJ} = \frac{3030}{34.0} = 89.1 \text{ g}$$

$$\text{Mass of carbon in this amount of black coal} = \frac{81.5}{100} \times 89.1 = 72.6 \text{ g}$$

Assuming the carbon produces carbon dioxide according to:



$$n(\text{C}) = \frac{72.6}{12.0} = 6.05 \text{ mol and } n(\text{C}) = n(\text{CO}_2)$$

Therefore, $m(\text{CO}_2) = 6.05 \times 44.0 = 267 \text{ g} = 0.267 \text{ kg}$.

Therefore, CO_2 production is 0.267 kg MJ^{-1} of electrical energy produced.

Revision questions

32. The molar heat of combustion for ethanol is $-1364 \text{ kJ mol}^{-1}$. Calculate the mass of carbon dioxide emitted when ethanol is used to produce 1.00 MJ of heat.
33. (a) Methanol is also a fuel. Its molar heat of combustion is -725 kJ mol^{-1} . What mass of carbon dioxide would be produced using methanol to generate 1.00 MJ of heat?
- (b) Comment on your answers to questions 32 and 33(a) in relation to the masses of CO_2 produced.
34. A coal-fired power station using brown coal as its fuel operates at 37.0% overall energy efficiency. The brown coal has a heat value of 16.0 kJ g^{-1} and a carbon content of 29.0% . Assuming that all the carbon present forms carbon dioxide, calculate the carbon dioxide produced per MJ of electrical energy produced in units of:
- (a) g MJ^{-1}
- (b) L MJ^{-1} (at SLC).

The energy available from a fuel may be estimated by using a known amount of fuel to heat a known mass of water. If the temperature change is noted, the formula $Q = mc\Delta T$ may be used to calculate the energy added to the water. Knowing the amount of fuel used, this can then be scaled up to an appropriate reference amount. Common units are kJ g^{-1} , kJ mol^{-1} and MJ tonne^{-1} .

study on

Unit 3

AOS 1

Topic 1

Concept 7

Do more
Heats of
combustion



How do we obtain the energy output of a fuel?

So far in this chapter, we have made predictions relating to fuel quantities and heat outputs using thermochemical equations. However, there are two issues that you may have been wondering about.

- How are ΔH values obtained in the first place?
- Thermochemical equations are fine for fuels that are pure substances and can therefore have an equation written for their combustion. But what about fuels that are mixtures? Many common fuels, such as petrol, diesel, wood and coal, fall into this category. How can we obtain heat outputs and make predictions for these fuels?

The answer to both these questions is to burn a small amount of fuel and 'capture' the heat evolved in some way so that it can be measured. The results obtained are then scaled up to a reference amount so that comparisons can be made. The values obtained are quoted in units that take into account the units used to measure the energy output and the particular reference amount being used. Common units are kJ mol^{-1} , kJ g^{-1} and MJ tonne^{-1} .

If this is to be done accurately, a device called a calorimeter must be used. There are two main types of calorimeters — solution calorimeters and bomb calorimeters. The features of these and their use are discussed in chapter 12.

An alternative method is to use the fuel to heat a known mass of water and measure the resultant temperature increase. This method produces only approximate results, the degree of accuracy depending on the steps taken to minimise heat loss to the surroundings.

You may remember from unit 1 that the formula:

$$Q = mc\Delta T$$

can be used to calculate the heat required to raise a given mass (m) of a substance of known specific heat (c) by a certain temperature (ΔT). The specific

heat capacity, c , of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1 °C or 1 K. This formula is used to calculate the heat added to the water. Sample problem 2.19 illustrates this method.

Sample problem 2.19

The heat content of kerosene was determined by using a kerosene burner to heat 250 mL of water. It was found that burning 0.323 g of kerosene raised the temperature of the water by 11.2 °C.

Given that the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, calculate the heat energy released from kerosene in kJ g^{-1} and MJ tonne^{-1} .

Solution: STEP 1

Calculate the heat energy (Q) transferred to the water.

$$250 \text{ mL of water} = 250 \text{ g}$$

$$\begin{aligned} Q &= mc\Delta T = 250 \text{ g} \times 4.18 \text{ J g}^{-1} \times 11.2 \text{ }^{\circ}\text{C} \\ &= 11\,704 \text{ J} = 11.7 \text{ kJ} \end{aligned}$$

STEP 2

Scale this value up to the chosen reference amount (in this case, 1 g).

$$\text{Heat evolved} = 11.7 \text{ kJ} \times \frac{1}{0.323 \text{ g}} = 36.2 \text{ kJ g}^{-1}$$

To convert this to MJ tonne^{-1} , $1 \text{ tonne} = 10^6 \text{ g} = 1\,000\,000 \text{ g}$; $1 \text{ MJ} = 1000 \text{ kJ}$

$$\text{Therefore, } 36.2 \text{ kJ g}^{-1} = \frac{36.2}{1000} \times 1\,000\,000 = 36\,200 \text{ MJ tonne}^{-1}.$$

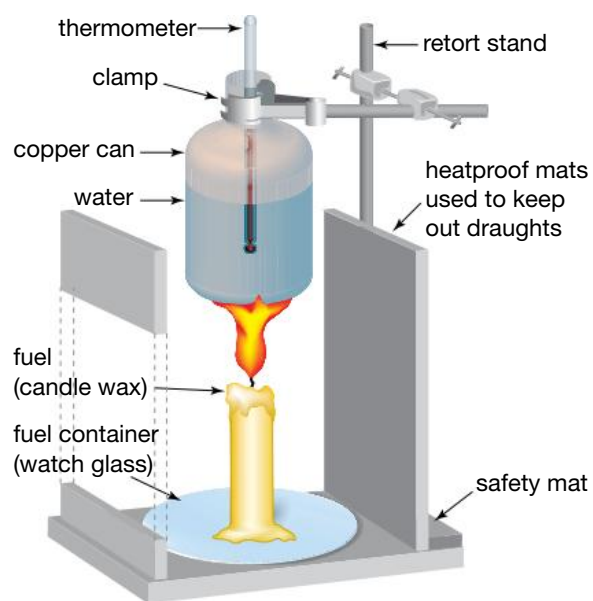
Note: This represents a minimum value. Not all of the heat from the kerosene would have gone into the water. Some of it would have been wasted in heating the surrounding air and the equipment used to hold the water.

Revision questions

An experiment to compare the energy output of candle wax, ethanol and butane was performed by setting up the apparatus shown in the figure at the top of the next page. The ethanol was poured into a crucible, a small wax candle stuck onto a watch glass and a gas cigarette lighter were each used as a 'burner' after being lit. Each burner was weighed before and after it was used to heat 200 g of water. The results are shown in table 2.2 on the next page. (Assume the formula for candle wax is $\text{C}_{20}\text{H}_{42}$.)

35. Copy and complete table 2.2.
36. Taking the specific heat capacity of water as $4.18 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$, calculate the energy produced from 1.00 gram of each substance. How do the results compare?
37. Calculate the heat of combustion (enthalpy per mole of substance used) for each substance. How do the results compare?
38. Describe a use for each of the fuels tested. Explain why each fuel is better suited for the purpose it is commonly used for than either of the other two fuels.
39. The molar heat of combustion of ethanol has been found experimentally to be $-1364 \text{ kJ mol}^{-1}$.
 - (a) Is combustion exothermic or endothermic?
 - (b) What was the percentage accuracy of the experiment above?
 - (c) List the sources of error in the experiment and describe how some of these errors can be minimised.
40. Write a report for the experiment.

Apparatus for testing the energy output of candle wax



Most of our energy is supplied by fossil fuels.

TABLE 2.2 Results of combustion of different fuels

Property	Ethanol	Candle wax	Butane
mass of 'burner' before heating (g)	23.77	32.72	43.94
mass of 'burner' after heating (g)	22.54	32.50	43.71
mass of fuel used (g)			
mass of water (g)	200	200	200
initial temperature of water (°C)	20.0	20.0	20.0
highest temperature of water (°C)	35.0	30.0	29.0
temperature rise (°C)			
molar mass (g mol ⁻¹)			

Chapter review

Summary

- The unit of energy is the joule (J).
- The study of energy changes that accompany chemical reactions is called thermochemistry or chemical thermodynamics.
- The total energy stored in a substance is called the enthalpy, or heat content, of the substance and is represented by the symbol H .
- The change in enthalpy as a reaction proceeds is known as the heat of reaction and can be determined according to the relationship:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- Exothermic reactions release energy to their surroundings and have a negative ΔH value.
- Endothermic reactions absorb energy from their surroundings and have a positive ΔH value.
- Energy diagrams or profiles may be used to visually represent changes in enthalpy.
- Thermochemical equations are chemical equations that, in addition to balancing charge and mass, include the enthalpy change and may be used in stoichiometric calculations to determine the energy changes associated with chemical reactions.
- The kinetic molecular theory of gases helps explain gas properties and begins with five assumptions about gas particles. These particles:
 - are moving constantly and at random
 - experience an increase in kinetic energy and move more quickly when temperature is increased
 - have insignificant attractive or repulsive forces between them
 - are very far apart and their volume is small compared to the volume they occupy
 - collide with one another and the walls of their container, exerting pressure.
- When considering gas behaviour, we are concerned with the pressure a gas exerts, the volume it occupies, its temperature and the number of gas molecules. We express these in SI units.
 - Pressure is measured in pascal (Pa).

$$760 \text{ mmHg} = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \\ = 101.3 \text{ kPa}$$

- Temperature is converted from degrees Celsius ($^{\circ}\text{C}$) to the absolute or Kelvin scale, where absolute zero is -273°C .

$$\text{K} = ^{\circ}\text{C} + 273$$

- Volume is measured in cubic metres (m^3), litres (L) or millilitres (mL).

$$1 \text{ m}^3 = 10^3 \text{ L} = 10^6 \text{ mL}$$

- Quantity is measured in moles (mol).

- Boyle's law states that the volume of a fixed mass of gas at constant temperature is inversely proportional to the pressure exerted on it.

$$P_1 V_1 = P_2 V_2$$

- Charles' law states that the volume of a fixed mass of gas at constant pressure is directly proportional to its absolute (Kelvin) temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- Gas volumes are measured using a standard set of fixed conditions, standard laboratory conditions (SLC), where temperature is 25°C (298 K) and pressure is 100.0 kPa.
- The molar gas volume is the volume that 1 mole of gas occupies. At SLC, this equals 24.8 L. To calculate amounts of gases at SLC, we use the equation:

$$n_{\text{SLC}} = \frac{V}{24.8} \text{ where } V \text{ is measured in litres.}$$

- The universal gas equation combines several of the gas laws and contains the universal gas constant (R).

$$PV = nRT \text{ where the constant } R \text{ is equal to } 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \text{ and } V \text{ is measured in litres, } T \text{ in kelvin and } P \text{ in kPa.}$$

- The universal gas equation enables stoichiometric calculations that link masses and volumes together (mass-volume calculations).
- Volume-volume stoichiometry can be performed using volumes rather than moles, since, for gases at the same pressure and temperature, mole ratios are equal to volume ratios.

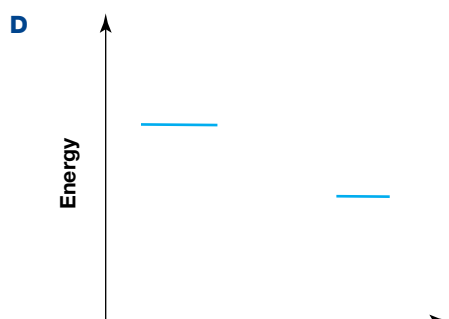
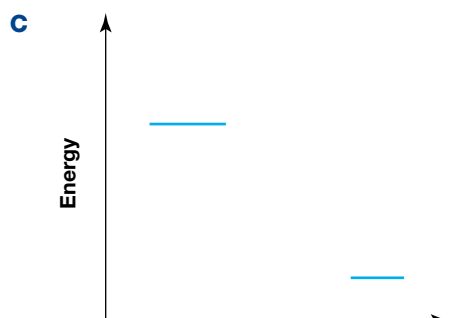
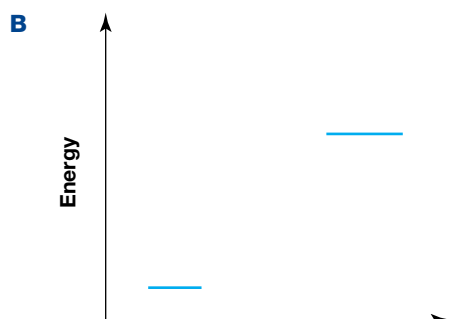
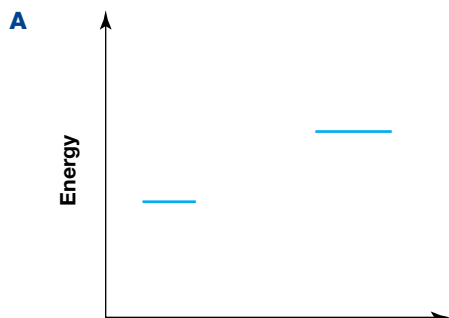
$$\frac{V(\text{unknown})}{V(\text{known})} = \frac{\text{coefficient of unknown}}{\text{coefficient of known}}$$

- ΔH values in thermochemical equations can be evaluated from experimental data and from the ΔH values of related equations.
- The environmental effect of a fuel can be measured in terms of its greenhouse gas emissions per megajoule of energy produced.
- The specific heat capacity (symbol c) of a substance is defined as the amount of energy needed to raise the temperature of 1 g of the substance by 1°C (or 1 K).

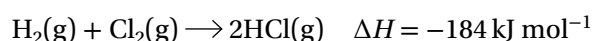
- The heat energy in a fuel can be estimated by using a known amount of the fuel to heat a known amount of water. The formula $Q = mc\Delta T$ is used to calculate the heat energy added to the water.

Multiple choice questions

1. Which of the energy profiles below represents the *most exothermic* reaction?



2. Consider the following equation for the formation of hydrogen chloride gas.



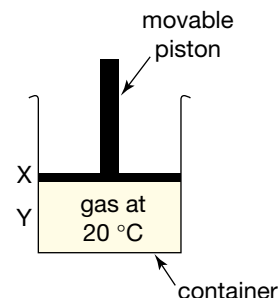
When 2 moles of hydrogen gas react completely with 2 moles of chlorine gas:

- A** 184 kJ of energy is released
 - B** 184 kJ of energy is absorbed
 - C** 368 kJ of energy is released
 - D** 368 kJ of energy is absorbed.
3. Which of the following processes is endothermic?
- A** Burning carbon
 - B** Evaporating kerosene
 - C** Condensing steam
 - D** A reaction with a negative heat of reaction
4. 'Dry ice' is solid carbon dioxide. It is stable at very low temperatures but sublimates at room temperature according to the reaction:



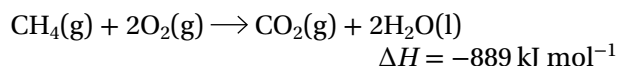
Handling dry ice with bare hands can cause severe skin damage because solid carbon dioxide:

- A** is a strong oxidising agent
 - B** releases considerable heat to the skin while subliming
 - C** absorbs considerable heat from the skin while subliming
 - D** forms a strong acid when dissolved in the moisture of the skin.
5. The diagram below shows a container filled with gas and sealed by a movable piston. There is sufficient gas to support the piston at point X when the temperature is 20 °C. Assume that the piston is locked at X. If the gas is heated, the pressure which it exerts will:
- A** increase
 - B** decrease
 - C** remain the same
 - D** change in an unpredictable manner.



6. The apparatus in question 5 remains at a constant temperature of 20 °C, but the piston is pushed down to point Y and locked, so that the volume of the container is halved. The average number of molecules striking a unit area of the wall of the container per unit time will:
- A** double
 - B** halve
 - C** remain the same
 - D** change in an unpredictable manner.
7. The pressure of the gas inside a scuba diver's lungs changes from 100 kPa to 150 kPa. If the diver's lungs initially held 6 L of gas, their volume at this depth would be:
- A** 3 L
 - B** 4 L
 - C** 6 L
 - D** 9 L.

8. A rigid container holds a fixed volume of gas at a certain temperature and pressure. In order to double the pressure of the gas inside the container, one could:
- A halve the amount of gas in the container
 - B halve the amount of gas, but double the absolute temperature
 - C double the amount of gas and double the absolute temperature
 - D double the absolute temperature.
9. 6.0 L of air at 400 K and 100 kPa is cooled to 300 K at constant pressure. The new volume will be:
- A 2.5 L
 - B 4.5 L
 - C 6.0 L
 - D 8.0 L.
10. Two litres of helium gas was measured at a temperature of 200 K and a pressure of 1 atmosphere. If the kinetic energy (temperature) of the molecules is doubled while the pressure remains constant, what volume will the gas occupy?
- A 0.5 L
 - B 1 L
 - C 2 L
 - D 4 L
11. 10 L of hydrogen gas is collected at 110 kPa and 20 °C. It is then compressed into a 2 L container at a pressure of 1100 kPa. The new temperature will be:
- A 40 °C
 - B 200 °C
 - C 273 °C
 - D 313 °C.
12. 200 mL of gas at 27 °C and 700 mmHg pressure became 210 mL at 1.05 atm pressure. The new temperature is:
- A 360 °C
 - B 87 °C
 - C 187 °C
 - D 260 °C.
13. Tired of working in laboratories that are either freezing or too hot, Jenny has proposed a third set of standard conditions. She has defined these as a temperature of 15 °C and a pressure of 100 kPa. Under these conditions, the molar volume of a gas would be:
- A less than 22.7 L
 - B 22.7 L
 - C between 22.7 L and 24.8 L
 - D greater than 24.8 L.
14. Methane, CH₄(g), burns in air to form carbon dioxide and water according to the following equation.

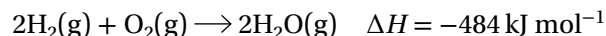


Which of the following statements about this reaction is false?

- A The reaction is exothermic.
- B The enthalpy (heat content) of the products is greater than the reactants, as shown by the sign of ΔH .

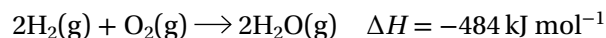
- C Heat is released to the environment by the reaction.
- D The volume occupied by the gaseous products is equal to that of the reactants, if all are measured at the same temperature and pressure.

15. Consider the following reaction.

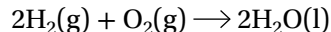


Energy is released when hydrogen burns in oxygen because:

- A the net strength of the chemical bonds within the reactant molecules is greater than the net strength of the chemical bonds within the product molecules
 - B the net strength of the chemical bonds within the reactant molecules is less than the net strength of the chemical bonds within the product molecules
 - C there are fewer product molecules than reactant molecules
 - D the reactants are elements while the product is a compound.
16. Consider the following reaction.



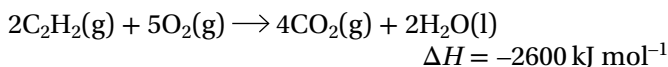
Compared with the reaction given above, the heat evolved in the reaction



will necessarily be:

- A greater, because extra heat is evolved in forming liquid water from gaseous water
- B less, because extra heat is absorbed in forming liquid water from gaseous water
- C the same, since the heat evolved is the same provided the chemical formulas of the reactants and products remain unchanged
- D the same, provided the same amounts of reactants are used.

Questions 17 and 18 refer to the following thermochemical equation for the combustion of ethyne, commonly known as acetylene.



17. The combustion of 0.26 g of ethyne will:

- A absorb 13 J of energy
- B evolve 13 J of energy
- C absorb 13 kJ of energy
- D evolve 13 kJ of energy.

18. The carbon dioxide contribution from the use of ethyne is:

- A 17 kg MJ⁻¹
- B 34 kg MJ⁻¹
- C 68 kg MJ⁻¹
- D 134 kg MJ⁻¹.

19. The amount of energy required to raise 150 g of water by 40 °C is:
A 25 J **C** 25 kJ
B 150 J **D** 150 kJ.
20. If burning 4.5 g of a fuel raises the temperature of 75 g of water by 30 °C, the heat of combustion of this fuel is:
A 0.0075 kJ g⁻¹ **C** 2.1 kJ g⁻¹
B 0.057 kJ g⁻¹ **D** 2.4 kJ g⁻¹.

Review questions

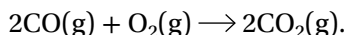
Energy changes in chemical reactions

- What is meant by the 'enthalpy change' of a chemical reaction?
- State whether each of the following reactions is exothermic or endothermic.
 - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
 $\Delta H = -185 \text{ kJ mol}^{-1}$
 - $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$
 $\Delta H = +41 \text{ kJ mol}^{-1}$
 - $\text{SnO}_2(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{Sn}(\text{s}) + 2\text{CO}(\text{g})$
 $\Delta H = +360 \text{ kJ mol}^{-1}$
 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
 $\Delta H = -92.2 \text{ kJ mol}^{-1}$
- Draw an energy profile diagram for each of the reactions in question 2. In each diagram, label the reactants and the products as given by the equation, and show the ΔH value and its magnitude.
- Compare endothermic and exothermic reactions with respect to:
 - the sign of ΔH
 - heat exchange with the surroundings
 - energy levels of reactants and products.
- Energy is lost during an exothermic reaction. Explain why this observation is consistent with the Law of Conservation of Energy.

Writing thermochemical equations

- Ethanol burns in oxygen to produce water and either carbon dioxide or carbon monoxide. The particular oxide produced depends on whether the oxygen supply is plentiful or limited. The molar heats of combustion for these two reactions are $-1364 \text{ kJ mol}^{-1}$ and $-1192 \text{ kJ mol}^{-1}$ respectively.
 - Write the thermochemical equation for the combustion of ethanol to produce carbon dioxide.
 - Write the thermochemical equation for the combustion of ethanol to produce carbon monoxide.
 - Use the equations from (a) and (b) to explain how the amount of oxygen consumed influences the oxide produced.

- (d) Calculate ΔH for the following reaction.



- Data tables give the heat output from the complete combustion of ethane and ethene as 51.9 kJ g^{-1} and 50.3 kJ g^{-1} respectively. Write thermochemical equations for the complete combustion of these fuels, showing ΔH values in units of kJ mol^{-1} .
- Dodecane has the formula $\text{C}_{12}\text{H}_{26}$. In an experiment, 3.10 g of dodecane was burned in a plentiful supply of oxygen. 137.0 kJ of heat was released. Write the thermochemical equation for the complete combustion of dodecane.
- While researching on the internet, a student found that candle wax is a mixture of hydrocarbons, but, as an approximation, it may be assumed to be pentacosane.
 - To what homologous series does pentacosane belong?
 - Write the formula for pentacosane given that its molecules contain 25 carbon atoms.
 - Write the equation for the combustion of pentacosane in a plentiful supply of oxygen. In an experiment, the student measured the heat given off by a burning candle. She discovered that 153 kJ of energy was evolved and that the mass of the candle decreased from 75.384 to 71.735 g.
 - On the assumption that candle wax may be approximated as pentacosane, determine the heat of combustion in kJ mol^{-1} and then write the thermochemical equation for its combustion. On further investigation, she found a source claiming tetracosane, $\text{C}_{24}\text{H}_{50}$, was a better approximation for candle wax.
 - How would this change affect the value of ΔH ?

Measuring gases

- Use the kinetic molecular theory to explain:
 - why gases exert pressure
 - why, for a fixed amount of gas at constant volume, pressure increases with temperature.
- Convert 1.34 atm to mmHg and kPa.
 - Convert 365 mmHg to Pa and atm.
 - Convert 102 576 Pa to atm and mmHg.
- Convert the following Celsius temperatures to Kelvin temperatures.

(a) 100 °C	(c) -200 °C
(b) -20 °C	(d) 345 °C
- Convert the following Kelvin temperatures to Celsius.

(a) 300 K	(d) 392 K
(b) 427 K	(e) 73 K
(c) 173 K	

14. Convert the following volumes to the second unit given.
- | | |
|---------------------------|-------------------------------------|
| (a) 125 L to m^3 | (d) 2.6 mL to L |
| (b) 125 L to mL | (e) 2 m^3 to L |
| (c) 300 mL to L | (f) $3 \times 10^3 \text{ mL}$ to L |

Standard conditions

15. Calculate the number of moles of the following gases at SLC.
- 1.5 L oxygen, O_2
 - 2.56 L of hydrogen, H_2
 - 250 mL of nitrogen, N_2
16. Calculate the volume of the following gases at SLC.
- 1.53 mol hydrogen, H_2
 - 13.6 g of methane, CH_4
 - 2.5×10^{30} molecules of nitrogen, N_2
17. Calculate the mass of the following gas samples. All volumes are measured at SLC.
- 150 mL of oxygen, O_2
 - 4.5 L of carbon dioxide, CO_2
18. (a) How many moles of nitrogen are contained in 26.0 L of nitrogen gas at SLC?
- (b) How many individual nitrogen molecules are present in 26.0 L of the gas?

Gas laws

19. What is absolute zero? Can one actually reach this temperature? Explain.
20. The pressure on 13.0 L of neon gas is increased from 90.0 kPa to 360 kPa. If the temperature remains constant, find the new volume of the gas.
21. 1.00 L of hydrogen gas in a cylinder under $5.0 \times 10^4 \text{ kPa}$ fills a balloon at 150 kPa at the same temperature. Determine the volume of the balloon.
22. The pressure on a gas remains constant. Its volume is 700 mL. The temperature is 27°C . Calculate the temperature needed to change the volume to:
- 14.0 mL
 - 420.0 mL.

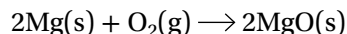
The universal gas equation

23. Calculate the number of moles of gas present in each of the following gas samples.
- 32.3 L of argon at 102.0 kPa and 15°C
 - 24.3 L of nitrogen at 13.2 atm and 35°C
 - 12.3 L of helium at 755 mmHg and -10°C
 - 24.8 L of argon at 100.0 kPa and 25°C
24. Calculate the volumes occupied by the following gas samples.
- 0.560 mol of carbon dioxide gas at 101.5 kPa and 17°C
 - 15.5 mol of ethyne gas at 10.35 atm and 20°C

- 0.800 g of oxygen gas at 98.9 Pa and 11°C
 - 5.279 g of nitrogen gas at 100 kPa and -50°C
25. An aerosol can of deodorant has a volume of 120 mL. The contents exert a pressure of $9.0 \times 10^5 \text{ Pa}$ at 27°C .
- Calculate the number of moles of gas present in the can.
 - How many particles are present in the can of deodorant?
 - If the contents of the can are transferred to a 200 mL container, what would be the temperature if the pressure drops to $6.0 \times 10^5 \text{ Pa}$?
26. Calculate the temperature, in $^\circ\text{C}$, of 0.25 mol of a gas that occupies a volume of $4.155 \times 10^{-3} \text{ m}^3$ at a pressure of 150 kPa.
27. A certain mass of unknown gas (molar mass = 30.0 g mol^{-1}) occupies 16.64 L at a pressure of 125 mmHg and a temperature of -73°C . Calculate the mass of gas present in the container.
28. Calculate the pressure needed to contain 3.0 mol of ammonia in a container of volume 20 L at a temperature of 27°C .
29. An empty 200 mL flask has a mass of 84.845 g. It is filled with a gas at 17.0°C and 770 mmHg pressure and then weighs 85.084 g. Calculate the molar mass of the gas. What is the gas?
30. A gas is at SLC and has a volume of 11.2 L. If its temperature is changed to 127°C , and its pressure changes to 253.3 kPa, calculate its new volume.
31. Each time Nicole breathes, she inhales about 400 mL of air. Oxygen makes up about 20% by volume of air. How many oxygen molecules does she inhale in one breath at 25°C and $1.0 \times 10^4 \text{ Pa}$ pressure?

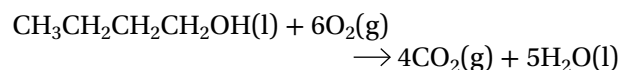
Mass-volume calculations

32. Magnesium burns according to the equation:



What mass of magnesium combines with 5.80 L of oxygen measured at SLC?

33. Butan-1-ol (density = 0.81 g mL^{-1}) burns according to the following equation.



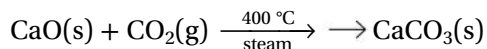
When 10.0 mL of butan-1-ol is burned, calculate:

- the mass of water produced
- the volume of carbon dioxide produced at SLC
- the volume of carbon dioxide produced at 200°C and 1.2 atm pressure.

The butan-1-ol is used to produce 100 mL of carbon dioxide at SLC.

- Calculate the volume of butan-1-ol needed.

34. A number of technologies either exist or are being developed for removing carbon dioxide from flue gases. Some of these are also being investigated for the removal of carbon dioxide directly from the air. One such process uses calcium oxide and steam (at 400 °C) to remove carbon dioxide. The overall equation for this reaction is:



- Calculate the maximum volume of carbon dioxide (at SLC) that can be removed per 1.00 tonne of calcium oxide.
- Calculate the maximum mass of calcium carbonate that would be formed per tonne of calcium oxide.

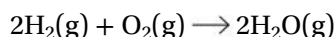
Volume–volume stoichiometry

35. Methane gas, CH₄, is a major constituent of the natural gas in Bass Strait. It readily burns in air to produce carbon dioxide and water vapour. If all gas volumes are measured at SLC calculate:

- the volume of oxygen gas that is required for the complete combustion of 12.5 L of methane gas
- the volume of air required for reaction, given that air contains 20% oxygen.

36. When propane, C₃H₈, is burned in a limited supply of oxygen, carbon monoxide is among its products. If 4.25 L of propane gas, measured at room temperature and pressure, is burned in a limited air supply, what volume of carbon monoxide gas would be produced at the same conditions?

37. Hydrogen reacts with oxygen in the reaction:

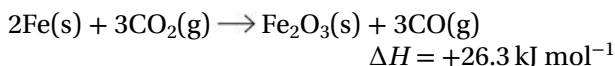


What volume of water vapour is produced when 4.0 L of hydrogen reacts with 10 L of oxygen? What volume of oxygen remains unreacted? (Assume that all volumes are measured at the same temperature and pressure.)

38. In the Haber process, nitrogen and hydrogen are combined under specific conditions of temperature and pressure to industrially manufacture ammonia.
- Write the balanced equation.
 - What volume of nitrogen combines with 45 m³ of hydrogen?
 - What volume of ammonia would be produced if the reaction went to completion?

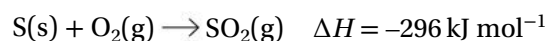
Calculations using thermochemical equations

39. Iron can react with carbon dioxide according to the following equation.



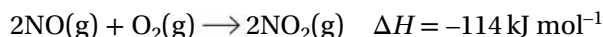
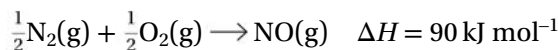
- Explain why this equation may be described as a thermochemical equation.
- Calculate the heat change, in kilojoules, when 2 g of iron reacts completely with excess carbon dioxide.
- Calculate the heat change, in kilojoules, when 200 mL of carbon dioxide is used at SLC.
- What mass of iron would be needed to absorb 1000 kJ of heat energy?
- What volume of carbon dioxide would be needed at SLC to absorb 1000 kJ of energy?

40. For the reaction:

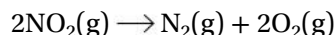


- how much heat is evolved when 2.00 moles of sulfur are burned in excess oxygen
- how much heat is evolved when 200 g of sulfur is burned in excess oxygen
- how much heat is evolved when 450 mL of oxygen at SLC reacts with excess sulfur
- how much heat is evolved when 200 g of sulfur reacts with 2 litres of oxygen at 80 °C and 101.3 kPa pressure?

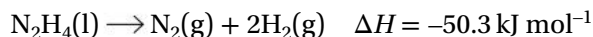
41. Given the following two equations:



calculate the enthalpy change for the following reaction:

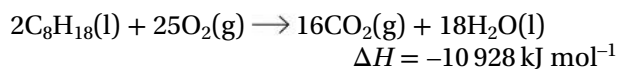


42. Butane, C₄H₁₀, is a gaseous fuel. For the combustion of butane, $\Delta H = -2874\text{ kJ mol}^{-1}$:
- write a balanced thermochemical equation
 - calculate the quantity of heat that would be evolved from the combustion of 12 L of butane measured at SLC.
43. Hydrazine, N₂H₄, is a liquid fuel that has been used for many years in the engines of space probes. It was famously used in the terminal-descent engines that successfully landed the *Curiosity* rover on the surface of Mars in 2012. When passed over a suitable catalyst, it decomposes quickly in a multi-step exothermic chemical reaction. The overall equation for this process is:



- Calculate the energy released per kilogram of hydrazine in the equation above.
- Given that the average temperature and pressure of the Martian atmosphere are -60 °C and 600 Pa respectively, calculate the total volume of gas added to the Martian atmosphere if 50 kg of hydrazine is used.

44. Octane burns according to the following equation.



- (a) Given that the density of octane is 0.70 g mL^{-1} , calculate the volume of carbon dioxide produced (at SLC) per litre of octane.
- (b) Calculate the mass of carbon dioxide evolved in the production of 1.00 MJ of energy through the reaction above.
- (c) Express your answer to (b) as litres of carbon dioxide (at SLC) per MJ.
45. Petrol and LPG are two fuels commonly used in Australia. It is claimed that LPG is 'better for the environment' as it releases less carbon dioxide. It is also attractive to motorists because, even though more litres are used, it is cheaper than petrol. As an approximation, petrol may be assumed to be octane, whereas LPG is a mixture of propane and butane. Some relevant data is shown in the table below.

Fuel	Molar enthalpy of combustion (kJ mol^{-1})	Density (g mL^{-1})
propane	-2217	0.51 (as LPG)
butane	-2874	0.51 (as LPG)
octane	-5464	0.70 (as petrol)

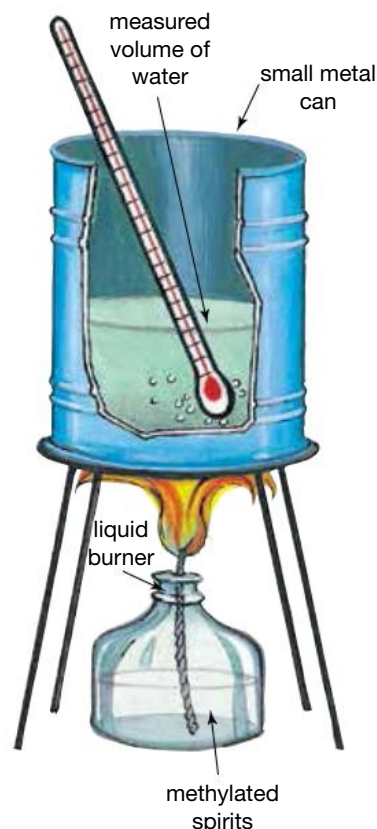
- (a) Calculate the mass of LPG (assuming it to be propane) required to produce 1.00 MJ of heat energy.
- (b) Calculate the mass of carbon dioxide produced from (a) and express your answer as g MJ^{-1} .
- (c) Calculate the mass of petrol (assuming it to be octane) required to produce 1.00 MJ of heat energy.
- (d) Calculate the mass of carbon dioxide produced from (c) and express your answer as g MJ^{-1} .
- (e) Hence state the net reduction (in g MJ^{-1}) of carbon dioxide emission when LPG is used in preference to petrol.
- (f) Repeat (a), (b) and (e) for LPG if it is assumed to be butane.
- (g) Calculate the volume of LPG (assuming it to be propane) required to produce the same energy as 1.00 litre of petrol (assuming it to be octane).
- (h) Is it true that LPG is better than petrol? Use your answers to (a)–(g) to explain your response.

Estimating heat energy in fuels

46. The specific heat capacity of aluminium is $0.900 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$. Calculate the energy needed to raise the temperature of a $7.20 \times 10^2 \text{ g}$ block of aluminium by $10.0 ^\circ\text{C}$.

47. It takes 78.2 J of energy to raise the temperature of 45.6 g of lead from $19.2 ^\circ\text{C}$ to $32.5 ^\circ\text{C}$. Calculate the specific heat capacity of lead.
48. A student investigated the heat output from some solid fuel blocks designed for use with model steam engines. In one experiment, it was found that the temperature of 80.0 mL of water increased from $23.2 ^\circ\text{C}$ to $68.5 ^\circ\text{C}$, and 0.300 g of fuel was burned in the process. Calculate the heat content of this fuel in kJ g^{-1} .
49. It is useful to know how much energy can be obtained from different fuels in order to determine which would be the best fuel for a particular purpose. The apparatus in the figure below can be constructed in the laboratory to measure the heat given out when a fuel such as ethanol is burned.

The heat produced when the fuel burns is absorbed by the water in the metal can. The temperature can be measured so, given that the specific heat of water is 4.18 J and the density of water is 1.00 g mL^{-1} , the heat of combustion may be determined.



Apparatus for measuring the heat of combustion of a fuel

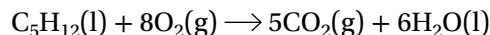
The results of one experiment are shown in the following table.

Volume of water in metal can =	200 mL
Thus, mass of water in can =	200 g
Rise in temperature of water =	11.0 °C
Mass of ethanol burned =	0.500 g

- (a) From these results, calculate the heat produced when 1 gram of ethanol is burned.
- (b) Calculate the heat of combustion for ethanol using the above results.
- (c) An accurate value for the heat produced when 1 mole of ethanol burns is 1364 kJ mol^{-1} . Calculate the percentage accuracy of this experiment.

- (d) Outline the sources of error in the experiment and then suggest how the design of the experiment could be improved so that more accurate heats of combustion for different fuels may be determined.

50. A student wished to estimate the ΔH value for the reaction:



using an identical experimental set-up to that in question 49. Using pentane in the liquid burner, it was found that the combustion of 0.735 g caused a temperature increase of 35.0°C .

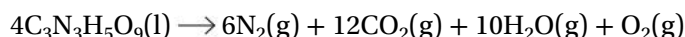
- (a) Estimate the ΔH value for the equation above using the data obtained.
- (b) Given that the molar enthalpy of combustion of pentane is $-3509 \text{ kJ mol}^{-1}$, comment on the value obtained in (a).

**Exam practice questions**

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

1. Nitroglycerine, $\text{C}_3\text{N}_3\text{H}_5\text{O}_9$, is a dangerous explosive that releases all gaseous products according to the equation:



Calculate the total volume of gaseous products that results when 1.00 kg of liquid nitroglycerine explodes at a temperature of 250°C and a pressure of 300 kPa.

3 marks

2. Kerosene is a hydrocarbon fuel that may be used in lamps, jet engines and camp stoves. It has a heat of combustion of $44\,100\text{ kJ kg}^{-1}$.

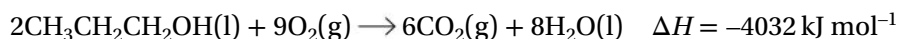
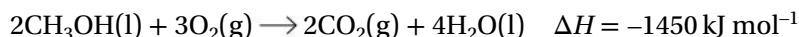
(a) Explain why the heat evolved from the combustion of kerosene is measured in kJ kg^{-1} rather than kJ mol^{-1} .

1 mark

(b) A cup of billy tea contains 250 g of water. How many cups of tea can be made if 12.5 mL of kerosene is used to heat the water? (Assume that the temperature of the water increases from 20.0°C to 100.0°C , the specific heat capacity of water is $4.18\text{ J g}^{-1}\text{ }^\circ\text{C}^{-1}$ and the heat of combustion of kerosene is $37\,000\text{ kJ L}^{-1}$.)

2 marks

3. Consider the following two equations.



(a) Calculate the mass of methanol required to produce 1.00 MJ of heat energy.

2 marks

(b) Calculate the mass of 1-propanol required to produce 1.00 MJ of heat energy.

2 marks

(c) Assuming that methanol and 1-propanol are made from non-renewable resources, calculate the net mass reduction (in g MJ^{-1}) of carbon dioxide when methanol is used as a fuel in preference to 1-propanol.

3 marks

(d) Calculate the net volume reduction (in L MJ^{-1}) from (c), assuming the carbon dioxide is at 101.3 kPa and 15°C .

3 marks

3 Converting chemical energy to electrical energy

In today's world of mobile phones and satellite communication, it is difficult to imagine what life would have been like before the invention of the telegraph and a suitable battery or cell to power it. What we now take for granted would have taken weeks and maybe even months just for communications within Australia. Overseas communications may have taken up to a year. In the late nineteenth century, redox reactions were responsible for bringing the world together via the telegraph. Today, redox reactions still perform this vital role. They are at the heart of the battery technology that powers our mobile phones and other electronic devices.

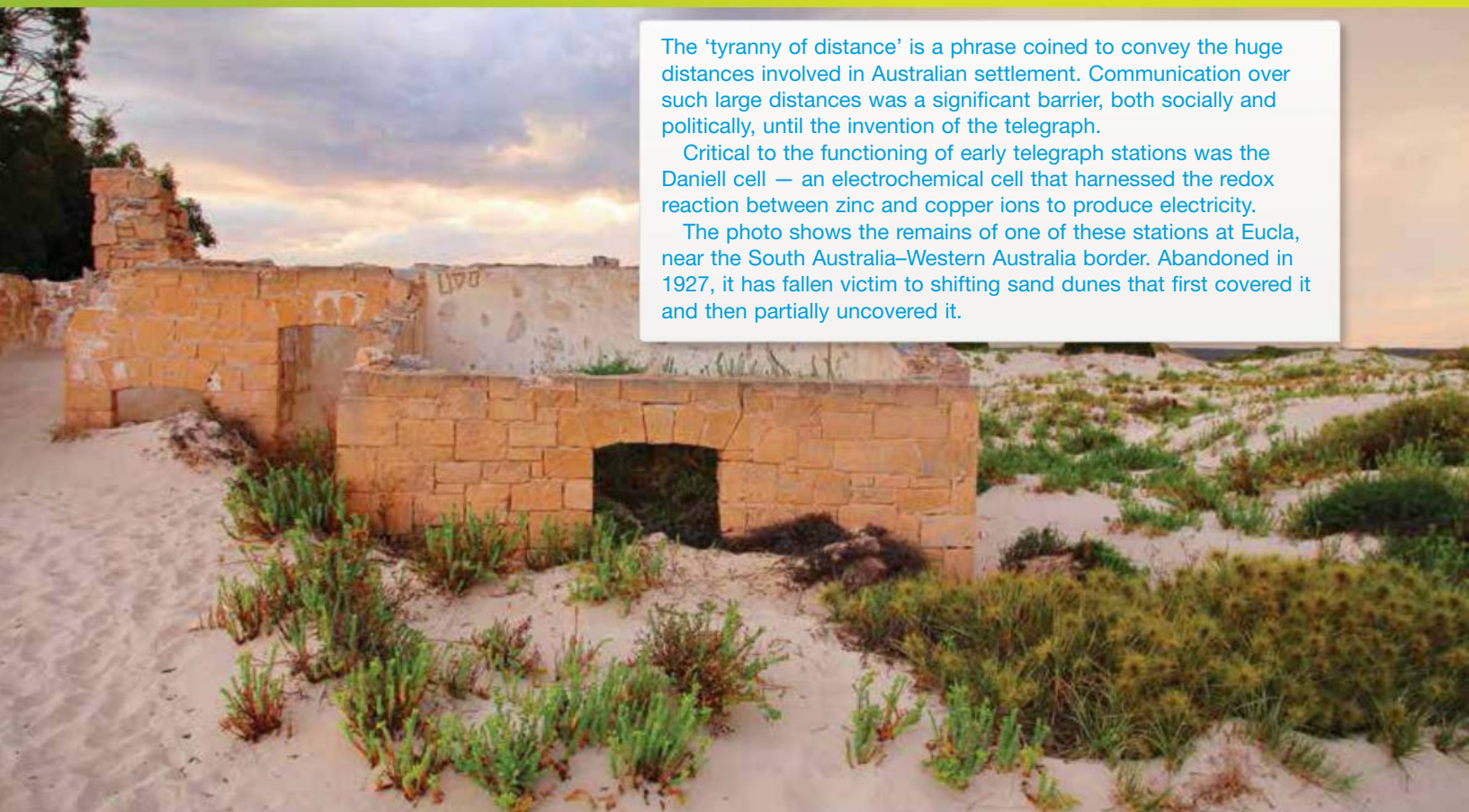
YOU WILL EXAMINE:

- definitions of oxidation and reduction, and of oxidising agent and reducing agent
- the use of oxidation numbers
- the description of redox processes by balanced half-equations and by balanced overall equations
- how spontaneous redox reactions may be harnessed to convert chemical energy into electrical energy through galvanic cells
- the design features of galvanic cells
- the electrochemical series and how it is obtained, constructed and used, and how it is used to predict spontaneous redox reactions and to make predictions concerning galvanic cells
- primary cells as batteries, which are practical applications of galvanic cells
- examples of some primary cells and how they function
- fuel cells as another type of device that converts chemical energy into electrical energy
- the design features of fuel cells
- examples of fuel cells and how they function.

The 'tyranny of distance' is a phrase coined to convey the huge distances involved in Australian settlement. Communication over such large distances was a significant barrier, both socially and politically, until the invention of the telegraph.

Critical to the functioning of early telegraph stations was the Daniell cell — an electrochemical cell that harnessed the redox reaction between zinc and copper ions to produce electricity.

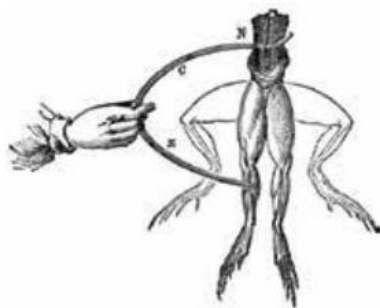
The photo shows the remains of one of these stations at Eucla, near the South Australia–Western Australia border. Abandoned in 1927, it has fallen victim to shifting sand dunes that first covered it and then partially uncovered it.



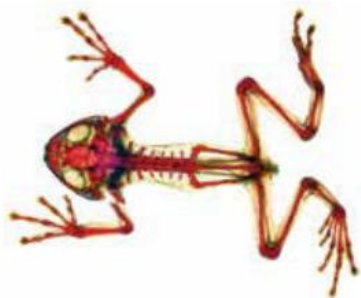
Redox reactions

Frog power?

The production of electricity from chemical reactions began in 1780 when Luigi Galvani (1739–1798), an Italian anatomist, began a series of experiments investigating the responses obtained from the hind legs of frogs when static electricity was applied to them. He found that the frogs' legs could be made to twitch by connecting the nerve and muscle tissues to different metals such as copper and iron. The dead frog was literally 'galvanised' into action. Galvani thought that the muscles of the frog must contain electricity and advocated the idea of 'animal electricity'.



One of Galvani's experiments on 'animal electricity'



During the eighteenth century, many people believed that the nerves and muscles of animals contained a fluid that acted like an electric current. How do Galvani's results support this idea?

Redox reactions involve the transfer of electrons. The process of oxidation produces electrons while the process of reduction consumes electrons.

A reducing agent is a substance that causes another substance (the oxidising agent) to be reduced.

An oxidising agent is a substance that causes another substance (the reducing agent) to be oxidised.

You will remember from unit 2 that **redox reactions** involve the transfer of electrons. The term 'redox' is derived from two separate words: **reduction** and **oxidation**. A substance is said to be reduced when it accepts (or gains) electrons. A substance is said to be oxidised when it donates (or loses) electrons. In a redox reaction, reduction and oxidation always occur simultaneously. Note that oxidation and reduction are *processes*.

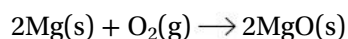
- Reduction is the *process* whereby electrons are added to a substance.
- Oxidation is the *process* whereby electrons are removed from a substance.

Oxidising agents (oxidants) and **reducing agents (reductants)**, on the other hand, are *substances* in a redox reaction. Because oxidation and reduction always occur together, an oxidising agent can be thought of as a substance that allows (or causes) another substance to undergo oxidation. It does this by accepting the electrons that are produced. In the same way, a reducing agent is a substance that permits another substance to undergo reduction (by supplying the electrons that are required). As a result, you will notice that oxidising agents undergo the *process* of reduction, while reducing agents undergo the *process* of oxidation.

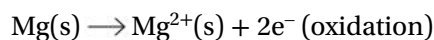
- Oxidising agents are substances that cause or permit another substance to be oxidised.
- Reducing agents are substances that cause or permit another substance to be reduced.

All of these definitions can be clarified if it is remembered that oxidation and reduction are *processes*, whereas oxidising agents and reducing agents are *substances* involved in these processes.

Redox reactions may be represented by balanced half-equations and by overall equations. For example, the burning of magnesium may be represented by the overall equation:



This equation may be 'deconstructed' into two half-equations that illustrate the transfer of electrons.



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Redox-electron transfer
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study on

Unit 3

AOS 1

Topic 2

Concept 1



Do more

Oxidation numbers

The oxidation number of an element is 0. The oxidation number of hydrogen is +1; the oxidation number of oxygen is -2.

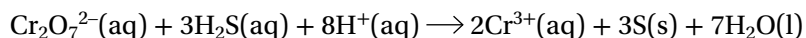
For a neutral compound, the sum of the oxidation numbers is 0.

For a polyatomic ion, the sum of oxidation numbers equals the charge on the ion.

In this reaction, magnesium is acting as a reducing agent while oxygen is acting as an oxidising agent. You will notice that, if the oxidation half-equation is multiplied by 2 and the two half-equations then added, the electrons cancel out and the *overall* equation is produced.

Oxidation numbers

The deconstruction of an equation into oxidation and reduction half-equations is proof that a reaction is a redox reaction. While this is a relatively simple process for some reactions, there are many redox reactions that are more complex. For example, the reaction:



is also a redox reaction. It is much harder to produce the half-equations for this reaction.

To assist in situations such as this, chemists use oxidation numbers. These are a set of rules that greatly assist in the identification of redox reactions. When using oxidation numbers:

- oxidation is an *increase* in the oxidation number of an atom
- reduction is a *decrease* in the oxidation number of an atom.

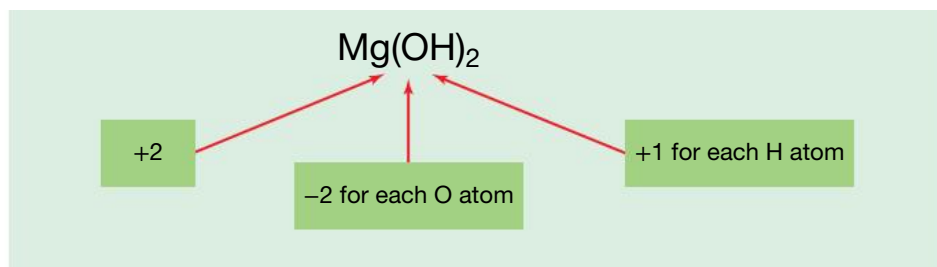
The following rules can be used to determine **oxidation numbers**. (Note: Oxidation numbers are theoretical numbers. They should not be confused with ionic charges.)

Rules for determining oxidation numbers

1. The oxidation number of an atom in its elemental form is 0. For example, the oxidation numbers of copper metal, $\text{Cu}(\text{s})$, and nitrogen gas, $\text{N}_2(\text{g})$, are both 0.
2. The oxidation number of a simple ion is the charge on the ion. For example, the Al^{3+} ion has an oxidation number of +3, and the S^{2-} ion has an oxidation number of -2. The charge must always be included.
3. The oxidation number of hydrogen is +1 in its compounds with non-metals. For example, the oxidation number of hydrogen in HCl , H_2O and NH_4^+ is +1. In metal hydrides such as NaH or CaH_2 , the oxidation number of hydrogen is -1.
4. The oxidation number of oxygen in a compound is usually -2. The exceptions to this rule are:
 - peroxide compounds, such as H_2O_2 and BaO_2 , in which oxygen has an oxidation number of -1
 - compounds in which oxygen is bonded to fluorine, where its oxidation number is +2. (Fluorine always has an oxidation number of -1 as it is the most electronegative element.)
5. In a neutral compound the sum of all the oxidation numbers must equal 0. For example, in MgCl_2 , they are added as follows: $+2 + (2 \times -1) = 0$.
6. In a polyatomic ion, the sum of the oxidation numbers must equal the charge on the ion. For example, in NO_3^- they are added as follows: $+5 + (3 \times -2) = -1$.
7. In covalent compounds that do not involve oxygen or hydrogen, the more electronegative element has the negative oxidation number. This is equal to the charge that it would have if it was a negative ion. For example, in ICl_3 , the chlorine is the more electronegative atom. It is therefore assigned an oxidation number of -1, as this is the charge on a chloride ion. (Note: This is just the way the oxidation number is worked out. This molecule is a covalent, neutral molecule; it *does not* contain chloride ions!) Using rule 5, we can now calculate that the oxidation number of the iodine in ICl_3 is +3.

Using oxidation numbers

The rules for determining oxidation numbers can be used to assign an oxidation number to each atom in a compound. Let us use the example of magnesium hydroxide, $\text{Mg}(\text{OH})_2$.



Note that the sum of the oxidation numbers must equal 0:

$$\begin{aligned}\text{Mg} + (2 \times \text{O}) + (2 \times \text{H}) &= +2 + (2 \times -2) + (2 \times +1) \\ &= 2 - 4 + 2 \\ &= 0\end{aligned}$$

The oxidation numbers of oxygen and hydrogen must be multiplied by 2 because each formula unit contains two of each of these atoms.

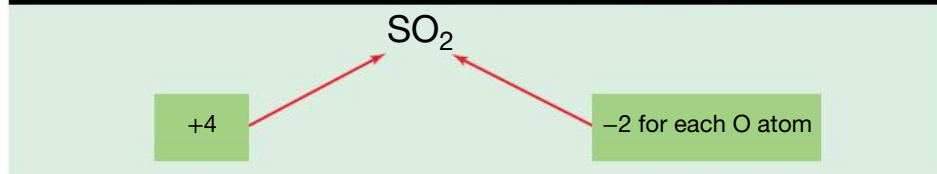
Sample problem 3.1

The photographs obtained by the *Voyager 1* space probe showed that one of the moons of Jupiter had active volcanoes and a surface composed of sulfur and sulfur dioxide, SO_2 . Assign oxidation numbers to each atom in the molecule sulfur dioxide.

Solution: Since the oxidation number for O is -2 and there are two O atoms, the oxidation number of S is $+4$.



Two of Jupiter's moons. Europa (left) has red stains on its surface caused by sulfur compounds. Io (right), has a thin atmosphere of sulfur dioxide, and sulfur compounds in liquid and solid states cover its surface.



Sample problem 3.2

The main compound in limestone statues or common chalk is calcium carbonate. What is the oxidation number of carbon in the carbonate ion, CO_3^{2-} ?

Solution: Assign as many oxidation numbers as possible, and then find the oxidation number of the unknown atom.

STEP 1

The oxidation number of oxygen is -2 .

STEP 2

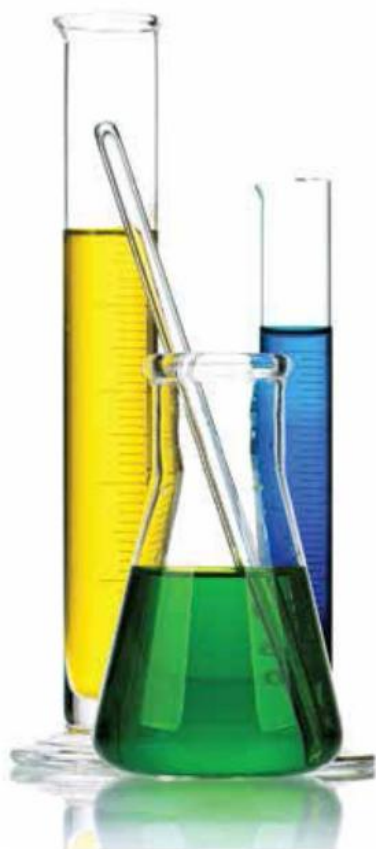
Obtain the oxidation number for carbon,

(oxidation number for C) + $3 \times$ (oxidation number for O) = -2 (-2 is the charge on the polyatom ion.)

(oxidation number for C) + $3 \times (-2) = -2$

(oxidation number for C) $- 6 = -2$

oxidation number for C = $+4$



Various chromium compounds dissolved in water. The solutions vary in colour due to the different oxidation states of chromium. Left to right: K_2CrO_4 , CrCl_3 , CrCl_2

Revision questions

- Assign oxidation numbers to the atoms in the following substances.
(a) HBr (c) CH_4 (e) Al_2O_3
(b) Na_2O (d) NaClO_3 (f) H_3PO_4
- Determine the oxidation number of S in each of the following compounds.
(a) H_2SO_4 (b) SO_2 (c) SO_3 (d) H_2S
- Solutions of chromium compounds are coloured due to the various oxidation states of chromium. Determine the oxidation number of chromium in each of the coloured solutions shown at left.
- Assign oxidation numbers to the atoms in the following ions.
(a) NH_2^- (c) HS^- (e) IO_3^-
(b) MnO_4^- (d) VO^{2+} (f) PO_4^{3-}

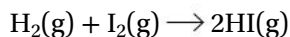
Identifying redox reactions

How can you decide whether a reaction is a redox reaction? The answer is that you can use oxidation numbers. If the oxidation number of an element changes between the reactant species and the product species, then that element has undergone either oxidation or reduction.

Given that oxidation cannot happen without reduction, it is easy to determine if the reaction can be classified as redox.

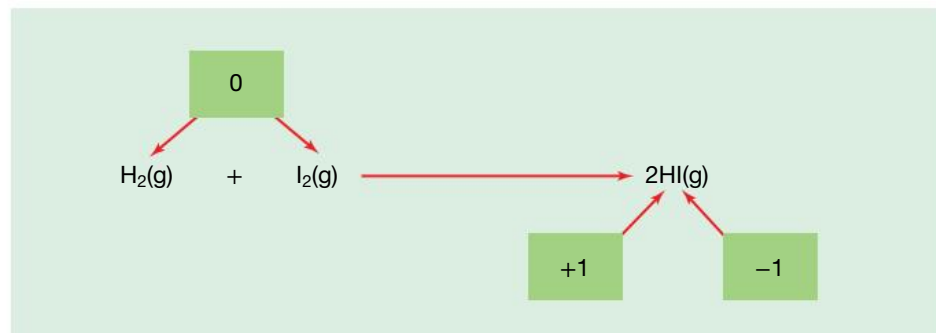
Sample problem 3.3

Determine whether the following reaction is a redox reaction.



Solution: **STEP 1**

Assign oxidation numbers to each element.



If the oxidation number of an element in a reacting species changes, the reaction is a redox reaction.

STEP 2

Determine whether a change in oxidation number has taken place.

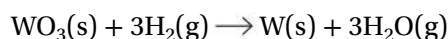
The oxidation number of hydrogen has changed from 0 to +1, so the hydrogen has been oxidised (as its oxidation number has increased).

The oxidation number of iodine has changed from 0 to -1, so the iodine has been reduced (as its oxidation number has decreased).

This is therefore a redox reaction.

Sample problem 3.4

Although tungsten, W, is a rare element, it is very common in light globes. Tungsten is used to make filaments for incandescent globes because it has both the highest melting point (3410 °C) and boiling point (5900 °C) of any metal. The metal is obtained from tungsten(VI) oxide by heating it with hydrogen, according to the equation:



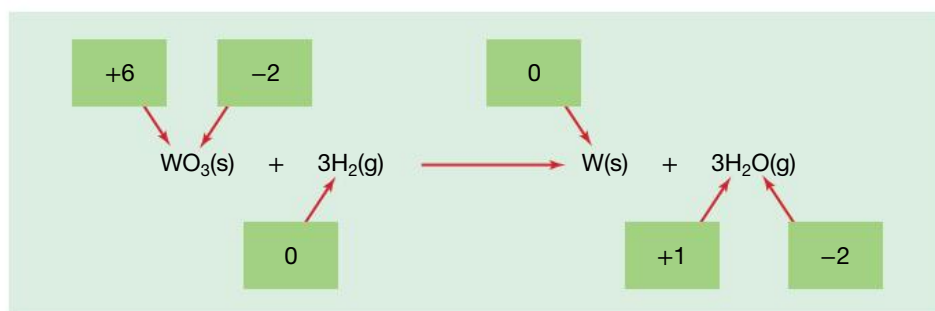
Using oxidation numbers, determine whether this equation represents a redox reaction and, if so, identify the oxidising agent and the reducing agent.

Solution: STEP 1

Assign oxidation numbers to each element.



The filaments of light globes are often made from tungsten metal, W. If hot tungsten is exposed to air, it oxidises to form tungsten oxide. This is why inert argon gas is used to fill the inside of light globes.



STEP 2

Determine whether a change in oxidation number has taken place.

Since the oxidation number of tungsten decreases (from +6 to 0), it must belong to the compound that is reduced. Similarly, the oxidation number of hydrogen increases (from 0 to +1), indicating oxidation.

Therefore, the reaction is redox. WO_3 (not just W) is the oxidising agent and H_2 is the reducing agent.

Oxidation involves an increase in oxidation number.

Reduction involves a decrease in oxidation number.

Revision questions

5. Which of the following equations are redox equations?

- (a) $2\text{Fe}(\text{s}) + 3\text{Cl}_2(\text{g}) \longrightarrow 2\text{FeCl}_3(\text{s})$
- (b) $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$
- (c) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$
- (d) $\text{NaOH}(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- (e) $\text{K}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{KOH}(\text{aq})$
- (f) $\text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{H}_3\text{PO}_4(\text{aq})$
- (g) $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g})$
- (h) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$

6. For each equation in question 5 that is a redox reaction, identify the substances that have been oxidised and reduced.
7. Prepare a multimedia presentation that describes the rules for assigning oxidation numbers and how they can be used to identify the oxidising agent and reducing agent in a redox reaction. Use examples in your presentation.

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Balancing redox equations

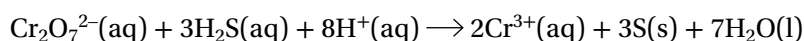
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Half-equations and redox equations

In unit 2, you learned that there is a set of rules for balancing redox equations. These are particularly useful for the more complicated types of redox reactions mentioned earlier. These rules are:

- Step 1 Identify the conjugate pairs that are involved in the reaction. Oxidation numbers may be useful in doing this. Write these pairs down with the reactant on the left and the product on the right.
 - Step 2 Balance all elements except oxygen and hydrogen.
 - Step 3 Balance oxygen atoms, where needed, by adding water molecules.
 - Step 4 Balance hydrogen atoms, where needed, by adding H^+ ions.
 - Step 5 Balance the overall charge by adding electrons.
- Once this process is done for each conjugate pair, the following steps then produce the overall equation.
- Step 6 Multiply each half-equation from step 5 by factors that produce the same number of electrons in each half-equation.
 - Step 7 Add the two half-equations together, cancelling the electrons. There may be other substances that partially cancel out as well at this stage.
 - Step 8 Identify the states for all species.

We can illustrate these steps by considering an equation mentioned earlier.



The conjugate pairs after using oxidation numbers are as follows.

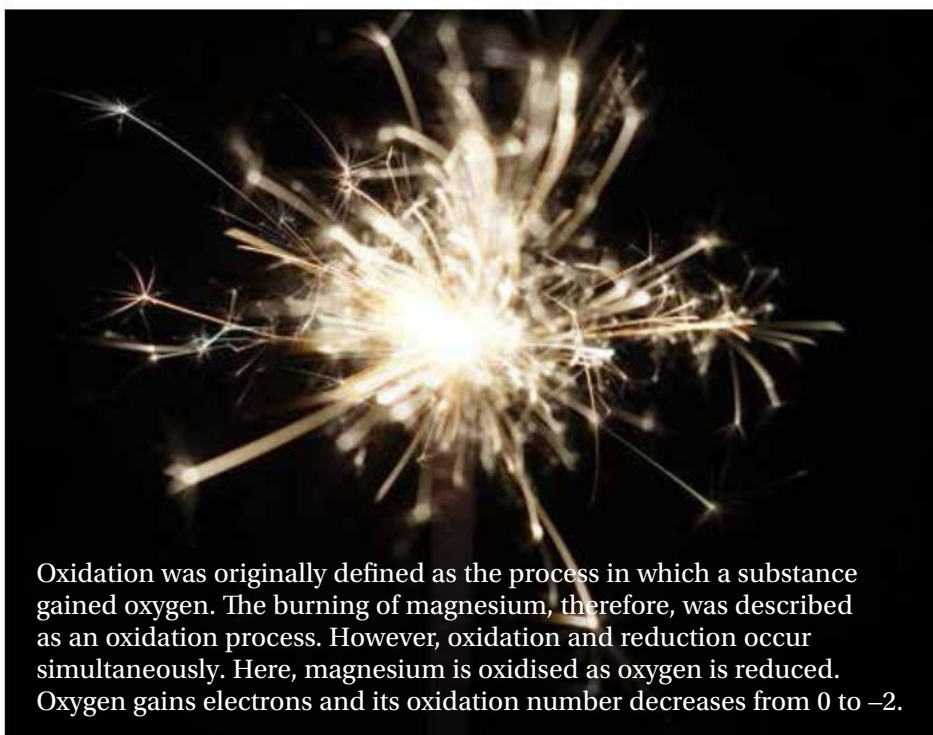
- Step 1 reduction: $\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}$
oxidation: $\text{H}_2\text{S} \longrightarrow \text{S}$
- Step 2 reduction: $\text{Cr}_2\text{O}_7^{2-} \longrightarrow 2\text{Cr}^{3+}$
oxidation: $\text{H}_2\text{S} \longrightarrow \text{S}$
- Step 3 reduction: $\text{Cr}_2\text{O}_7^{2-} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
oxidation: $\text{H}_2\text{S} \longrightarrow \text{S}$
- Step 4 reduction: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
oxidation: $\text{H}_2\text{S} \longrightarrow \text{S} + 2\text{H}^+$
- Step 5 reduction: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
oxidation: $\text{H}_2\text{S} \longrightarrow \text{S} + 2\text{H}^+ + 2\text{e}^-$

At this stage, the two half-equations have been produced and reduction and oxidation can be confirmed from the position of the electrons. If this was all that was required, symbols of state would now be added.

However, if the overall equation is required, the following two steps are used.

- Step 6 reduction: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ (not necessary to adjust)
oxidation: $3\text{H}_2\text{S} \longrightarrow 3\text{S} + 6\text{H}^+ + 6\text{e}^-$ (multiplied by 3 so that there are 6e^- on both sides)
- Step 7 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- + 3\text{H}_2\text{S} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{S} + 6\text{H}^+ + 6\text{e}^-$
After cancelling the electrons and hydrogen ions, this becomes
 $\text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{S} + 8\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O}$
- Step 8 Adding symbols of state now gives the original equation.
 $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{H}_2\text{S}(\text{aq}) + 8\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{S}(\text{s}) + 7\text{H}_2\text{O}(\text{l})$

8. Permanganate ions, $\text{MnO}_4^-(\text{aq})$, are strong oxidising agents. They can be used to oxidise ethanol, $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$, to ethanal, $\text{CH}_3\text{CHO}(\text{l})$. In the process, they are converted to $\text{Mn}^{2+}(\text{aq})$ ions.
 - (a) Write the equation for the above oxidation.
 - (b) Write the equation for the reduction reaction that also occurs.
 - (c) From your answers to (a) and (b), write the overall redox equation for this reaction.
 - (d) Identify the oxidising agent and the reducing agent in this reaction.
9. The oxidising strength of permanganate ions permits the ethanal produced in question 8 to be further oxidised to ethanoic acid, CH_3COOH . ($\text{Mn}^{2+}(\text{aq})$ is produced in this stage as well.)
 - (a) Write the equation for the oxidation that takes place in this situation.
 - (b) Write the equation for the reduction reaction.
 - (c) Write the overall redox equation for this reaction.
10. Nitric acid may act as an oxidising agent, especially when hot and concentrated. Many otherwise unreactive metals may be oxidised in this way. Write the overall redox equation for the oxidation of copper metal by $\text{NO}_3^-(\text{aq})$ ions to produce $\text{Cu}^{2+}(\text{aq})$ ions and $\text{NO}_2(\text{g})$ gas using this method.



Magnesium powder burning in a Bunsen burner flame. Burning magnesium powder gives out a great deal of light. It is commonly used in flash bulbs and fireworks.

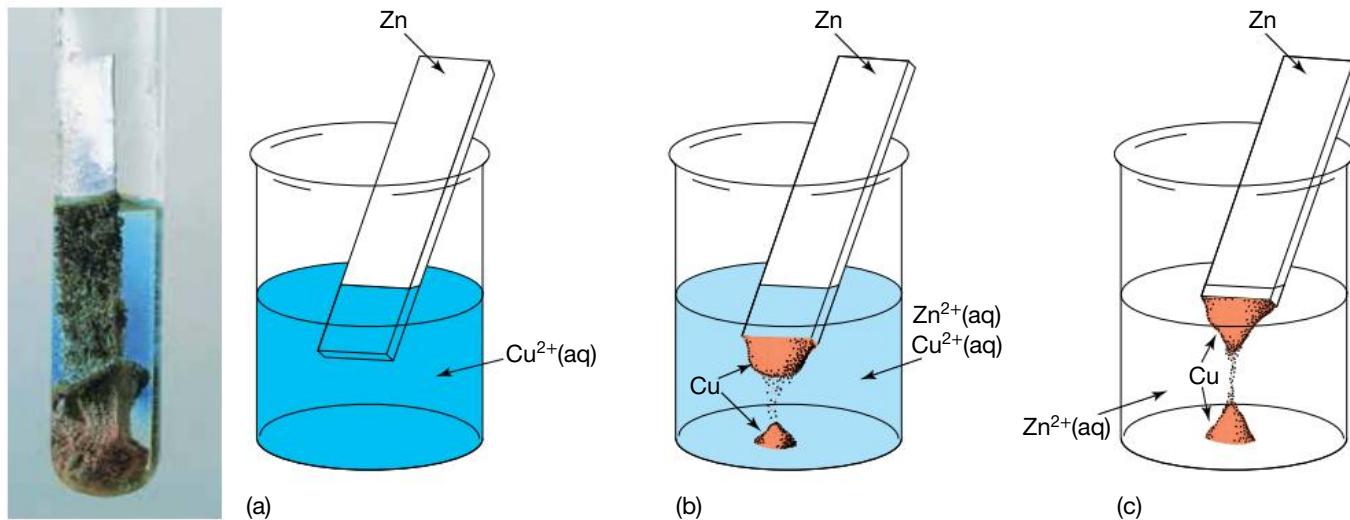
What happens when a zinc strip is placed in copper(II) sulfate solution?
As zinc is oxidised, electrons flow from the zinc metal to the copper ions.



This is a spontaneous reaction and requires no energy; in fact, it releases energy. Energy may be released in a number of forms such as heat, light, electricity or sound. The set-up of the reaction determines the form of energy that

Chemical energy can be converted into electrical energy in an electrochemical cell.

is released. For example, when zinc metal is placed in direct contact with copper ions, all the chemical energy of the reaction is released as thermal energy (heat) and the transfer of electrons from zinc to copper ions occurs on the surface of the zinc metal.



- (a) When a zinc strip is dipped into a copper(II) sulfate solution, a spontaneous redox reaction begins.
- (b) As the zinc dissolves, copper ions are reduced to copper metal and the original blue colour of the solution begins to fade.
- (c) If the zinc strip remains in the solution for an extended period of time, the solution in the beaker becomes colourless. All the copper ions in solution are reduced to form copper metal, and the zinc goes into solution as zinc ions.

As zinc reacts with copper(II) ions, it goes into solution as Zn^{2+} ions. Solid copper is deposited on the surface of the zinc.



If, however, the site of oxidation is physically separated from the site of reduction (for example, if each of the solutions is in a separate beaker), and a connecting wire is placed between them, the electrons are forced to travel through this wire to complete the redox reaction. Such movement of electrons constitutes an electric current. This arrangement, therefore, converts chemical energy directly into electrical energy.

To do this for the $\text{Zn(s)}/\text{Cu}^{2+}(\text{aq})$ reaction that we have been discussing, a strip of zinc metal is placed in a beaker containing zinc sulfate solution (see the diagram on the next page). This is connected by a wire to a strip of copper placed in a beaker containing a copper sulfate solution. The wire provides a pathway for the electrons to pass from the zinc atoms to the copper cations. No reaction is observed, however, because the circuit is not complete.

As the zinc atoms donate electrons and become zinc cations in the first beaker, the electrical neutrality must be maintained, so anions are required. These anions are supplied by the **salt bridge**, which can be a simple filter paper or a U-tube with cotton wool in it. It is soaked in a salt solution, such as potassium nitrate solution, $\text{KNO}_3(\text{aq})$, and used to connect the two beakers. Potassium nitrate solution provides NO_3^- anions for the first beaker to balance the positive charges created by zinc cations. In the second beaker, copper

The salt bridge provides ions to balance ions consumed or produced in each cell.

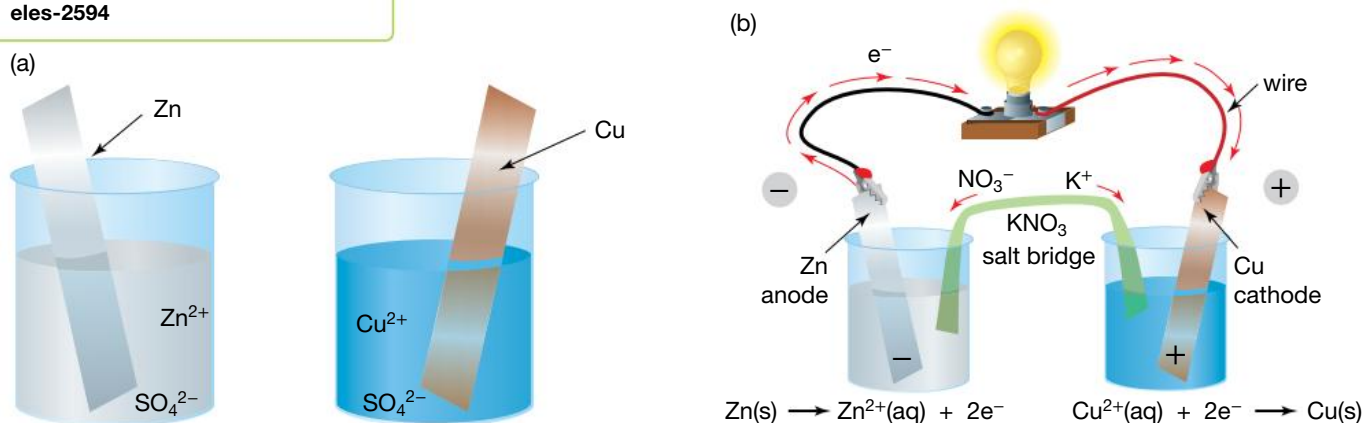
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Experiment 3.1 Investigating the Daniell cell
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eLesson

Galvanic cells 1
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cations accept electrons and become copper atoms, leaving behind negative sulfate ions in solution that must be balanced. So the salt bridge supplies cations (in this case, $\text{K}^+(\text{aq})$). Electrons carry the current in the wire from zinc to copper, and ions carry the current in solution. The flow of ions completes the circuit. It is important that the ions in the salt bridge do not react with chemicals in the beakers. The movement of ions in the solutions is called the **internal circuit**.



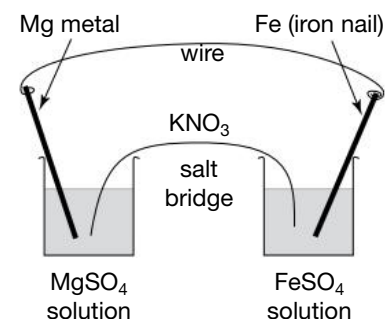
A simple galvanic cell consists of:

- two half-cells, containing two electrodes (anode and cathode) and two electrolytes
- a conducting wire
- a salt bridge, containing another electrolyte.

An electrolyte is a solution containing ions that can conduct electricity.

An electrode is a conductor through which electrons enter or leave a galvanic cell.

The anode is the electrode where oxidation occurs. The cathode is the electrode where reduction occurs.



Solution:

Each beaker is a **half-cell**. The metal conducting strips are called **electrodes** and, combined with the wire, they are referred to as the **external circuit**. Electrons in the external circuit can be made to do useful work such as lighting a light bulb.

Chemical energy has been converted into electrical energy. Solutions that can conduct a current are known as **electrolytes**. The electrode at which oxidation occurs is called the **anode**, and it has a negative charge. The electrode at which reduction occurs is called the **cathode**, and it has a positive charge. All of these components together are known as a galvanic cell or an **electrochemical cell**.

The example above of an electrochemical cell containing the half-cells $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq})$ and $\text{Cu(s)}/\text{Cu}^{2+}(\text{aq})$ is known as the Daniell cell.

Sample problem 3.5

A galvanic cell was set up in the following way. A strip of clean magnesium was dipped into a beaker containing a solution of MgSO_4 and, in a separate beaker, an iron nail was dipped into a solution of FeSO_4 . The iron nail and magnesium strip were connected with a wire, and the circuit was completed with a salt bridge consisting of filter paper dipped into a solution of KNO_3 , as shown in the diagram at left. The magnesium electrode was known to have a negative charge. Predict the following.

- The substance that is oxidised and the one that is reduced
- The anode and cathode
- The direction of electron flow
- The half-cell reactions
- The overall redox reaction

(a) Since electrons flow from negative to positive, they are produced at the magnesium electrode and consumed at the zinc electrode. Therefore, magnesium is being oxidised and iron (II) ions are being reduced.

- (b) Since oxidation occurs at the anode, magnesium is the anode and iron is the cathode.
- (c) Electrons flow from the magnesium electrode through the wire to the iron electrode.
- (d) The following half-cell reactions occur.
- $$\text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \text{ (oxidation)}$$
- $$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe(s)} \text{ (reduction)}$$
- (e) Adding these half-equations and cancelling the electrons, results in the following overall redox reaction.



Revision questions

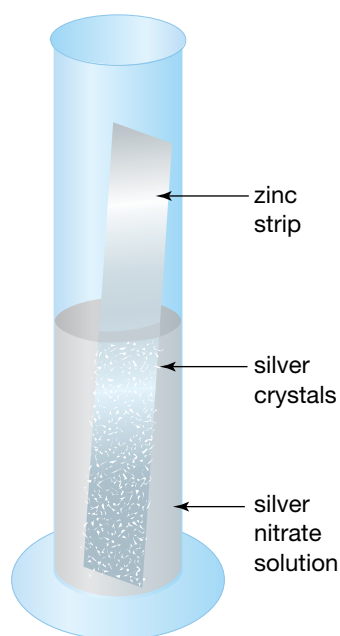
11. When zinc metal is dipped into a solution of silver nitrate, it forms a coating of silver, as shown in the diagram at left.

Use this reaction to draw a diagram of a galvanic cell, using KNO_3 in the salt bridge and zinc sulfate as one of the electrolytes. Complete the following steps in constructing your diagram.

- Draw the two half-cells.
- Write half-equations for the oxidation and reduction reactions.
- Write the overall cell reaction.
- Label the flow of:
 - electrons in the wire
 - anions in the salt bridge
 - cations in the salt bridge.
- Label the anode and the cathode.

12. A galvanic cell was set up by combining half-cells containing zinc and magnesium electrodes dipped into the appropriate sulfate solutions. A conducting wire and a salt bridge completed the circuit. After 3 hours, the two electrodes were removed and weighed. The mass of the Zn electrode had increased, while the mass of the Mg electrode had decreased. Draw this galvanic cell, clearly indicating the following.

- The anode and the cathode
- The ions present in the half-cells
- The electrolyte in the salt bridge
- Anion and cation flow within the salt bridge
- The direction of the flow of electrons
- The anode reaction and the cathode reaction
- The oxidation reaction and the reduction reaction
- The overall cell reaction
- The oxidising agent and the reducing agent



study on

Unit 3

AOS 1

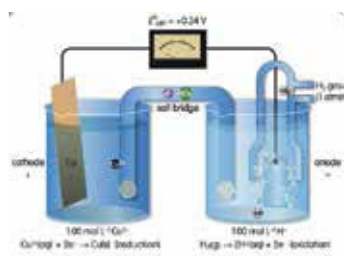
Topic 2

Concept 3



See more

Features of galvanic cells



Galvanic cells in the laboratory

Galvanic cells constructed in the laboratory have the following features in common.

- Two separate half-cells that contain electrolytes: Oxidation occurs in one half-cell and reduction in the other. Each half-cell contains a different **conjugate redox pair**. A conjugate redox pair consists of an electron donor and its corresponding electron acceptor form: for example, $\text{Cu}^+(\text{aq})$ (donor) and $\text{Cu}^{2+}(\text{aq})$ (acceptor). Each half-cell also has spectator ions that balance

Oxidising agents accept electrons to undergo reduction. Reducing agents lose electrons to undergo oxidation.

- the reacting ions and make the cell electrically neutral. So, in the Daniell cell, Cu^{2+} (present as $\text{CuSO}_4(\text{aq})$) is reacting and Zn^{2+} (present as $\text{Zn}(\text{NO}_3)_2(\text{aq})$) is produced; the $\text{SO}_4^{2-}(\text{aq})$ and the $\text{NO}_3^-(\text{aq})$ are spectator ions.
2. One electrode in each half-cell: Each electrode may be one of the reactant pairs or may be inert such as graphite or platinum. Redox half-cell reactions occur at the electrode surface. The polarity refers to the charge on the electrode; the anode is negative and the cathode is positive.
 3. A connecting wire between the electrodes that forms an external circuit: This allows electrons to flow from the reducing agent to the oxidising agent; that is, from the anode to the cathode.
 4. A salt bridge connecting the two solutions: This contains a strong electrolyte (often potassium nitrate or potassium chloride) that allows a slow migration of ions (such as K^+ and NO_3^-) to maintain the cell's electrical neutrality. The negative ions flow into the cell containing the anode; they are needed to balance the positive ions that are produced at the anode surface. The positive ions flow into the cell containing the cathode. Because electrons are accepted by the ions in this cell, positive ions are consumed. The original negative ions remaining must be balanced by additional positive charges from the salt bridge. The ions from the salt bridge must not react with the electrolytes in the cells. That would interfere with the cell's operation.

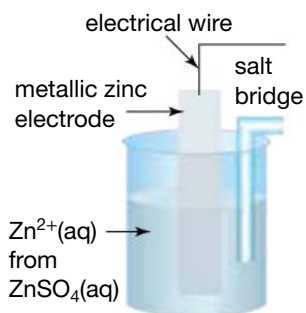
Types of half-cell

Each half-cell in a laboratory galvanic cell contains a conjugate oxidising agent-reducing agent pair. Oxidation occurs in one of the half-cells and reduction occurs in the other. Half-cells are constructed by dipping an electrode into an electrolyte. The electrode may or may not take part in the reaction.

It is convenient to group half-cells into three types based on design. The three types are:

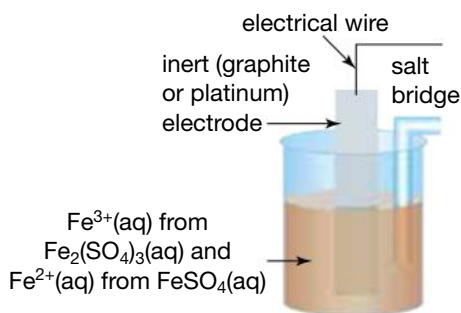
- the metal ion-metal half-cell
- the solution half-cell
- the gas-non-metal half-cell.

(a) The metal ion-metal half-cell



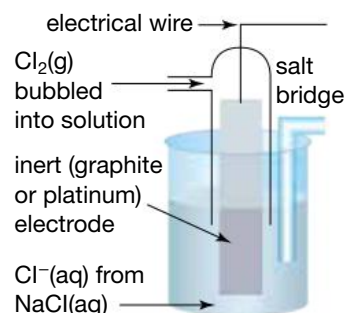
This cell consists of a metal rod in a solution of its ions, usually from the sulfate salt. The sulfate ion is unreactive. More reactive ions such as bromide ions or nitrate ions may set up a competing reaction.

(b) The solution half-cell



This cell uses an inert electrode in the reacting solution. The reacting solution may contain an oxidising agent, e.g. $\text{MnO}_4^-(\text{aq})$ in solution (with $\text{Mn}^{2+}(\text{aq})$), or a reducing agent, e.g. $\text{Fe}^{2+}(\text{aq})$ in solution (with $\text{Fe}^{3+}(\text{aq})$).

(c) The gas-non-metal ion half-cell



Although gases are reactive, they are usually more difficult to manage in the laboratory. As a result, gaseous half-cells are not very common. In a gaseous half-cell, the gas bubbles over an inert electrode that is connected to the external wire. Its conjugate redox non-metal ion is in solution.

Revision questions

13. A half-cell containing $\text{Cr}_2\text{O}_7^{2-}(\text{aq})/\text{Cr}^{3+}(\text{aq})$ is connected to one containing $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$. A voltmeter indicates that electrons flow from the beaker containing $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ to the one containing $\text{Cr}_2\text{O}_7^{2-}(\text{aq})/\text{Cr}^{3+}(\text{aq})$.
- Draw a labelled diagram of this set-up, indicating the contents of each beaker, the salt bridge and the materials that each electrode is made from. Also mark the direction of electron flow.
 - Write the equation for each half-reaction under the appropriate half-cell.
 - On your diagram, label the anode, cathode and the polarity of each electrode.
 - Why is it necessary to acidify the $\text{Cr}_2\text{O}_7^{2-}(\text{aq})/\text{Cr}^{3+}(\text{aq})$ half-cell?

Standard electrode potentials

The **electrical potential** of a galvanic cell is the ability of the cell to produce an electric current. Electrical potential is usually measured in volts (V). Although we cannot measure the electrode potential for an isolated half-cell, we can measure the difference in potential between two connected half-cells.

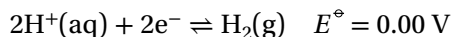
The electrical potential of a cell results from competition between the two half-cells for electrons. The half-cell with the greater tendency to attract electrons undergoes reduction. The other half-cell loses electrons and is oxidised. The half-cell in which reduction occurs has a greater reduction potential than the half-cell in which oxidation occurs.

The **reduction potential** of a half-cell is a measure of the tendency of the oxidising agent to accept electrons and so undergo reduction. The difference between the reduction potentials of the two half-cells is called the **cell potential difference**.

The **standard cell potential difference** (E°_{cell}) is the measured cell potential difference, under standard conditions, when the concentration of each species in solution is 1 M, the pressure of a gas, where applicable, is 1 atm (101 325 Pa), and the temperature is 25 °C (298 K).

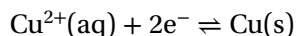
$$E^\circ_{\text{cell}} = E^\circ_{\text{oxidising agent}} - E^\circ_{\text{reducing agent}}$$

To obtain a comparative measure of the reduction potentials of different half-cells, the **standard hydrogen half-cell** is used as a standard reference electrode. It has been assigned an arbitrary value of 0.00 V and the reaction that occurs at the electrode surface is as follows.



The standard hydrogen electrode is used with other half-cells so that the reduction potentials of those cells may be measured. If a species accepts electrons more easily than hydrogen, its electrode potential is positive. If it accepts electrons less easily than hydrogen, its electrode potential is negative.

When a standard hydrogen half-cell is connected to a standard $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cell, the voltmeter measures a potential difference of 0.34 volts (see the diagram at the top of the next page). Since electrons flow towards the $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cell, $\text{Cu}^{2+}(\text{aq})$ has a greater tendency to accept electrons (it is a stronger oxidising agent) than $\text{H}^+(\text{aq})$. The measured E° value for the half-cell reaction:



is therefore positive in sign and equal to +0.34 volts.

The reduction potential is a measure of the tendency of an oxidising agent to accept electrons.

The cell potential difference E° is calculated by the difference between the two half-cell E° values.

Half-cell E° values are measured against the standard hydrogen half-cell, which is arbitrarily assigned 0.00 volts.

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Galvanic cells 2 (part 1)

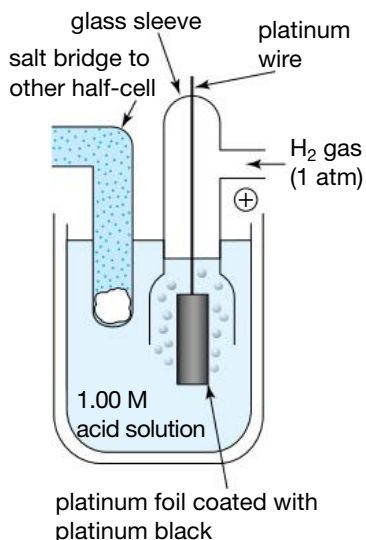
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Galvanic cells 2 (part 2)

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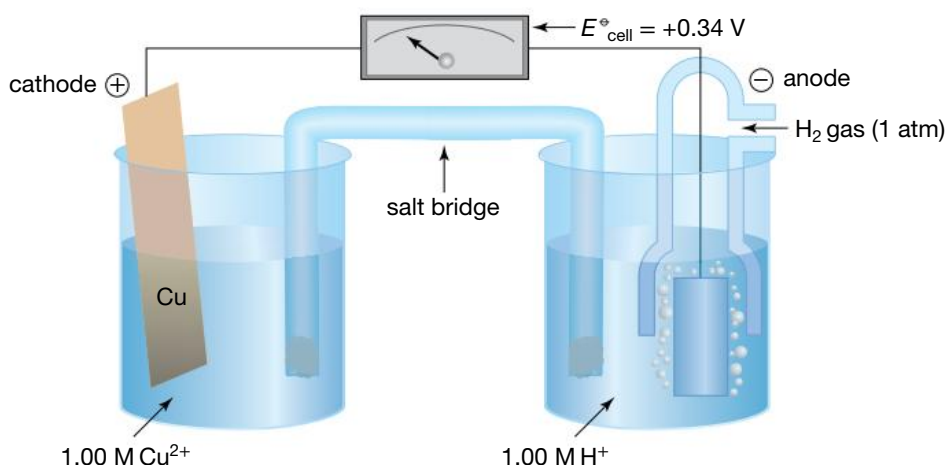


A hydrogen half-cell

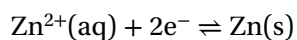


The hydrogen half-cell, which is used as a reference half-cell for the determination of a redox half-cell's ability to accept electrons, consists of hydrogen gas bubbling around an inert platinum electrode in a solution of hydrogen ions. The standard hydrogen half-cell is arbitrarily assigned a standard reduction potential of 0.00 V at 25 °C.

Measuring the standard half-cell potential of a Cu^{2+}/Cu half-cell

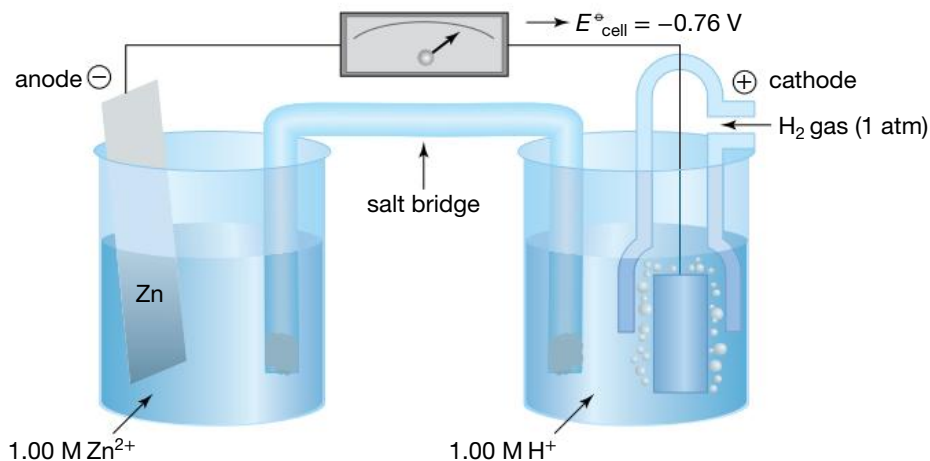


When a standard hydrogen half-cell is connected to a standard $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ half-cell, the voltmeter measures a potential difference of 0.76 volts (see diagram below). Since electrons flow to the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ half-cell, $\text{H}^+(\text{aq})$ has a greater tendency to accept electrons than $\text{Zn}^{2+}(\text{aq})$. The measured E° value for the half-cell reaction:



is therefore negative in sign and equal to -0.76 volts.

Measuring the standard half-cell potential of a Zn^{2+}/Zn half-cell



Half-cell potentials are often listed in a table such as table 3.1. Such tables may be referred to as tables of standard electrode potentials or standard reduction potentials, and may also be termed an **electrochemical series**. The half-cell potentials are usually arranged from the largest E° value to the smallest.

TABLE 3.1 The electrochemical series

Half-reaction			E° (volts)
strongest oxidising agent	reducing agent	weakest reducing agent	
	$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$		+2.87
	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$		+1.77
	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$		+1.52
	$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$		+1.46
	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$		+1.36
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$		+1.33
	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$		+1.23
	$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$		+1.09
	$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$		+0.95
	$\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$		+0.81
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$		+0.80
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$		+0.77
	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2(\text{l})$		+0.68
	$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$		+0.54
	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$		+0.40
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$		+0.34
	$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$		+0.20
	$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$		+0.15
	$\text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{S}(\text{g})$		+0.14
	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ (defined)		0.00
	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$		-0.13
	$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s})$		-0.14
	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$		-0.23
	$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$		-0.36
	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$		-0.44
	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$		-0.76
	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$		-0.83
	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$		-1.67
	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s})$		-2.34
	$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$		-2.71
	$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca}(\text{s})$		-2.87
weakest oxidising agent	$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K}(\text{s})$	strongest reducing agent	-2.93
	$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$		-3.02

Note: Standard electrode reduction potentials at a temperature of 25 °C, a pressure of 1 atm and a concentration of 1 M for all aqueous species

In the E° table, the strongest oxidising agent, top left, reacts with the strongest reducing agent, bottom right.

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Experiment 3.2 Predicting redox reactions

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Experiment 3.3 Galvanic cells and redox potentials

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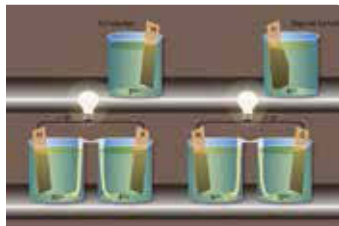
Unit 3

AOS 1

Topic 2

Concept 4

Do more
Electrochemical series



Use of standard half-cell reduction potentials

A table such as the electrochemical series on the previous page provides a great deal of information about a redox reaction. This includes:

- determination of the relative strengths of oxidising agents and reducing agents
- prediction of whether a redox reaction will occur
- prediction of the overall reaction occurring in a cell and the potential difference of that cell.

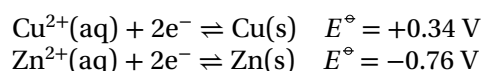
However, the table does not tell us the rate of a reaction or if intermediates form. E° values and their order are temperature dependent, and the E° table predicts reactions only at standard conditions of 25 °C, 1 atm and 1 M concentration for solutions.

Predicting spontaneous reactions in galvanic cells

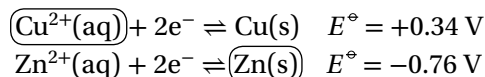
In galvanic cells, at least two oxidising agents and two reducing agents are present. Which oxidising agent reacts with which reducing agent?

The following procedure may be useful in predicting which spontaneous reaction occurs in a galvanic cell. Use the Daniell cell as an example.

- Write the half-equations occurring in the galvanic cell in descending order of E° . For example:



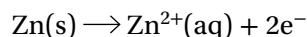
- Circle the species present in the galvanic cell that could participate.



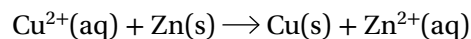
- Select the oxidising agent with the highest E° . This is reduced at the cathode since it accepts electrons more easily than an oxidising agent with a lower E° .



- Select the reducing agent with the lowest E° . This is oxidised at the anode since it donates electrons more easily than a reducing agent with a higher E° . Write this equation as an oxidation equation; that is, reverse it.



- Balance electrons if necessary from the half-equations.
- Write the full equation.

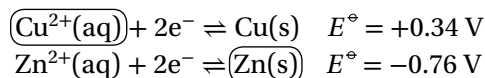


- Determine the cell potential difference by using the formula:

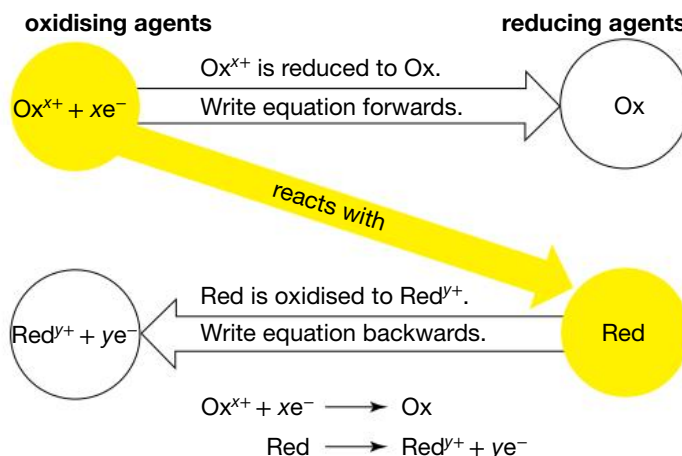
$$\begin{aligned}\text{cell potential difference} &= E^\circ_{\text{oxidising agent}} - E^\circ_{\text{reducing agent}} \\ &= +0.34 - (-0.76) \\ &= 1.10 \text{ V}\end{aligned}$$

Summary

When the electrode reactions are written in descending order of E° values, the strongest oxidising agent (highest E°) on the left-hand side of the equation reacts with the strongest reducing agent (lowest E°) on the right.



Summary
of how to
predict redox
reactions:
Ox = oxidising
agent; Red =
reducing agent



Sample problem 3.6

The standard half-cell potentials of some metal-metal ion half-cells are as follows.

Half-cell	E° (volts)
Ag ⁺ (aq)/Ag(s)	+0.80
Co ²⁺ (aq)/Co(s)	-0.28
Ba ²⁺ (aq)/Ba(s)	-2.90

Determine which species is the best oxidising agent and which is the best reducing agent.

Solution: Oxidising agents accept electrons to undergo reduction. Ag⁺(aq), Co²⁺(aq) and Ba²⁺(aq) are all oxidising agents.

Reducing agents lose electrons to undergo oxidation. Ag(s), Co(s) and Ba(s) are all reducing agents.

In a conventional table of standard half-cell reduction potentials, the strongest oxidising agent has the most positive E° value, while the strongest reducing agent has the most negative E° value. So, in this example, Ag⁺(aq) is the strongest oxidising agent, while Ba(s) is the strongest reducing agent.

study on

Unit 3

AOS 1

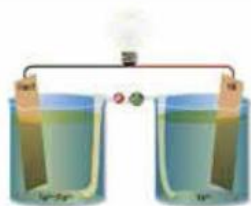
Topic 2

Concept 5



See more

Predicting products
of redox reactions



Revision questions

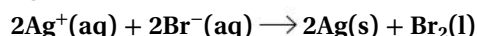
14. Consider the following conjugate redox pairs and their E° values.

Cl ₂ (g)/Cl ⁻ (aq)	+1.36 V
I ₂ (s)/I ⁻ (aq)	+0.54 V
Al ³⁺ (aq)/Al(s)	-1.67 V
MnO ₄ ⁻ (aq)/Mn ²⁺ (aq)	+1.52 V
Pb ²⁺ (aq)/Pb(s)	-0.13 V

- (a) Which species is:
- the strongest oxidising agent
 - the strongest reducing agent
 - the weakest oxidising agent
 - the weakest reducing agent?

(b) Write fully balanced half-equations for each conjugate redox pair.

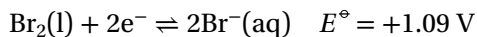
15. Use a table of standard electrode potentials to determine whether the following reaction is a spontaneous redox reaction.



Justify your decision.

Sample problem 3.7

Given the two half-equations:

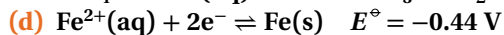
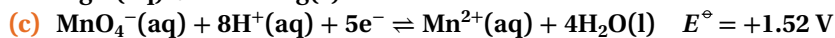
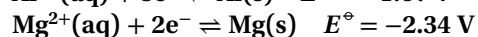
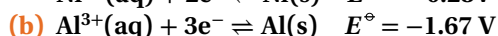
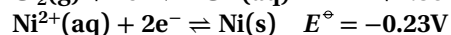
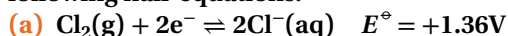


predict the likely spontaneous redox reaction.

Solution: For a redox reaction to occur, a reducing agent must react with an oxidising agent. $\text{Br}_2(\text{l})$ does not react with $\text{Mg}^{2+}(\text{aq})$ (since both can act only as oxidising agents) and $\text{Br}^-(\text{aq})$ does not react with $\text{Mg}(\text{s})$ (since both can act only as reducing agents). For a spontaneous redox reaction to occur, the E° of the oxidising agent must be more positive than the E° of the reducing agent. $\text{Br}_2(\text{l})$ reacts spontaneously with Mg .

Revision questions

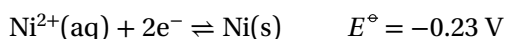
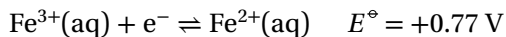
16. Write the likely spontaneous redox reactions that would occur given the following half-equations.



17. Suggest reasons why the reactions that you predicted in question 16 may not be observed.

Sample problem 3.8

Given the two half-equations:



identify the anode and cathode, write the overall equation and calculate the standard cell potential that would be produced in a galvanic cell made from these half-cells.

Solution: Reduction occurs at the cathode and oxidation occurs at the anode. Reduction occurs at the half-cell with the more positive reduction potential. In this cell, $\text{Fe}^{3+}(\text{aq})$ is reduced and $\text{Ni}(\text{s})$ is, therefore, oxidised. Since reduction occurs in the $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$ half-cell, the electrode in this half-cell acts as the cathode. The nickel electrode in the $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$ half-cell acts as the anode, and undergoes oxidation.

The half-cell reactions may be written as follows.



So, to balance the electrons in each half-reaction:



Before the half-reactions are added, care must be taken to balance and cancel the electrons. The overall equation will be written as:



The standard cell potential can be calculated as follows.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{oxidising agent}} - E^\circ_{\text{reducing agent}} \\ &= +0.77 \text{ V} - (-0.23 \text{ V}) \\ &= +1.00 \text{ V} \end{aligned}$$

(Note: The E° of a half-cell remains the same even if the half-equation is multiplied by a number to cancel electrons in the overall equation. While a nickel electrode could be used in one half-cell, an iron electrode is unsuitable for the other as there could be a further interaction between iron and Fe^{2+} .)

Revision questions

18. Identify the anode and cathode, write the overall equation, label the direction of electron flow and calculate the standard cell potential that would be produced in a galvanic cell constructed from half-cells using the following redox half-equations.
- (a) $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb(s)}$ $E^\circ = -0.13 \text{ V}$
 $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$ $E^\circ = -0.76 \text{ V}$
- (b) $\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag(s)}$ $E^\circ = +0.80 \text{ V}$
 $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ $E^\circ = +0.77 \text{ V}$
- (c) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O(l)}$ $E^\circ = 1.23 \text{ V}$
 $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$ $E^\circ = -0.44 \text{ V}$
19. Sketch the galvanic cells based on the following overall equations, labelling the direction of electron flow, cathode, anode, polarity and direction of cation movement in the salt bridge.
- (a) $\text{Cu}^{2+}(\text{aq}) + \text{Mg(s)} \longrightarrow \text{Cu(s)} + \text{Mg}^{2+}(\text{aq})$
- (b) $2\text{Co}^{3+}(\text{aq}) + \text{Pb(s)} \longrightarrow \text{Pb}^{2+} + 2\text{Co}^{2+}(\text{aq})$
20. A galvanic cell constructed by a VCE student in a school laboratory recorded zero cell voltage after it had been operating previously at 0.38 V. Suggest three possible reasons for this observation.

The unpredictability of the rate of electrochemical reactions

Although E° values can be added to decide whether a spontaneous reaction will occur between an oxidising agent and a reducing agent, they do not provide any information about the rate of the reaction. Although you may predict that a redox reaction is possible between two reactants, in practice no reaction may be observed if the reaction proceeds very slowly.

If the redox reaction conditions deviate significantly from those at which standard electrode potentials are measured, the relative order of redox conjugate pairs in the table of standard electrode potentials could be altered. This could mean that previously favourable reactions become unfavourable under the new conditions.

Redox predictions may be checked by experiment.

Non-standard conditions may change redox reaction E° values.

Cells and batteries

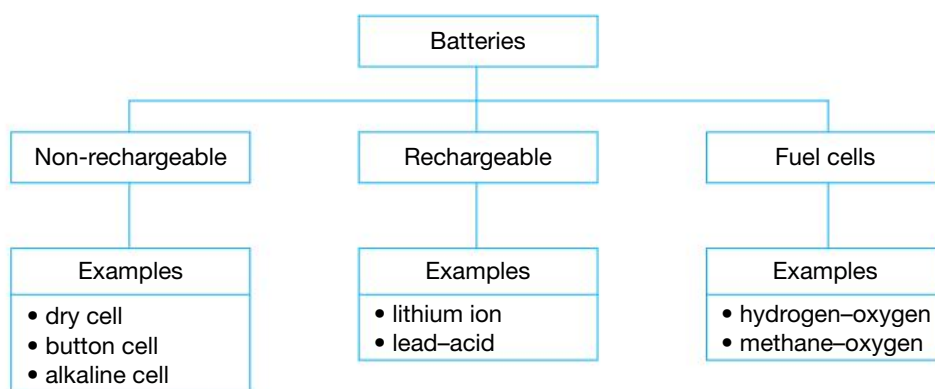
One of the first electrochemical cells used widely was invented by Daniell in 1836 and was used extensively at the time in telegraph and telephone work as a reliable source of electricity. Daniell cells are examples of wet cells, where the electrolyte is in a liquid state. However, since Daniell cells could not be stored easily and were easily spilled, their application was limited. The demand for portable, leakproof electrochemical cells led to the development of the Leclanché or dry cell.

Batteries are practical applications of electrochemical cells. They are used as small, portable and efficient sources of electrical energy. A battery is a combination of cells in series or parallel, but common cells such as the dry cell are also often referred to as batteries.

Some cells, such as the common dry cell, are used until the supply of electrical energy is exhausted and are then discarded. These cells are sometimes called **primary cells** and are not rechargeable. Once the chemical reaction is over, they are useless. Other cells, such as the lead–acid accumulator battery or nickel–cadmium cells, are **rechargeable**. Rechargeable batteries are sometimes referred to as **secondary cells**, which are discussed in chapter 4.

Another type of cell is the fuel cell, which uses a supply of fuel in order to create a flow of electrons.

Primary cells are not rechargeable. Secondary cells can be recharged.



Cells can be primary (non-rechargeable) cells, secondary (rechargeable) cells or fuel cells.

Factors affecting selection of cells

Many factors must be considered when selecting a cell for a particular use. These include:

- *initial and operating cost*: This depends on the materials used and the technology involved in development and production.
- *size and shape*: The main shapes are cylindrical, coin, button, pouch and prismatic.
- *mass*: In portable devices, lightness is a priority, whereas transport vehicles can accommodate heavier or bulkier cells.
- *single use or rechargeable*
- *memory effect*: Some cells have decreased capacity to be fully charged. This occurs when rechargeable batteries are not fully discharged before recharging.
- *voltage provided*: For example, cells with aqueous electrolytes cannot provide more than 2 volts.
- *discharge curve*: This is how the voltage changes over time. For some batteries, the voltage decreases steadily; other batteries supply relatively constant voltage until most of the charge is consumed.
- *current*: The greater the surface area of the electrodes, the greater the current, although this limits the amount of electrolyte present.

- *shelf life*: Some cells discharge over time even when not being used.
- *ease of disposal and other environmental factors*: The mercury button cell has been phased out due to environmental concerns, and there is also concern about the toxicity of cadmium in nickel-cadmium (NiCd) cells. All rechargeable batteries should be recycled.

Primary cells

The dry cell

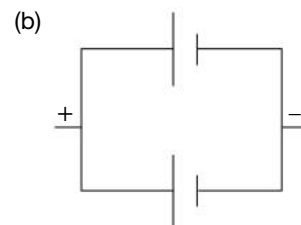
The dry cell is a primary cell that is suitable for devices requiring intermittent use.

The dry cell is a good general-purpose battery but it can produce only a small current and its voltage output drops with use.

An electrochemical cell in which the electrolyte is a paste, rather than a liquid, is known as a **dry cell (Leclanché cell)**. The most commonly used dry cell is a C battery, which has a voltage of 1.5 V.

Dry cells are commonly used in torches, toys and transistor radios since they are cheap, small, reliable and easy to use. The oxidising agents and reducing agents used in such cells should have the following properties:

- be far enough apart in the electrochemical series to produce a useful voltage from the cell
- not react with water in the electrolyte too quickly, or they will 'run out' early (therefore, highly reactive metals such as sodium, potassium and calcium are not found in such batteries)
- be inexpensive.



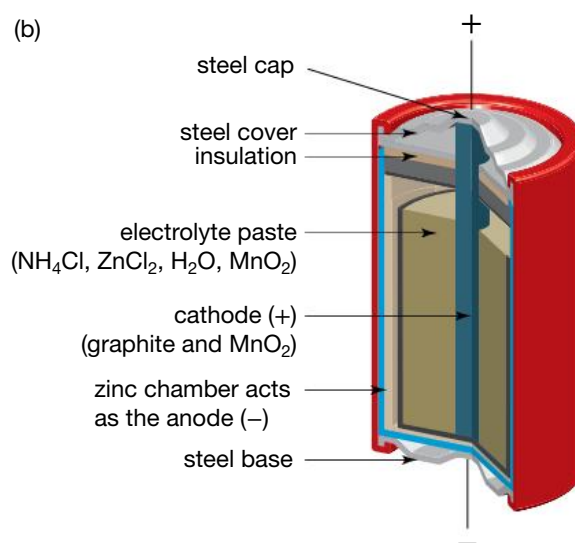
Arrangement of cells in circuits: (a) Two 1.5 V cells connected in series make a 3.0 V battery. (b) Two 1.5 V cells connected in parallel allow a higher current at 1.5 V.

Once the materials around the electrodes have been used up, the cell stops operating.

(a)



(b)



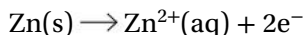
(a) Dry cells in a torch (b) A simplified cross-section of a dry (Leclanché) cell

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Experiment 3.4 Looking at a dry cell
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A dry cell consists of a zinc container filled with an electrolyte paste. This paste contains manganese(IV) oxide, MnO_2 , zinc chloride, ZnCl_2 , ammonium chloride, NH_4Cl , and water. A carbon rod is embedded in the paste and forms the cathode. The zinc container is the anode. The thick paste prevents the contents of the cell from mixing, so a salt bridge is not needed. The electrode half-equations are as follows.

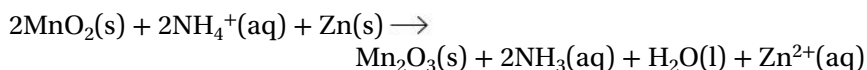
Anode (oxidation):



Cathode (reduction):



The overall cell reaction can be written as:



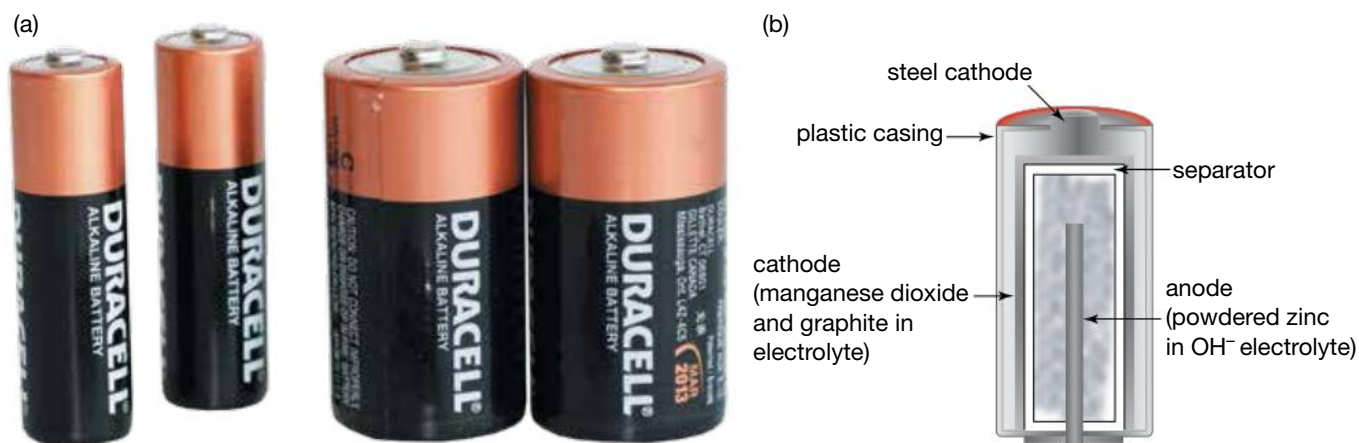
Intermittent use or slight warming of the cell prevents the build-up of these products around the electrodes, increasing the life of the cell.

The alkaline zinc/manganese dioxide cell

The alkaline cell is a primary cell that is more expensive than a dry cell but lasts much longer.

Alkaline cells were developed as a consequence of the greater demand for a higher capacity portable energy source than the dry cell could provide. An alkaline cell is designed to give a greater current output than the standard dry cell. The voltage output falls off more slowly. Alkaline batteries have longer shelf lives than dry cells. Since less electrolyte needs to be used in an alkaline cell than in a dry cell, more electrode reactants can be packed into the cell. Alkaline cells are commonly used in electronic flash guns, high-drain toys and radios.

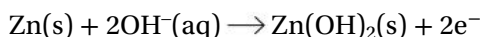
The cell has a powdered zinc anode in an electrolyte paste of potassium hydroxide. The cathode is a compressed mixture of manganese dioxide and graphite. A separator consisting of a porous fibre soaked in electrolyte prevents mixing of the anode and cathode components. The cell is contained within a steel shell.



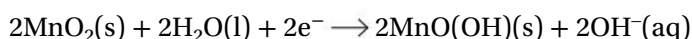
(a) Alkaline zinc/manganese dioxide cells (b) A simplified cross-section of an alkaline zinc/manganese dioxide cell

The electrode half-equations are as follows.

Anode (oxidation):



Cathode (reduction):



The overall cell reaction is:



The alkaline cell has a voltage of 1.55 V, but this drops slowly with time. Although it may last up to five times longer than a dry cell, it is more difficult to make and more expensive. It is also bulky, making it unsuitable for smaller devices such as watches and calculators.

Revision questions

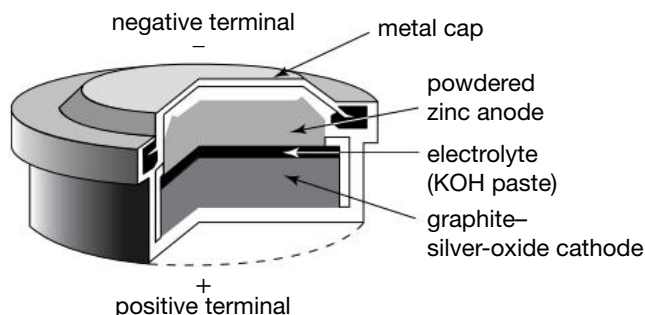
21. Describe the difference between a primary cell and a secondary cell.
22. Name the reducing agent in a Leclanché cell.
23. Calculate the change in oxidation number of manganese during discharge in a Leclanché cell.

Button cells

Button cells were developed because of the need for a very small cell with a constant voltage over a long period.

The silver oxide cell is ideal for use in watches, cameras, calculators and hearing aids. It has a good shelf life and a long operating life. It will keep a watch going all day for many years. More substantial silver oxide batteries are used in submarines and missiles. The cell has a zinc anode in silver oxide paste and uses a potassium hydroxide electrolyte.

Some appliances require the use of very small electrochemical cells. **Button cells** are primary cells that were developed to meet this need, although they are expensive to produce. However, they have an added advantage that they give a very steady voltage during operation. Button cells are small, long-life cells used in such devices as calculators, hearing aids, pacemakers, cameras and watches. In relation to their size, button cells last longer than dry cells and alkaline cells. There are a number of different types of button cells, including the silver oxide cell and the zinc-air cell.

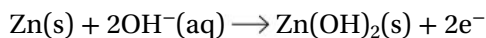


Silver oxide cell

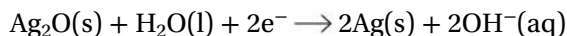
Silver oxide cells are ideal for very small devices.

The reactions at each electrode may be written as follows.

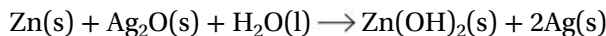
Anode (oxidation):



At the cathode in the zinc/silver cell, silver(I) oxide is reduced.



so the overall equation for this reaction is:



This cell has a flat discharge curve and the voltage is 1.5 V.

Zinc–air cells are used in hearing aids. They use oxygen from air as a reactant.

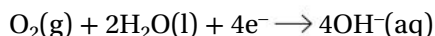
Zinc–air cell

A **zinc–air cell** makes use of oxygen from the air as a reactant (see the diagram below). It is less expensive to produce than the silver oxide cell and is mainly used for hearing aids. The electrolyte is potassium hydroxide and the half-equations for each electrode may be written as follows.

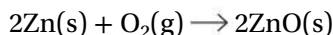
Anode (oxidation):



Cathode (reduction):

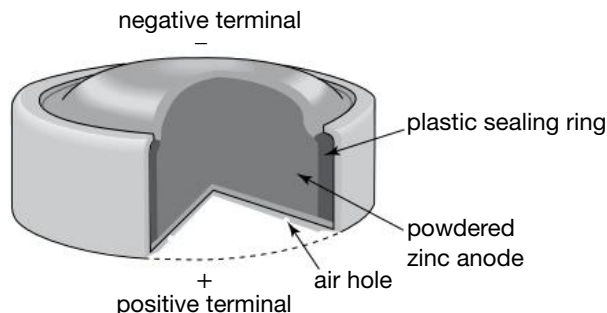


Overall:



A zinc–air cell produces a voltage of about 1.4 V and can be considered a fuel cell as the oxygen is continually drawn from the air. Fuel cells use a continuous supply of fuel to produce a flow of electrons. Fuel cells will be investigated in the following section.

The zinc–air cell has a small vent that is open to the air. This air vent is sealed until the cell is ready to use; this prolongs the life of the cell. A material to absorb the carbon dioxide from the air must be included to prevent the carbon dioxide from reacting with the hydroxide electrolyte.



Lithium cells

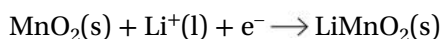
Lithium cells provide double the voltage of conventional cells.

Lithium cells are cells based on lithium anodes. Since lithium is a very reactive metal, and also very light, these batteries can produce a high cell voltage. However, they require a more robust construction. They are far more expensive than common batteries but have a shelf life of 10 years. Their main application is as power sources for electronic memory. Owing to their relatively long shelf life, lithium cells may also be used in such equipment as electronic switchboards, navigation systems, industrial clocks and even poker machines. In many applications they outlast the probable useful lifetime of the equipment they power.

Primary lithium cells include lithium manganese dioxide and lithium thionyl chloride cells. The most common is the lithium–manganese cell. This has a lithium anode, a manganese dioxide cathode, and a non-aqueous electrolyte such as propylene carbonate. The anode (oxidation) reaction is:



The cathode reaction is:

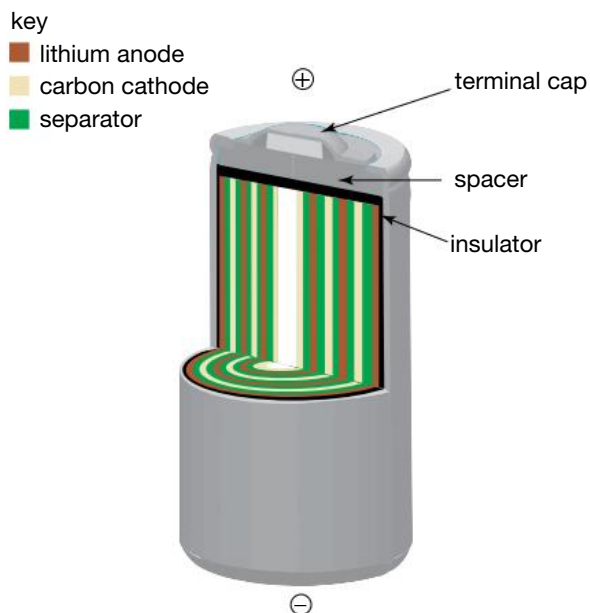


These cells can be used in watches, calculators, games and cameras. Lithium cells come in button, flat, cylindrical, solid core or spiral wound form.

Spiral wound cells consist of two coiled sheets, one of lithium foil and one of manganese dioxide, separated by a sheet containing electrolytic salts. They have a good shelf life and the voltage produced is about 3 volts.



Cardiac arrhythmias cause problems with the heart's rhythm or pulse rate. This can be controlled by using a pacemaker, a small device inserted in the chest or abdomen. The pacemaker uses electrical stimulation to ensure that the heart beats at a normal rate. The device is powered by a lithium battery. A magnetic switch operates the device, and the lithium battery usually lasts for 3 to 5 years.

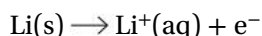


A simplified diagram of a spiral-wound lithium cell

Another type of lithium battery, the lithium thionyl chloride cell, consists of a lithium anode, a carbon cathode and an electrolyte solution of lithium aluminium chloride, LiAlCl_4 , in thionyl chloride, SOCl_2 . The cathode is a highly porous Teflon-coated carbon cylinder that is saturated with the electrolyte material. The SO_2 produced at the cathode dissolves in the thionyl chloride. The anode and cathode are kept apart by a separator.

The half-equations at each electrode may be written as follows.

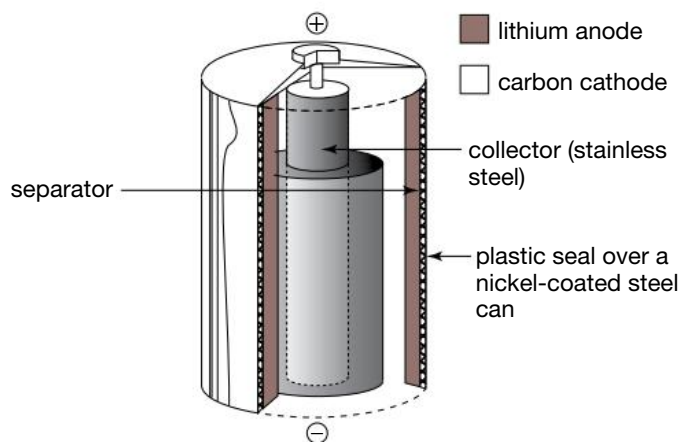
Anode (oxidation):



Cathode (reduction):



The overall equation for the reaction is:



A simplified cross-section of a lithium/thionyl chloride battery

Revision questions

24. Draw a diagram of a galvanic cell, consisting of two half-cells, that could be constructed in the laboratory to investigate the half-reactions in a silver oxide button cell. Label the electrodes and the direction of the electron flow.
25. At the cathode of a zinc–air cell, has the oxidation number of the substance reacting increased or decreased?
26. What property of lithium batteries makes them so useful for electronic devices?

Fuel cells

It is very frustrating when the battery of a mobile phone goes flat in the middle of a phone call. If the phone was powered by a fuel cell instead of a battery, then you would just insert a small cartridge of fuel to get it functioning again without the need for any electricity.

A **fuel cell** is an electrochemical device that converts chemical energy into usable DC electricity and heat without combustion as an intermediary step. First demonstrated in 1839, fuel cells produce electricity without combustion by combining fuels such as hydrogen and oxygen in the presence of an electrolyte. In this example, water and heat are the only by-products of the process. Fuel cell technology was not used extensively until the 1960s in the US space program.

The search for energy alternatives that have greater operating efficiencies at lower costs has spawned advancement of fuel cell technology, since power generation from fuel cells averages between 40–60% efficiency compared with 30–35% efficiency of power generation through fossil fuel combustion.

Where are fuel cells used?

Fuel cells are used, or are being investigated for use, in the following situations.

- As a portable power source to power small appliances, such as recharging batteries in laptops or smartphones
- For larger scale, stationary applications including back up power in hospitals and industry
- Transport applications such as forklifts, boats and buses. Their silent operation is advantageous for submarines and considerable research is being undertaken to improve the efficiency and reduce costs of fuel cell cars.

Fuel cell design

Not surprisingly, when compared with galvanic cells, fuel cells share many design features in common. As with galvanic cells, the site of oxidation is physically separated from the site of reduction. They both contain an anode, which is the negative electrode, and a cathode, which is the positive electrode. Oxidation occurs at a negative electrode and reduction at a positive electrode in both types of cells. There is also an electrolyte between these electrodes, necessary for the flow of ions that make up the internal circuit. Both convert chemical energy into electrical energy through a spontaneous redox reaction. Although fuel cells are often expensive to manufacture, the low operating and maintenance costs over their lifetime make them a more efficient method for generating electricity than many ‘use-and-discard’ primary cells in current use.

There are two major differences, however. The design of the electrodes themselves can have a significant effect on a fuel cell. Typically, electrodes in a fuel cell are porous in nature. This provides a high surface area and also the

A fuel cell is similar to a battery but does not ‘go flat’ or need recharging. It continues to convert chemical energy to electrical energy as long as the fuel is supplied.

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Experiment 3.5 Investigating the hydrogen–oxygen fuel cell
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Unit 3

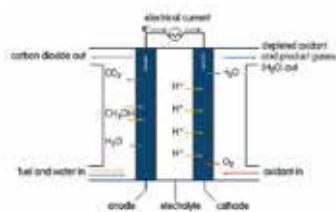
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Concept 1



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Fuel cells



opportunity to introduce catalysts, thus making the reactions that take place on their surfaces more efficient. This structure also allows more effective 'contact' between fuels, which are often gases, and the electrolyte. The other difference is that fuel cells do not 'go flat'. They continue to provide electricity as long as a fuel and an oxidising agent are supplied. The input fuel passes over the anode (and oxygen over the cathode) where it is split into ions and electrons. The electrons go through an external circuit while the ions move through the electrolyte towards the oppositely charged electrode. At this electrode, ions combine to create by-products, primarily water and carbon dioxide. Depending on the input fuel and electrolyte, different chemical reactions occur.

Like batteries, fuel cells are combined into groups, called stacks, to obtain a usable voltage and power output. Unlike batteries, however, fuel cells do not release energy stored in the cell, running down when the energy is gone. Instead, they convert the energy in hydrogen-rich fuels directly into electricity and operate as long as they are supplied with fuel. Fuel cells therefore do not have to be recharged. They can be designed to emit no air pollution and to operate more quietly and more cheaply than a conventional electric generator. Fuel cells emit almost none of the sulfur and nitrogen compounds released by the burning of fossil fuels and can use a wide variety of fuels including methane, coal-derived gas, landfill gas, biogas, alcohols, hydrogen and other hydrocarbons.

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Types of fuel cell

There are six main types of fuel cell. They are categorised according to the type of electrolyte and/or the fuel used:

- alkaline fuel cell (AFC)
- proton exchange membrane fuel cell (PEMFC)
- phosphoric acid fuel cell (PAFC)
- molten carbonate fuel cell (MCFC)
- solid oxide fuel cell (SOFC)
- direct methanol fuel cell (DMFC).

Typical applications for these are shown in table 3.2.

TABLE 3.2 Some typical applications of fuel cells

Application	Fuel cell type
• powering small devices • other portable applications	PEMFC, DMFC
• stationary power generation • larger scale electricity production	SOFC, MCFC, PAFC, PEMFC
• transportation • submarines	PEMFC

Research continues into new designs for fuel cells, not only for new fuels, but also new electrolytes. For example, there is a current line of research investigating the use of biological materials as electrolytes.

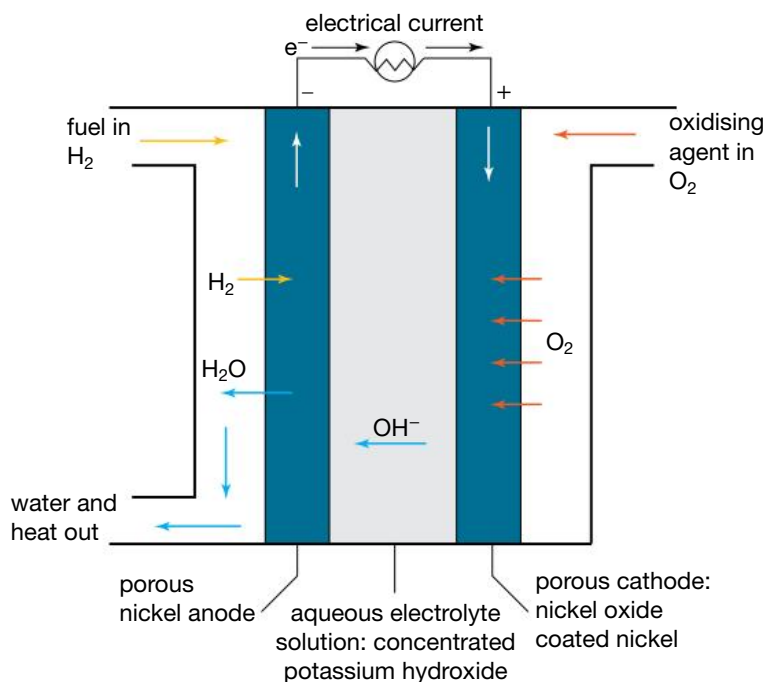
The alkaline, proton exchange membrane and direct methanol fuel cells will now be discussed.

Alkaline fuel cell

The **alkaline fuel cell** (AFC), also known as the hydrogen-oxygen fuel cell, is one of the oldest and most travelled fuel cells. It was used in the Gemini and Apollo space missions to produce electrical energy and water. It is clean and very efficient but requires pure hydrogen and oxygen.

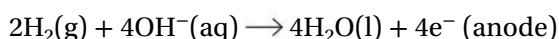
The alkaline fuel cell uses potassium hydroxide as the electrolyte; it was used in the US space program.

A cross-section of an alkaline fuel cell



In this cell, three compartments are separated from each other by two electrodes. Oxygen (the oxidising agent) is fed into the cathode compartment. Hydrogen (the fuel) is fed into the anode compartment. The gases diffuse slowly through the electrodes. The electrolyte in the central compartment is a hot concentrated solution of potassium hydroxide. Electrons from the oxidation reaction at the anode pass through an external circuit to enter the reduction reaction at the cathode.

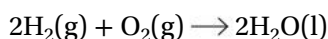
Oxidation:



Reduction:



The equation for the overall reaction may be written as:



Proton exchange membrane fuel cell

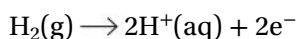
PEM fuel cells are used for transport and some stationary power supplies.

The **proton exchange membrane fuel cell (PEMFC)** offers high power density and operates at relatively low temperatures. They are used in cars, forklifts and buses as well as some large-scale systems. Suitable fuels include hydrogen gas, methanol and reformed fuels.

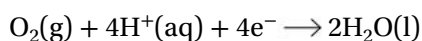
The use of a solid polymer electrolyte eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells. Its low operating temperature provides instant start-up and requires no thermal shielding to protect personnel. A typical PEMFC uses a polymer membrane as its electrolyte. Although it is an excellent conductor of hydrogen ions, the membrane is an electrical insulator. The electrolyte is sandwiched between the anode and cathode, forming a unit less than a millimetre thick (see the diagram at the top of the next page).

The reactions that occur in a PEMFC are as follows.

Anode:



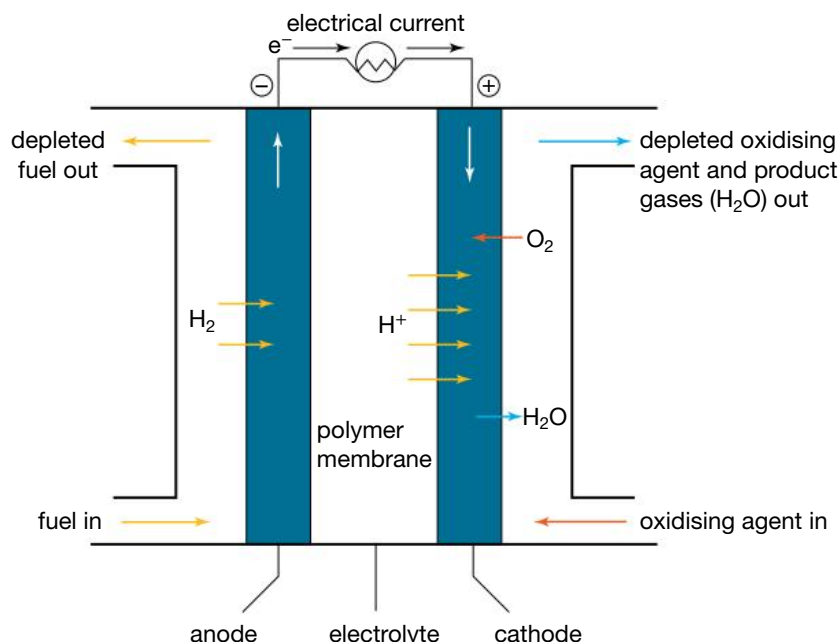
Cathode:





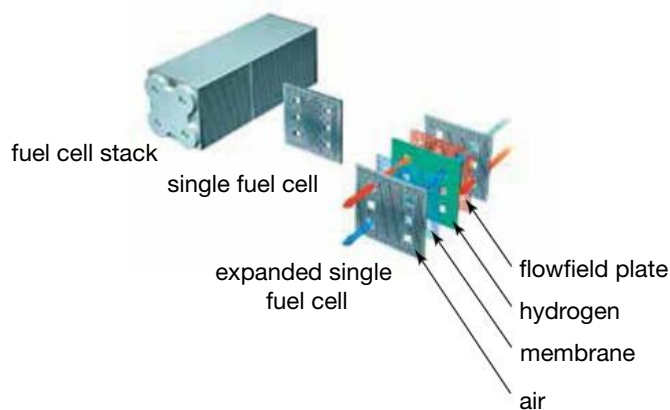
The Toyota Mirai went on sale in Japan in late 2014 and is now on sale in California. It is powered by a fuel cell stack that uses hydrogen stored in specially constructed tanks and oxygen from the air. The electricity generated is used to either power its electric motor directly or to charge a battery that can be used to power the motor. Water is the only significant emission.

Honda and Hyundai sell similar vehicles.



A typical PEMFC

Hydrogen from the fuel gas stream is consumed at the anode, producing electrons that flow to the cathode via the electric load and hydrogen ions that enter the electrolyte. At the cathode, oxygen combines with electrons from the anode and hydrogen ions from the electrolyte to produce water. Since the PEMFC operates at about 80 °C, the water does not dissolve in the electrolyte and is collected from the cathode as it is carried out of the fuel cell by excess oxidising agent flow.



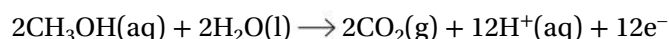
The design of a PEM fuel cell allows the depleted gases and excess oxidising agent gas to flow through the cell stack.

The direct methanol fuel cell is ideal for small devices because it has a low operating temperature and it does not require a fuel reformer.

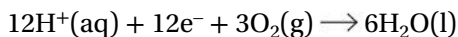
Direct methanol fuel cell

The **direct methanol fuel cell** (DMFC) is relatively new technology and is powered by pure methanol. The anode catalyst withdraws hydrogen from the liquid methanol. Methanol has a higher energy density than hydrogen and is easier to transport. The small size of these cells makes them suitable for mobile phones, portable music devices and laptops, allowing devices to operate for longer periods of time before 'refuelling'.

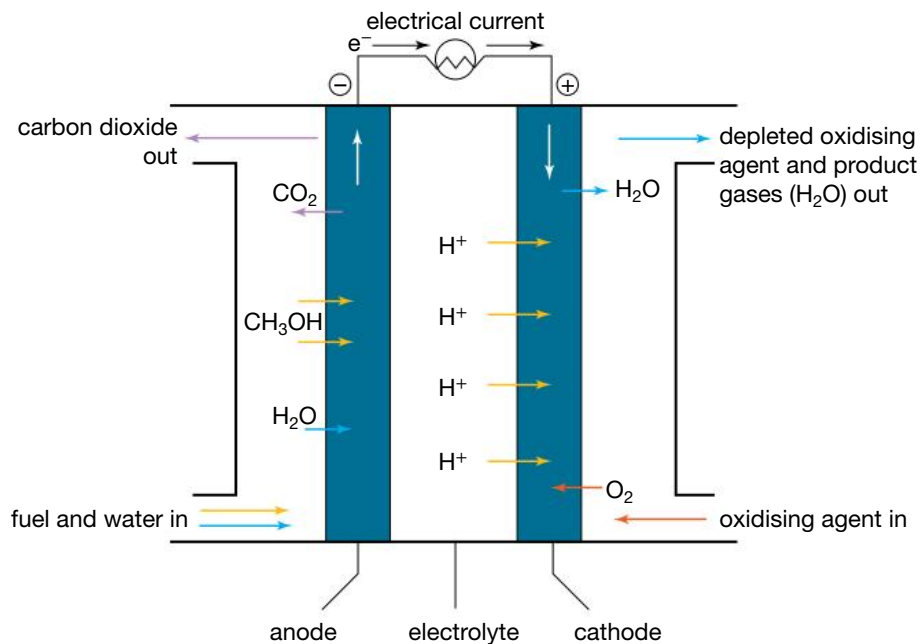
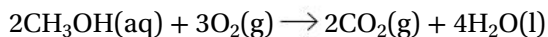
Anode (oxidation):



Cathode (reduction):



Overall:



A typical direct methanol fuel cell

TABLE 3.3 Comparison of fuel cells

Fuel cell type	Electrolyte	Anode gas	Cathode gas	Temperature	Efficiency
alkaline (AFC)	potassium hydroxide	hydrogen	pure oxygen	below 80 °C	50–70%
phosphoric acid (PAFC)	phosphoric acid	hydrogen, reformed hydrocarbon fuels	oxygen and air	210 °C	35–50%
molten carbonate (MCFC)	alkali, carbonates	hydrogen, carbon monoxide, methane, reformed hydrocarbon fuels	oxygen and air, carbon dioxide	650 °C	45–60%
proton exchange membrane (PEMFC)	solid polymer membrane	hydrogen	pure oxygen or oxygen mixed with air	75 °C	35–55%
solid oxide (SOFC)	ceramic oxide	hydrogen, methane, reformed hydrocarbon fuels	oxygen and air	800–1000 °C	45–60%
direct methanol (DMFC)	solid polymer membrane	methanol solution in water	oxygen and air	75 °C	35–45%

Advantages of the use of fuel cells include:

- high energy conversion efficiency
- modular design, different sizes available
- low chemical pollution

- fuel flexibility
- co-generation capability by using heat produced
- quiet operation
- unlimited run time while fuel is supplied
- no need to be recharged
- low maintenance due to lack of moving parts
- low running costs
- lower weight and volume than conventional batteries for electric-powered vehicles
- potential to power portable devices for longer times than conventional batteries.

Disadvantages include:

- manufacturing process and materials are expensive; infrastructure required for pumping gases
- need reliable and continual supply of fuel
- distribution, storage and transportation of hydrogen difficult
- technology of producing hydrogen from other fuels still being developed
- few refuelling stations available for fuel-cell vehicles
- some technological issues with water regulation and temperature control in some fuel cells
- electrodes expensive because they must also function as catalysts.

Environmental and safety considerations

The most common fuel used in fuel cells is hydrogen, which can be obtained by a reforming process using hydrocarbon fuels or by using renewable sources to provide electricity to break down water into hydrogen and oxygen.

Molten carbonate and solid oxide cells use methanol or a hydrocarbon, such as natural gas, directly because the high operating temperatures allow the reforming (conversion) to hydrogen to occur within the fuel cell structure, usually after some initial reforming. Direct methanol fuel cells use the anode catalyst to remove the hydrogen from the liquid methanol without a fuel reformer. This process is a more efficient way of producing energy than burning fuel to produce steam to drive a turbine. This means that less fuel is wasted and that fewer amounts of greenhouse gases are generated.

In general, fuel cells rely on hydrogen as a fuel. The hydrogen can be obtained from the electrolysis (decomposition using electricity, see chapter 4) of water or reformed from another fuel, such as methanol, natural gas, petrol and diesel. Moreover, enzymes in cyanobacteria can generate hydrogen biologically. As the reformation process produces less greenhouse gases than combustion of these fuels, using these fuels is environmentally favourable. If, however, hydrogen can be produced by renewable means, then the use of hydrogen results in water being the main product of the use of fuel cells. Solar power, wind power or bioethanol can be used to power the electrolysis of water into hydrogen and oxygen. Fuel cells do not have the same problems of disposal as lead-acid batteries or the fumes associated with the use of diesel generators.

Hydrogen storage

Hydrogen has a high energy content by weight but not by volume. Storing hydrogen can be difficult, as it is the lightest element and must undergo considerable compression to be contained in a suitably sized tank, which must withstand the extreme pressures required. It can be stored as a liquid but this requires keeping its temperature at -252.8°C in very well-insulated containers. Another method is combining hydrogen with certain metal or complex hydrides that can absorb the hydrogen; then it can be released by heating or adding water. Carbon nanomaterials or glass microspheres and other chemical methods are also being investigated as a means of storage.

Hydrogen can be stored using compression, liquefying or chemical means.

Hydrogen is a low molecular mass, colourless, odourless, non-toxic and flammable gas that requires particular safety precautions, as do all fuels.

Safety of hydrogen

Hydrogen is a fuel and an awareness of its properties is essential in producing, storing and using it safely, as is necessary with all other fuels.

Hydrogen has a lower ignition point than hydrocarbons and is highly flammable. It has a much lower radiant heat when ignited than burning hydrocarbons. The flame of burning hydrogen is almost invisible, and this would pose a problem to fire fighters. It is a colourless, tasteless and odourless gas, so leaks would be difficult to detect. Hydrogen is not toxic, however, and, due to its lightness, leaks would rise and rapidly dissipate into the air. Vapour from petrol leaks by contrast, being denser than air, can collect below a vehicle and could potentially ignite. Hydrogen can be explosive at relatively higher concentrations than petrol, but, because of its tendency to rise rapidly, it is less likely to explode than heavier hydrocarbon gases.

Fuel cells offer great potential for the future. The reactions in fuel cells are the same as for burning the fuels in a combustion reaction. A check of the overall reactions in the AFC, PEMFC and DMFC illustrates this point. As infrastructure is developed for the distribution and storage of their fuels (particularly hydrogen), and electrode manufacturing techniques are improved and become cheaper, their use should become more widespread. Generally speaking, they are safe to use — certainly no more dangerous than generating electricity by currently used methods.

Revision questions

27. Draw a timeline to show past achievements and possible future developments in fuel cell technology with respect to their use in vehicles.
 28. Discuss four applications of fuel cells.
 29. Produce a poster or a multimedia presentation that:
 - (a) illustrates the operation of fuel cells
 - (b) summarises advantages and disadvantages of fuel cells.
 30. List the different types of fuel cell and describe one in detail. Include chemical reactions and a diagram.
-

Chapter review

Summary

- Redox reactions involve the transfer of electrons between an oxidising agent and a reducing agent.
- Redox reactions can be divided into a reduction process and an oxidation process.
- Reduction is the process of gaining electrons whereas oxidation is the process of losing electrons.
- Redox reactants can be divided into oxidising agents and reducing agents. Reducing agents allow (or cause) another substance to undergo reduction because they supply electrons (as they undergo the process of oxidation). Oxidising agents allow another substance to undergo oxidation because they consume electrons (as they undergo the process of reduction).
- Spontaneous redox reactions can transform chemical energy into either heat or electrical energy, depending on the physical arrangements under which the reactions are carried out.
- A set of rules can be used for balancing the half-equations that represent the oxidation and reduction processes.
- Oxidation numbers can be used to determine the species in a redox reaction that may act as an oxidising agent or a reducing agent, since reduction corresponds to a decrease in oxidation number, whereas oxidation corresponds to an increase in oxidation number.
- Galvanic cells (also called electrochemical or voltaic cells) convert chemical potential energy into electrical energy.
- An electrolyte is a solution containing ions that can conduct electricity.
- Galvanic cells consist of two separate half-cells, each half-cell containing a different conjugate redox pair. A connecting wire between the electrodes forms the external circuit through which electrons travel from the reducing agent to the oxidising agent, and a salt bridge forms an internal circuit through which ions can travel to maintain cell neutrality.
- In a galvanic cell, oxidation occurs at the negatively charged anode whereas reduction occurs at the positively charged cathode.
- The electrical potential of a galvanic cell is the ability of the cell to produce an electric current and is measured in volts (V).
- The reduction potential of a half-cell is a measure of the tendency of the oxidising agent to accept electrons and thus undergo reduction.
- The difference between the reduction potentials of two electrically connected half-cells is called the cell potential difference.
- The standard cell potential difference (E°_{cell}) is the measured cell potential when the concentration of each species in solution is 1 M, the pressure of a gas is 1 atm and the temperature is 25 °C. It may be calculated according to:
$$E^\circ_{\text{cell}} = E^\circ_{\text{oxidising agent}} - E^\circ_{\text{reducing agent}}$$
- The standard hydrogen half-cell is used as a standard reference electrode and has been assigned an arbitrary value of 0.00 volts.
- The standard electrode potential (SEP) table, also known as the electrochemical series, can be used to predict whether a particular redox reaction can proceed to an appreciable extent.
- The SEP table gives no indication of the rate of a reaction.
- Strong oxidising agents have high E° values and are found at the top left of the SEP table, whereas strong reducing agents have low E° values and are found at the bottom right of the SEP table.
- 'Wet' cells are electrochemical cells where the electrolyte is in a liquid state.
- An electrochemical cell in which the electrolyte is a paste, rather than a liquid, is known as a dry cell.
- A battery is a small, portable, efficient source of electrical energy that is constructed from a combination of electrochemical cells connected in series or in parallel.
- Electrochemical cells that are used until the supply of electrical energy is exhausted are called primary cells. Primary cells cannot be recharged.
- Different types of primary cells currently in use include Leclanché cells (dry cells), alkaline Zn(s)/MnO₂(s) cells, button cells, Zn(s)/air cells and lithium cells. Each of these contains an anode, cathode and an electrolyte, and is a practical application of a galvanic cell.
- A fuel cell is an electrochemical device that converts chemical energy into usable DC electricity and heat using a continuous supply of fuel, without combustion as an intermediary step.
- The simplest fuel cell is the alkaline fuel cell. Its function can be represented by the equation:
$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$$
- There are six basic types of fuel cells based on the electrolyte used: alkaline fuel cell; phosphoric acid fuel cell; molten carbonate fuel cell; solid oxide fuel cell; proton exchange membrane fuel cell; direct methanol fuel cell.
- Fuel cells have higher efficiencies than generating electricity by combustion of the fuel.
- Fuel cells have many design features in common with galvanic cells. They have an anode and a cathode,

- and an electrolyte to carry ions between these electrodes. A major difference is that the reactants (fuel and oxidising agent) are supplied continuously in a fuel cell. It generates electricity as long as this supply is maintained.
- The structure and nature of the electrodes in a fuel cell are critical to the effective operation of the cell. They are often porous and may also contain catalysts.
 - The most common fuel for fuel cells is hydrogen, which can be obtained by a reforming process using hydrocarbon fuels or by using renewable sources to provide electricity to break down water into hydrogen and oxygen.
 - Hydrogen is a low molecular mass, colourless, odourless, non-toxic and flammable gas that requires particular safety precautions as do all fuels.
 - Hydrogen can be stored using compression, liquefying or chemical means.

Multiple choice questions

- In a particular reaction, it is observed that electrons are transferred from substance A to substance B. Which of the following statements is correct?
 - A undergoes oxidation and is an oxidising agent.
 - A undergoes oxidation and is a reducing agent.
 - B undergoes oxidation and is a reducing agent.
 - A undergoes reduction and is an oxidising agent.
- The oxidation number of each sulfur atom in $\text{S}_2\text{O}_3^{2-}$ is:

A -2	C +6
B +2	D +4.
- For the reaction

$$\text{NO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{e}^- + \text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq})$$
 the oxidation number of nitrogen changes from:
 - 0 to +1
 - 0 to -1
 - +2 to -3
 - +4 to +5.
- In a reaction the oxidation numbers of two elements were found to change as follows.
 X changes from +2 to +5.
 Y changes from +7 to +5.
 Which of the following describes the changes correctly?
 - X and Y are both oxidised.
 - X is oxidised and Y is reduced.
 - X is reduced and Y is oxidised.
 - X and Y are both reduced.
- The half-equation for the reduction of NO_3^- to N_2O can be represented as follows.

$$a\text{NO}_3^-(\text{aq}) + b\text{H}^+(\text{aq}) + 8\text{e}^- \longrightarrow c\text{N}_2\text{O}(\text{g}) + d\text{H}_2\text{O}(\text{l})$$
 where the values of a and b respectively are:

A 2 and 5	C 1 and 4
B 2 and 10	D 1 and 5.
- When iron filings are mixed with $\text{CuSO}_4(\text{aq})$ solution, it is observed that 1 mole of Fe displaces 1 mole of copper from solution. From this observation it can be stated that:
 - iron and copper are equally reactive
 - the iron ions and copper ions each carry two electrical charges
 - the iron ions and copper ions each carry one electrical charge
 - the iron ions and copper ions all carry equal electrical charges.
- The tarnish on silverware, Ag_2S , can be removed by placing the articles in an aluminium pan and covering them with a warm solution of dilute sodium hydroxide. The following half-reactions show why this method is effective.

$$\text{Ag}_2\text{S}(\text{s}) + 2\text{e}^- \longrightarrow 2\text{Ag}(\text{s}) + \text{S}^{2-}(\text{aq})$$

$$\text{Al}(\text{s}) + 3\text{OH}^-(\text{aq}) \longrightarrow \text{Al}(\text{OH})_3(\text{s}) + 3\text{e}^-$$
 Which of the following equations represents a balanced ionic equation for the reaction that occurs?
 - $3\text{Ag}_2\text{S}(\text{s}) + 2\text{Al}(\text{s}) + 6\text{OH}^-(\text{aq}) \longrightarrow 6\text{Ag}(\text{s}) + 3\text{S}^{2-}(\text{aq}) + 2\text{Al}(\text{OH})_3(\text{s})$
 - $\text{Ag}_2\text{S}(\text{s}) + \text{Al}(\text{s}) + 3\text{OH}^-(\text{aq}) \longrightarrow 2\text{Ag}^+(\text{aq}) + \text{S}^{2-}(\text{aq}) + \text{Al}(\text{OH})_3(\text{s}) + \text{e}^-$
 - $\text{Ag}_2\text{S}(\text{s}) + \text{Al}(\text{OH})_3(\text{s}) \longrightarrow 2\text{Ag}^+(\text{aq}) + \text{S}^{2-}(\text{aq}) + \text{Al}(\text{s}) + 3\text{OH}^-(\text{aq})$
 - $\text{Al}(\text{s}) + 3\text{OH}^-(\text{aq}) + 2\text{Ag}(\text{s}) + \text{S}^{2-}(\text{aq}) \longrightarrow \text{Ag}_2\text{S}(\text{s}) + \text{Al}(\text{OH})_3(\text{s}) + 3\text{e}^-$
- The permanganate ion, MnO_4^- , can oxidise H_2S to elemental sulfur according to the equations:

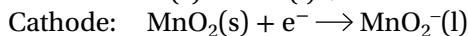
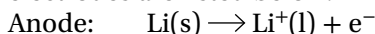
$$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$$

$$\text{H}_2\text{S}(\text{g}) \longrightarrow \text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$$
 When these equations are balanced, the coefficients of MnO_4^- and S respectively are:

A 1 and 1	C 2 and 5
B 1 and 2	D 5 and 2.
- An electrochemical cell functions only when there is a complete circuit for electrical flow. For reactions to occur that produce an electric current, it is necessary to have an:
 - external and internal circuit for the flow of ions
 - external circuit for electron flow and an internal circuit for ion flow
 - external circuit for ion flow and an internal circuit for electron flow
 - internal and external circuit for the flow of electrons.
- In any electrochemical cell, the cathode is the electrode:
 - that is closest to the outside of the cell
 - at which electrons are liberated by some species

- C** at which reduction occurs
D at which hydrogen is liberated.

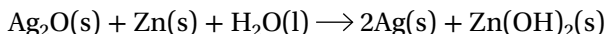
- 11.** In a lithium–manganese dioxide button battery, the anode is made from lithium foil on a stainless steel backing and the cathode is manganese dioxide mixed with carbon black to act as an organic electrolyte. The equations occurring at the electrodes are listed below.



The lithium manganese dioxide button battery is a primary cell. Which of the following is the strongest oxidising agent?

- A** Li(s) **C** $\text{MnO}_2(\text{s})$
B $\text{Li}^+(\text{aq})$ **D** $\text{MnO}_2^-(\text{aq})$

- 12.** Silver oxide–zinc cells can be produced in a very compact form to be used in calculators. The overall equation for the operation of a silver oxide–zinc cell is:



The reduction half-equation that occurs in the silver oxide–zinc cell can be written as:

- A** $\text{Zn(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{H}^+(\text{aq}) + \text{Zn(OH)}_2(\text{s}) + 2\text{e}^-$
B $\text{Zn(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow 2\text{H}^+(\text{aq}) + \text{Zn(OH)}_2(\text{s})$
C $\text{Ag}_2\text{O(s)} + 2\text{H}^+(\text{aq}) \rightarrow 2\text{Ag(s)} + \text{H}_2\text{O(l)} + 2\text{e}^-$
D $\text{Ag}_2\text{O(s)} + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag(s)} + \text{H}_2\text{O(l)}$

- 13.** A small piece of silver was placed in a solution containing both magnesium nitrate and copper(II) nitrate. Which one of the following will occur?

- A** No reaction occurs.
B The silver dissolves and only copper is precipitated.
C The silver dissolves and only magnesium is precipitated.
D A mixture of copper and magnesium forms on the silver.

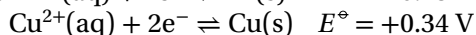
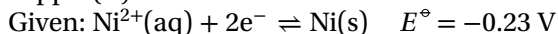
- 14.** In which of the following pairs of elements does neither metal release hydrogen gas when dilute hydrochloric acid is added?

- A** Zn and Ag **C** Fe and Al
B Cu and Ag **D** Mg and Ni

- 15.** Which of the following reactions does *not* occur spontaneously?

- A** $\text{Cu}^{2+}(\text{aq}) + \text{Pb(s)} \rightarrow \text{Pb}^{2+}(\text{aq}) + \text{Cu(s)}$
B $\text{Fe(s)} + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{Pb(s)} + \text{Fe}^{2+}(\text{aq})$
C $2\text{Ag(s)} + 2\text{H}^+(\text{aq}) \rightarrow 2\text{Ag}^+(\text{aq}) + \text{H}_2(\text{g})$
D $\text{Li(s)} + \text{H}^+(\text{aq}) \rightarrow \frac{1}{2}\text{H}_2(\text{g}) + \text{Li}^+(\text{aq})$

- 16.** A piece of nickel is placed in a solution of copper(II) sulfate.



which one of the following statements is incorrect?

- A** Copper is precipitated from solution.
B Copper ions are oxidised.

- C** Nickel dissolves into solution.

- D** There is no increase in electrical charge in the solution.

- 17.** Which of the following metals could be used to make a container to store an aqueous copper sulfate solution?

- A** Sn **C** Ag
B Pb **D** Fe

- 18.** A VCE student is given five metals and 1 M solutions of nitrates of the metals. The metals are labelled *M*, *N*, *O*, *P* and *Q*, and the solutions are labelled M^{2+} , N^{2+} , O^{2+} , P^{2+} and Q^{2+} .

The student carries out a number of experiments and the results obtained are listed below.

- (i) Metal *M* remains unchanged in all solutions.
(ii) Metal *O* becomes coated with another metal when placed in each of solutions M^{2+} , N^{2+} , P^{2+} and Q^{2+} .
(iii) Metal *P* becomes coated with another metal when placed in each of solutions M^{2+} and N^{2+} , but not when placed in solution Q^{2+} .

Considering the experimental data above, which of the following reactions takes place spontaneously with the greatest observed cell voltage?

- A** $\text{M(s)} + \text{O}^{2+}(\text{aq}) \rightarrow \text{M}^{2+}(\text{aq}) + \text{O(s)}$
B $\text{O(s)} + \text{M}^{2+}(\text{aq}) \rightarrow \text{O}^{2+}(\text{aq}) + \text{M(s)}$
C $\text{N(s)} + \text{P}^{2+}(\text{aq}) \rightarrow \text{N}^{2+}(\text{aq}) + \text{P(s)}$
D $\text{Q(s)} + \text{O}^{2+}(\text{aq}) \rightarrow \text{Q}^{2+}(\text{aq}) + \text{O(s)}$

- 19.** Which of the following reactions occurs spontaneously in the direction indicated?

- A** $2\text{I}^-(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{I}_2(\text{s})$
B $\text{Br}_2(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + \text{Cl}_2(\text{g})$
C $\text{I}_2(\text{s}) + 2\text{Br}^-(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{Br}_2(\text{aq})$
D $2\text{F}^-(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{F}_2(\text{g}) + 2\text{Cl}^-(\text{aq})$

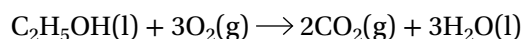
- 20.** In an experiment, bromine gas is bubbled into a solution containing a mixture of chloride ions and iodide ions. It would be expected that the bromine reacts with:

- A** the chloride ions only
B the iodide ions only
C both the chloride ions and the iodide ions
D neither the chloride ions nor the iodide ions.

- 21.** In a hydrogen–oxygen fuel cell that uses an acidic electrolyte:

- A** hydrogen gas is oxidised at the anode to form hydrogen ions
B hydrogen gas is reduced at the anode to form hydrogen ions
C hydrogen ions are oxidised at the cathode to form hydrogen ions
D hydrogen ions are reduced at the cathode to form hydrogen ions.

- 22.** A fuel cell designed to produce electricity from the reaction between grain alcohol and oxygen has the following overall equation.



Which of the following statements is true?

- A** Carbon dioxide is evolved at the negatively charged anode.
 - B** The grain alcohol and oxygen are mixed together in a 1 : 3 ratio within the electrolyte.
 - C** The grain alcohol undergoes reduction at the negatively charged electrode.
 - D** Oxide ions travel through the external circuit to the cathode.
- 23.** A major hurdle to the widespread use of fuel cells that use hydrogen and oxygen is:
- A** the difficulty in obtaining the oxygen required
 - B** that they cannot function without the use of an alkaline electrolyte
 - C** the current difficulty of transporting and storing the hydrogen fuel required
 - D** the voltage produced is too small.
- 24.** Which of the following is a feature of a fuel cell but not a galvanic cell?
- A** Small size
 - B** An anode and a cathode
 - C** A suitable electrolyte
 - D** Input connections for chemicals
- 25.** The process of fuel reforming involves:
- A** adding oxygen to a fuel to assist combustion
 - B** converting a fossil fuel into carbon monoxide
 - C** removing carbon monoxide from a fossil fuel
 - D** converting a fossil fuel into hydrogen.
- 26.** When hydrogen burns in air, it reacts to form:
- | | |
|-------------------------------|--------------------------|
| A H_2O | C CO_2 |
| B N_2 | D CH_4 . |
- 27.** Hydrogen can be stored as a:
- | | |
|-------------------------|----------------------------|
| A compressed gas | C metal hydride |
| B liquid | D all of the above. |

Review questions

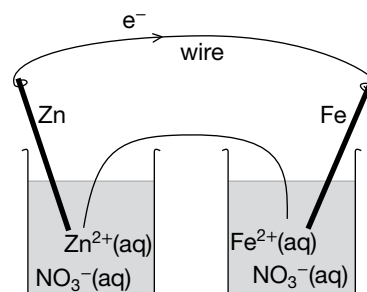
Redox reactions

- 1.** Early definitions of oxidation were:
- the addition of oxygen
 - the loss of hydrogen
- whereas early definitions of reduction were:
- the removal of oxygen
 - the addition of hydrogen.
- (a) Choose an example of a reaction that illustrates the *adequacy* of each of these definitions.
- (b) Choose an example of a reaction that illustrates the *inadequacy* of each of these definitions.
- (c) Use the examples chosen in (b) to show the redox nature of the reaction by considering the modern definitions of oxidation as the loss of electrons and reduction as the gain of electrons.
- (d) Provide a definition of oxidation and reduction with respect to oxidation numbers and illustrate your definition with an example.

- 2.** Define the following terms.
- (a) Oxidising agent
 - (b) Reducing agent
 - (c) Oxidation number
- 3.** In each of the following reactions use oxidation numbers to find which species has been reduced and which has been oxidised.
- (a) $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(s)} + \text{H}_2\text{(g)}$
 - (b) $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$
 - (c) $\text{Mg(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{MgSO}_4\text{(aq)} + \text{H}_2\text{(g)}$
 - (d) $2\text{Al(s)} + 3\text{Cl}_2\text{(g)} \rightarrow 2\text{AlCl}_3\text{(s)}$
- 4.** Identify the oxidising agent and reducing agent in each of the following reactions.
- (a) $2\text{Na(s)} + \text{S(s)} \rightarrow \text{Na}_2\text{S(aq)}$
 - (b) $2\text{K(s)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{KCl(aq)}$
 - (c) $4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)}$
 - (d) $\text{Cl}_2\text{(g)} + 2\text{HBr(aq)} \rightarrow 2\text{HCl(aq)} + \text{Br}_2\text{(l)}$
 - (e) $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$
 - (f) $\text{Zn(s)} + 2\text{MnO}_2\text{(s)} + 2\text{NH}_4\text{Cl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{Mn}_2\text{O}_3\text{(s)} + 2\text{NH}_3\text{(g)} + \text{H}_2\text{O(l)}$
- 5.** Identify the oxidising agent and reducing agent in each of the following redox equations.
- (a) $2\text{I}^-\text{(aq)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{Cl}^-\text{(aq)} + \text{I}_2\text{(s)}$
 - (b) $\text{Br}_2\text{(aq)} + 2\text{Cl}^-\text{(aq)} \rightarrow 2\text{Br}^-\text{(aq)} + \text{Cl}_2\text{(g)}$
 - (c) $\text{I}_2\text{(s)} + 2\text{Br}^-\text{(aq)} \rightarrow 2\text{I}^-\text{(aq)} + \text{Br}_2\text{(aq)}$
 - (d) $2\text{Co}^{3+}\text{(aq)} + \text{Pb(s)} \rightarrow \text{Pb}^{2+}\text{(aq)} + 2\text{Co}^{2+}\text{(aq)}$
 - (e) $\text{Fe(s)} + \text{Pb}^{2+}\text{(aq)} \rightarrow \text{Pb(s)} + \text{Fe}^{2+}\text{(aq)}$
 - (f) $\text{Hg(l)} + 2\text{H}^+\text{(aq)} \rightarrow \text{H}_2\text{(g)} + \text{Hg}^{2+}\text{(aq)}$
 - (g) $2\text{F}^-\text{(aq)} + \text{Cl}_2\text{(g)} \rightarrow \text{F}_2\text{(g)} + 2\text{Cl}^-\text{(aq)}$
- 6.** Balance the following equations using half-equations.
- (a) $\text{Br}^-\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \rightarrow \text{SO}_2\text{(g)} + \text{Br}_2\text{(l)}$
 - (b) $\text{Al(s)} + \text{Cl}_2\text{(g)} \rightarrow \text{AlCl}_3\text{(s)}$
 - (c) $\text{I}_2\text{(s)} + \text{H}_2\text{S(g)} \rightarrow \text{I}^-\text{(aq)} + \text{S(s)}$
 - (d) $\text{Cu(s)} + \text{HNO}_3\text{(aq)} \rightarrow \text{Cu}^{2+}\text{(aq)} + \text{NO(g)}$
 - (e) $\text{Cu(s)} + \text{HNO}_3\text{(aq)} \rightarrow \text{Cu}^{2+}\text{(aq)} + \text{NO}_2\text{(g)}$
 - (f) $\text{CuO(s)} + \text{NH}_3\text{(g)} \rightarrow \text{N}_2\text{(g)} + \text{Cu(s)}$
 - (g) $\text{PbS(s)} + \text{H}_2\text{O}_2\text{(l)} \rightarrow \text{PbSO}_4\text{(s)} + \text{H}_2\text{O(l)}$
 - (h) $\text{Cr}_2\text{O}_7^{2-}\text{(aq)} + \text{CH}_3\text{CH}_2\text{OH(aq)} \rightarrow \text{CH}_3\text{COOH(aq)} + \text{Cr}^{3+}\text{(aq)}$

Galvanic cells in the laboratory

- 7.** Consider the reaction occurring in the diagram shown, and complete the following.
- (a) State the anode reaction.
 - (b) State the cathode reaction.
 - (c) Find the overall cell reaction.



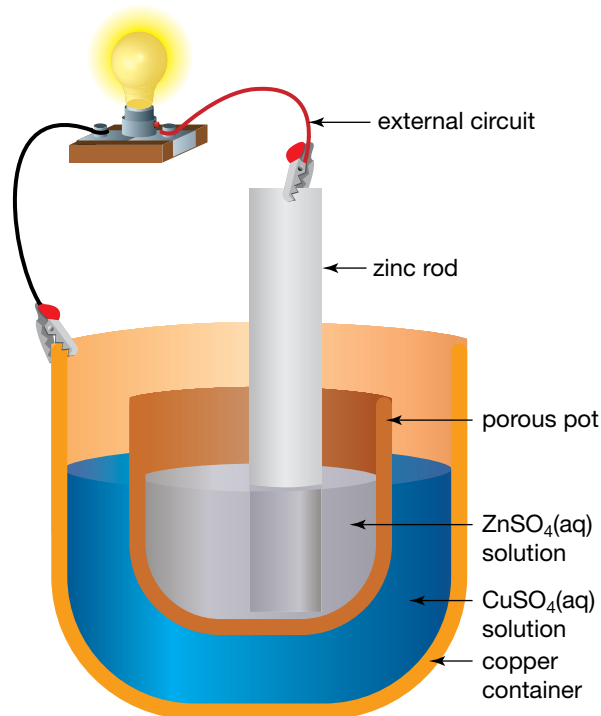
8. A student was doing an experiment in the school laboratory. She placed a fresh piece of zinc metal into a beaker of silver nitrate solution and left it to stand for a short period of time. She then noted the following observations:
- The temperature of the solution increased.
 - The zinc metal became coated with silver.
- Write the ionic equation for the reaction occurring in the beaker.
 - Draw a galvanic cell that allows the energy released during the reaction to be readily used. On your diagram, identify the anode and the cathode and the polarity of these electrodes. Indicate the direction of electron flow.
 - Write half-equations for the reactions occurring at each electrode.
 - Explain the significance of the increase in temperature of the solution.
9. Define the following terms.
- | | |
|----------------------|---------------------|
| (a) Galvanic cell | (e) Anode |
| (b) Internal circuit | (f) Salt bridge |
| (c) External circuit | (g) Inert electrode |
| (d) Cathode | |
10. Why is a salt bridge or porous barrier used to connect two half-cells in a galvanic cell?

The electrochemical series

11. Refer to a table of standard electrode potentials to predict whether each of the following reactions could occur spontaneously.
- $2\text{Al(s)} + 3\text{Zn}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Zn(s)}$
 - $\text{Ni(s)} + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + \text{Zn(s)}$
 - $2\text{Cr}^{3+}(\text{aq}) + 3\text{Mg(s)} \rightarrow 2\text{Cr(s)} + 3\text{Mg}^{2+}(\text{aq})$
 - $2\text{H}^{+}(\text{aq}) + \text{Sn(s)} \rightarrow \text{H}_2(\text{g}) + \text{Sn}^{2+}(\text{aq})$
 - $\text{Fe(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Cu(s)}$
 - $\text{Fe}^{2+}(\text{aq}) + \text{Cu(s)} \rightarrow \text{Fe(s)} + \text{Cu}^{2+}(\text{aq})$
 - $\text{Zn(s)} + \text{Mg}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Mg(s)}$
 - $\text{Cu(s)} + \text{Ca}^{2+}(\text{aq}) \rightarrow \text{Ca(s)} + \text{Cu}^{2+}(\text{aq})$
 - $\text{Cl}_2(\text{g}) + 2\text{Br}^{-}(\text{aq}) \rightarrow 2\text{Cl}^{-}(\text{aq}) + \text{Br}_2(\text{l})$
 - $3\text{Ag(s)} + \text{Fe}^{3+}(\text{aq}) \rightarrow 3\text{Ag}^{+}(\text{aq}) + \text{Fe(s)}$
12. By referring to a table of standard electrode potentials, state whether you would expect:
- bromine gas to form if chlorine gas was bubbled into a solution of bromide ions
 - chlorine gas to form if bromine gas was bubbled into a solution of chloride ions
 - iron(II) ions to be oxidised by acidified hydrogen peroxide solution
 - iron(II) ions to be reduced when reacted with hydrogen peroxide solution.
13. Design a galvanic cell that produces electricity from each of the following reactions.
- $2\text{Ag}^{+}(\text{aq}) + \text{Mg(s)} \rightarrow 2\text{Ag(s)} + \text{Mg}^{2+}(\text{aq})$
 - $2\text{Al(s)} + 3\text{I}_2(\text{s}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 6\text{I}^{-}(\text{aq})$
 - $\text{Cl}_2(\text{g}) + \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$
 - $2\text{Fe}^{3+}(\text{aq}) + \text{Fe(s)} \rightarrow 3\text{Fe}^{2+}(\text{aq})$

For each cell, show how it is constructed. Identify the anode and cathode, showing the equations occurring at each. Indicate the direction of electron flow and the migration of each kind of ion in the cell and the salt bridge.

14. Galvani's 'frogs' legs' experiment was basically an electrochemical cell consisting of two dissimilar metals that acted as electrodes, and an electrolyte that was aqueous frog-body fluid. Draw a diagram of Galvani's experiment showing its galvanic cell nature. Label the cathode, anode and direction of electron flow.
15. The diagram below represents a Daniell cell. When the zinc rod and the copper container are connected as part of a completed electrical circuit, a current flows in this circuit.
- Use the electrochemical series and the diagram to determine the following:
- the direction of the electron flow
 - the anode
 - the cathode
 - the anode reaction
 - the cathode reaction
 - the overall cell reaction
 - the component that serves the purpose of the salt bridge.



16. Draw a galvanic cell that uses the reaction between solid aluminium metal and an aqueous solution of blue copper sulfate. Potassium nitrate can be used in the salt bridge.
- Clearly label the following:
 - the anode, the cathode and the appropriate electrolytes

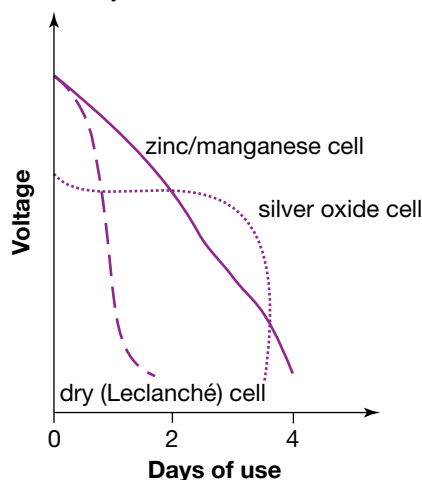
- equations for the reactions at the anode and cathode, marked as either oxidation or reduction
 - the overall cell reaction
 - the direction of electron flow
 - the direction of flow of anions and cations in the salt bridge.
- (b) What would happen if the salt bridge was removed? Explain.
- (c) What happens to the colour of the copper sulfate solution? Explain.
17. Each of the pairs of half-cells below are combined to form galvanic cells. Draw a diagram for each, showing:
- the direction of electron flow in the external circuit
 - the half-equation at the electrode labelled the anode
 - the half-equation at the electrode labelled the cathode
 - the full equation for the overall reaction in the galvanic cell
 - the flow of negative and positive ions in the salt bridge
 - the cell potential.
- (a) $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ and $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$
- (b) $\text{Sn}^{2+}(\text{aq})/\text{Sn}(\text{s})$ and $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$
- (c) $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$ and $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$
18. Explain why:
- (a) a paint containing powdered aluminium metal would form a protective coating for objects made of iron
- (b) aluminium windows should not be held in place with copper or iron nails.
19. Considering the positions of iron, magnesium and zinc in the electrochemical series, explain why iron is protected from rusting when blocks of magnesium or zinc are attached to it.
20. Three metals are represented by the symbols A, B and C. If metals B and C react with a solution containing ions of metal A, and metal C does not react with a solution containing ions of metal B, determine the relative reducing strengths of the three metals.

Galvanic cells and batteries

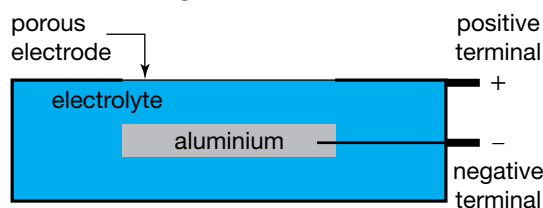
21. Explain the difference between a cell and a battery.
22. Electrochemical cells constructed in the laboratory often consist of two separate half-cells connected by electrical wire and a salt bridge.
- (a) Explain the features of commercial cells that enable electrical power to be generated from chemicals in only one cell.
- (b) Select a commercial cell and construct a corresponding laboratory-type, two-half-cell galvanic system. Label all parts, including

cathode, anode, direction of electron flow and half-cell reactions.

23. Some dry cells have a longer 'life' than other dry cells. Describe the modifications that could be made to:
- (a) the zinc anode
- (b) the quantity of manganese dioxide
- (c) the concentration of electrolyte to increase the life of a cell.
24. The figure below shows the comparative performance of batteries over time. Describe a practical situation in which each of these batteries would be ideally suited. Justify your choice in each case, explaining why the other two types of battery would be less desirable.

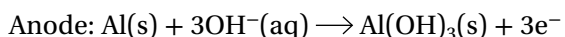


25. One type of heart pacemaker contains metallic lithium, which is reduced to lithium ions when the pacemaker is in use. Silver chromate, Ag_2CrO_4 , acts as the oxidising agent and is reduced to silver metal.
- (a) How do pacemaker cell designers use the electrochemical series when deciding which materials to use in the device?
- (b) Write the half-equations that would occur at each electrode in the pacemaker, and then derive the overall equation.
- (c) The electrolyte in a lithium pacemaker is lithium chlorate(VII), LiClO_4 , dissolved in propene carbonate. Why is it essential that the electrolyte does *not* contain any water?
- (d) Pacemaker cells could be designed to be even smaller than 'button' cells. List two advantages and disadvantages of reducing the size of pacemaker cells.
26. The structure of an aluminium-air battery is shown in the figure below.



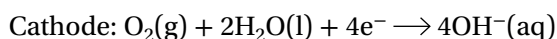
In the aluminium–air battery, a piece of aluminium is immersed in an electrolyte near a porous electrode. This porous electrode has air on one side and the electrolyte on the other. The electrolyte can be a common salt, NaCl, solution, an alkali solution, such as potassium hydroxide, KOH, or sea water. Although the choice of electrolyte is quite flexible, only special alloys of aluminium can be used. With ordinary alloys, the aluminium immediately becomes coated with a protective oxide layer or simply dissolves as aluminium oxide, giving off hydrogen gas.

In this battery, the aluminium anode reacts with hydroxide ions to form aluminium hydroxide, with the release of three electrons.

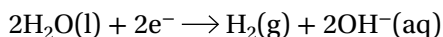


The OH^- ions are present either because the electrolyte is an alkali solution or because they are produced at the cathode.

At the porous cathode, the water in the electrolyte reacts with oxygen from the air and the electrons from the anode to produce hydroxide ions.



If the cathode is covered (for example, with water) so that oxygen cannot enter the cell, a slightly different reaction occurs in the cell in which hydrogen gas is produced.



- (a) Write the overall equation for the aluminium–air battery operating under optimal conditions.
- (b) Write the overall equation if the cathode is covered with water.

Fuel cells

27. (a) What is a fuel cell?
(b) List the advantages of a fuel cell over a primary galvanic cell.
28. Fuel cells have been used in spacecraft for a number of years as a source of electrical energy. To obtain sufficient current, two gases, hydrogen and oxygen, are kept in cylinders under high pressure. The gases are passed over nickel electrodes. The product of these fuel cells is water,

which is used by the astronauts for drinking. Each hydrogen–oxygen fuel cell used in the Apollo spacecraft weighed approximately 100 kg.

- (a) What advantages do fuel cells have over internal combustion engines for use in spacecraft?
- (b) What are the limitations of fuel cells, compared with the internal combustion engine?
29. Fuel cells have been developed to run on methane. Assuming that the electrolyte is acidic:
 - (a) write the half-equation for the oxidation reaction
 - (b) write the half-equation for the reduction reaction.
 Draw a diagram of this cell, labelling the following.
 - (c) The methane and oxygen inlets
 - (d) The anode and cathode and their polarities
 - (e) The direction of electron flow
 - (f) The ion flow in the electrolyte
30. Obtaining hydrogen for use in fuel cells is not yet economically viable. But researchers have come up with a fuel cell that runs on octane, the main component of petrol. Previously, the reforming process caused a build-up of carbon on the electrodes in the fuel cell, reducing efficiency. A new system combines the reformer and the fuel cell and uses a more advanced catalyst.
 - (a) Write the equation for the combustion of octane, C_8H_{18} .
 - (b) This reaction is the same as the one that occurs in the fuel cell and produces the same amount of carbon dioxide. Explain what benefit there is in using a fuel cell to supply energy to power a vehicle.
 - (c) Write the half-equations for the anode and cathode reactions in this fuel cell assuming an acidic electrolyte.
 - (d) Add the two half-equations from (c) to get the overall reaction. Compare your answer with (a). What do you notice?
31. Discuss the statement ‘Electrochemical cells may help decrease our use of fossil fuels as an energy source.’
32. Describe how the method of producing electricity from an electrochemical cell differs from the method of producing electricity from:
 - (a) a hydro-electricity scheme
 - (b) a coal-fired power station.

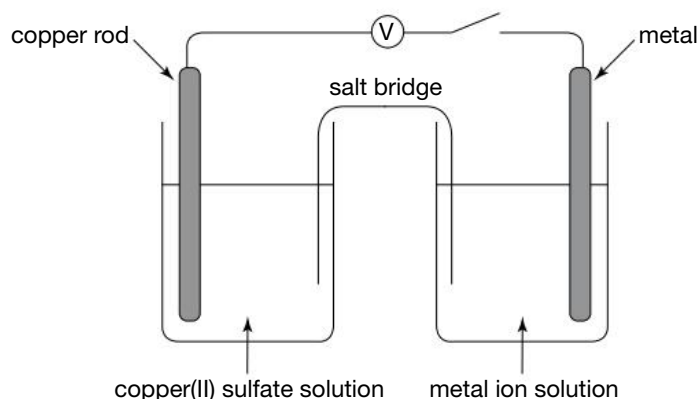


Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

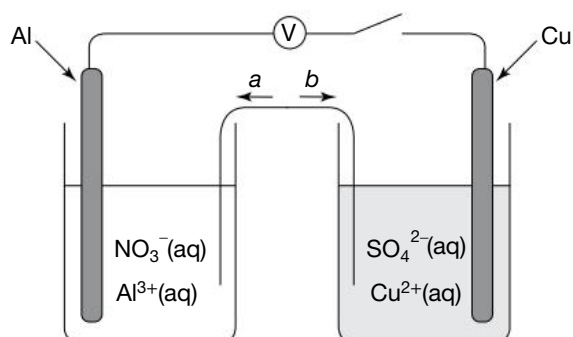
1. A student set up an electrochemical experiment as shown in the figure.



He kept the copper half-cell constant, but changed the other half-cell. For each cell, he recorded the metal that was used as the anode and the overall cell voltage.

Cell	Anode	Voltage (V)
copper-lead	lead	0.49
copper-silver	copper	0.31
copper-magnesium	magnesium	1.45
copper-iron	iron	0.57
copper-aluminium	aluminium	0.94
copper-copper	copper	0.00
copper-nickel	nickel	0.31

- (a) How did the student determine which of the metals in the cell acted as the anode? **2 marks**
- (b) Why did the copper-copper cell produce no voltage? **1 mark**
- (c) Determine the likely order of reactivity of the metals. Justify your placements. **2 marks**
2. A half-cell is constructed with a copper electrode in a 1.0 M copper(II) sulfate solution. It is connected by a salt bridge to another half-cell containing an aluminium electrode in a 1.0 M aluminium nitrate solution.



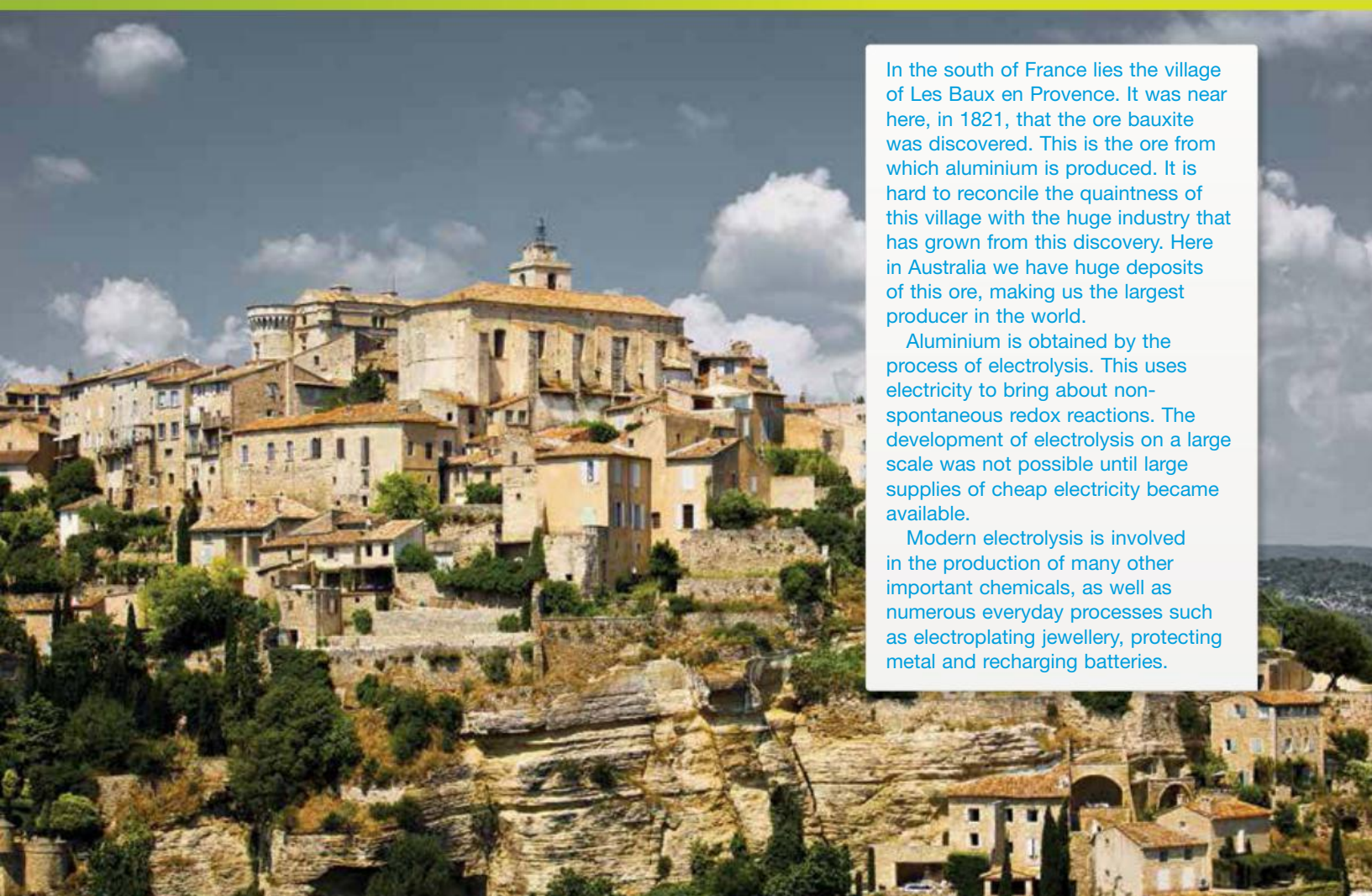
- (a) A voltmeter is connected into the external circuit. What would be the expected $E^\ominus$ value for this cell? **1 mark**
- (b) Give two changes that might be observed in the copper half-cell if a large current flowed for many hours. **2 marks**
- (c) What is the polarity of the copper electrode? **1 mark**
- (d) Which arrow, *a* or *b*, shows the direction of negative ions in the salt bridge? **1 mark**
- (e) Write a balanced half-equation for the reaction occurring at the anode. **1 mark**
3. Fuel cells have been developed to use different alkanes for fuels. An example is the propane–oxygen fuel cell. The overall reaction (assuming an acidic electrolyte) is identical to the combustion of propane in oxygen.
- $$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$$
- (a) Write an equation showing the reaction occurring at the anode. **1 mark**
- (b) Write an equation showing the reaction occurring at the cathode. **1 mark**
- (c) Describe two advantages in using propane in a fuel cell instead of burning propane in a power station. **2 marks**
- (d) How do the electrodes in a fuel cell differ from those in a primary cell? **1 mark**

4 Electrolysis

Galvanic cells convert chemical energy to electrical energy from spontaneous chemical reactions. The reverse process occurs in electrolytic cells. During electrolysis, an electrical current is passed through an electrolyte causing a chemical reaction that would not otherwise occur. Electrolysis reactions form the basis of a number of important industrial processes.

YOU WILL EXAMINE:

- energy transformations in electrolytic cells
- the differences between galvanic and electrolytic cells
- how to use the electrochemical series to predict the products of redox reactions in electrolytic cells and the limitations of these predictions
- some examples of commercial electrolysis
- rechargeable batteries
- some of the factors that affect battery life
- how to apply Faraday's laws to calculate quantities in redox reactions.



In the south of France lies the village of Les Baux en Provence. It was near here, in 1821, that the ore bauxite was discovered. This is the ore from which aluminium is produced. It is hard to reconcile the quaintness of this village with the huge industry that has grown from this discovery. Here in Australia we have huge deposits of this ore, making us the largest producer in the world.

Aluminium is obtained by the process of electrolysis. This uses electricity to bring about non-spontaneous redox reactions. The development of electrolysis on a large scale was not possible until large supplies of cheap electricity became available.

Modern electrolysis is involved in the production of many other important chemicals, as well as numerous everyday processes such as electroplating jewellery, protecting metal and recharging batteries.

Metals through the ages

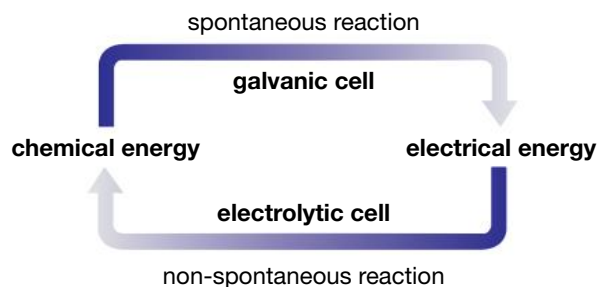
The more reactive metals could be obtained in significant quantities only after the discovery of electrolysis.

The metals in use during ancient times, such as copper, lead, zinc and tin, were easily smelted or extracted from their ores. Iron, however, proved to be more difficult to extract, so weapons and tools made of iron were not in use until long after the copper-based alloys of the Bronze Age had been discovered.

The extraction of metals such as aluminium, magnesium, calcium and sodium was not achieved until the nineteenth century. Not until electrolysis was discovered could these elements be obtained from their compounds in significant amounts.



We have already seen how a spontaneous chemical reaction can be used to generate a flow of electrons (an electric current). In this chapter, you will see how an electric current can be used to make a non-spontaneous redox reaction occur.

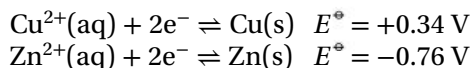


Electrolysis — the process

Electrolysis is a chemical reaction caused by the passage of a current through an electrolyte.

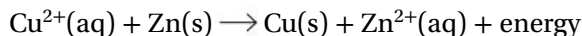
In an electrochemical cell or galvanic cell, a spontaneous chemical reaction produces an electric current. In an electrolytic cell, the reverse process takes place. The passage of an electric current through an electrolytic solution causes a chemical reaction. This process is known as **electrolysis**.

In galvanic cells, chemical reactions can be used to generate a flow of electrons (an electric current). If a zinc rod is placed in copper(II) sulfate solution, a coating of copper appears on the zinc rod. This may be explained by considering the standard electrode potentials of each half-equation:



In electrolysis, electrical energy is converted into chemical energy.

Since the E° value for the Cu^{2+}/Cu redox pair is greater than the E° value for the Zn^{2+}/Zn redox pair, Cu^{2+} ions react spontaneously with zinc metal. A galvanic cell constructed from these two half-cells would produce electrical energy. The overall equation for such a galvanic cell would be:



However, if a copper rod is placed in a zinc sulfate solution, no reaction occurs. Since this reaction is the reverse of the one that produces energy, energy must be supplied for the reaction to occur:



Electrolytic cells

The chemical reaction that occurs when electricity passes through a molten ionic compound or through an electrolyte solution is called **electrolysis**. Solutes that form solutions that can conduct electricity are called **electrolytes**. An electrolyte solution conducts electricity. Positive ions gain electrons at the cathode and negative ions lose electrons at the anode. This transfer of electrons has the same effect as a flow of electrons, and the solution conducts electricity. The apparatus in which electrolysis occurs is called an **electrolytic cell**.

Conducting solutions are known as electrolytes.

Electrolysis occurs in an electrolytic cell.

study on

Unit 3

AOS 2

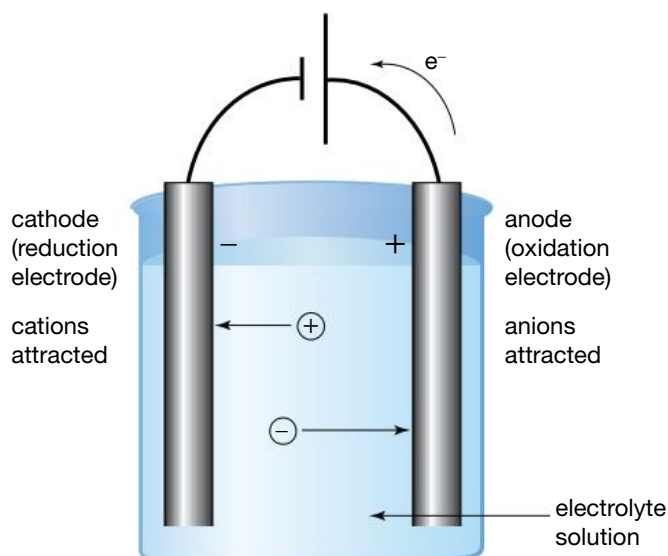
Topic 2

Concept 1



See more

Features of electrolytic cells



An electrolytic cell

An electrolytic cell consists of an electrolyte, electrodes and a power supply.

Electrons are supplied to the cathode and withdrawn from the anode by the power supply.

An electrolytic cell has three essential features:

1. an electrolyte solution that contains free-moving ions. These ions can donate or accept electrons, allowing electrons to flow through the external circuit.
2. two electrodes at which the electrolysis reactions occur
3. an external source of electrons, such as a battery or power pack. This electron flow is in one direction only and is termed DC (direct current).

The electrode to which electrons flow from the external power source is the negative electrode and is called the **cathode**, since reduction occurs there. The electrode from which electrons are withdrawn by the power source is the positive electrode and is called the **anode**, since oxidation occurs there. Cations are attracted to the cathode, while anions are attracted to the anode. The cations gain electrons from the cathode and the anions give up electrons to the anode.

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Unit 3

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Topic 3

Concept 6

Do more

Comparison of galvanic and electrolytic cells

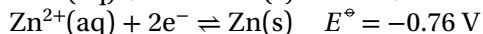


In both galvanic and electrolytic cells, oxidation always occurs at the anode and reduction at the cathode.

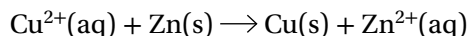
In an electrolytic cell, the anode is positive and the cathode is negative.

Comparing galvanic and electrolytic cells

Consider the following redox half-equations:

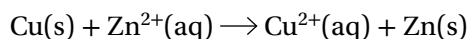


Electrical energy can be obtained from the spontaneous reaction between copper(II) ions and zinc metal in a galvanic cell:



When standard half-cells are used, 1.1 volts may be generated by the cell.

If, however, an external DC power source is placed in the external circuit and connected so that the applied voltage is opposite to that generated by the galvanic cell, the reverse reaction proceeds:



When standard half-cells are used, more than 1.1 volts is needed to force this non-spontaneous reaction to occur.

Note (i): Although a knowledge of E° values for cell half-reactions may enable a prediction to be made of the overall minimum voltage required for an electrolytic reaction to occur, the actual observed voltage may vary by as much as 1 volt, owing to a phenomenon known as ‘overpotential’.

Note (ii): A full analysis of this situation would also involve the possibility that water molecules from the solution could also be ‘made’ to react. This is examined further later in this chapter.

In both galvanic and electrolytic cells, oxidation occurs at the anode and reduction occurs at the cathode. However, in an electrolytic cell, the cathode is negative since the external DC source forces electrons onto it. Zinc ions, Zn^{2+} , are therefore attracted to the cathode where they pick up electrons to form zinc atoms.

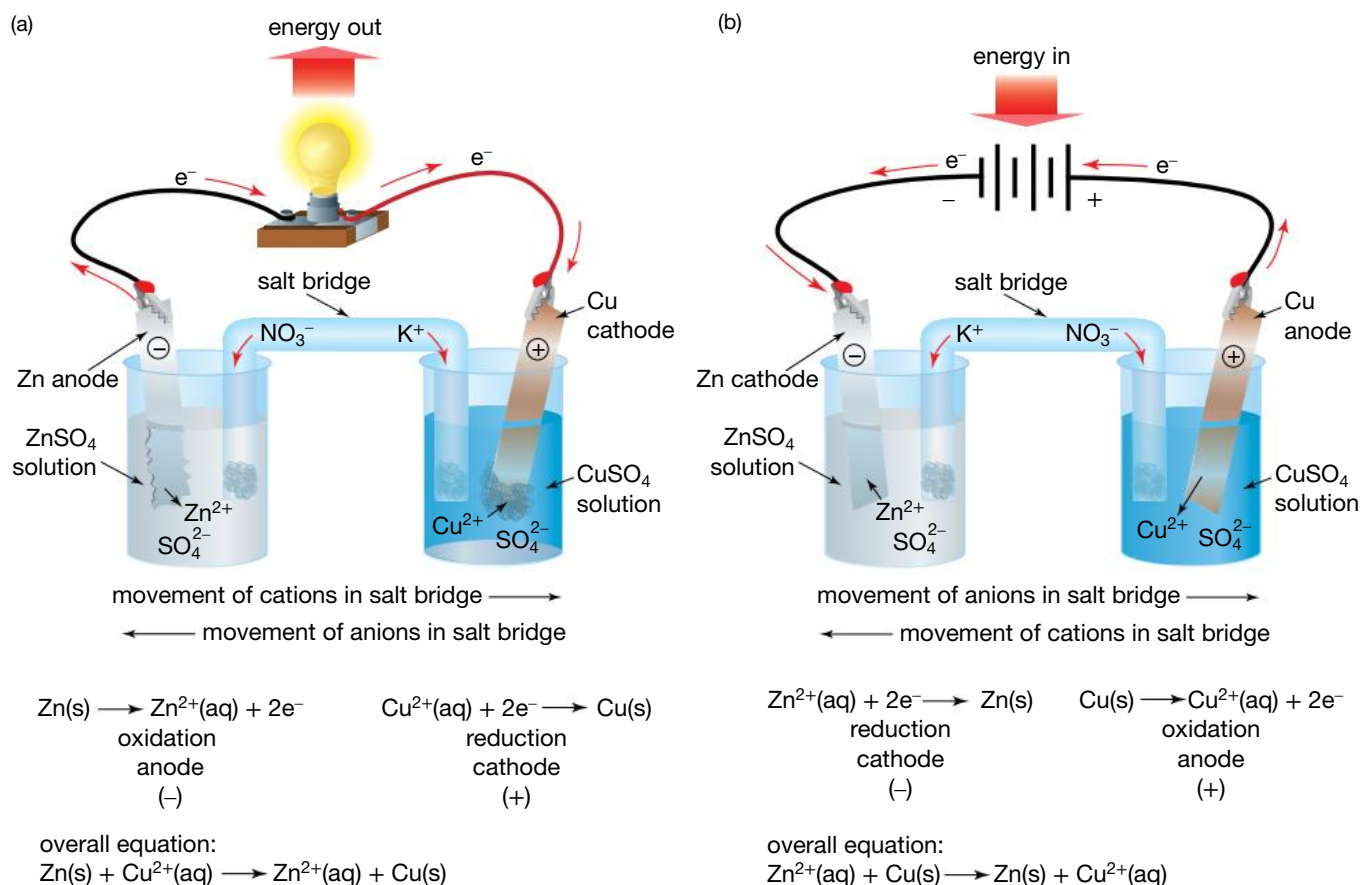
The anode in an electrolytic cell is positive since the DC source withdraws electrons from it. Electrons are supplied to the positive anode by the oxidation of the copper electrode itself.

In an electrolytic cell, the polarity of the electrodes is determined by the external DC source. In contrast, the polarity of the electrodes in a galvanic cell develops due to the spontaneous redox reaction occurring within the cell itself.

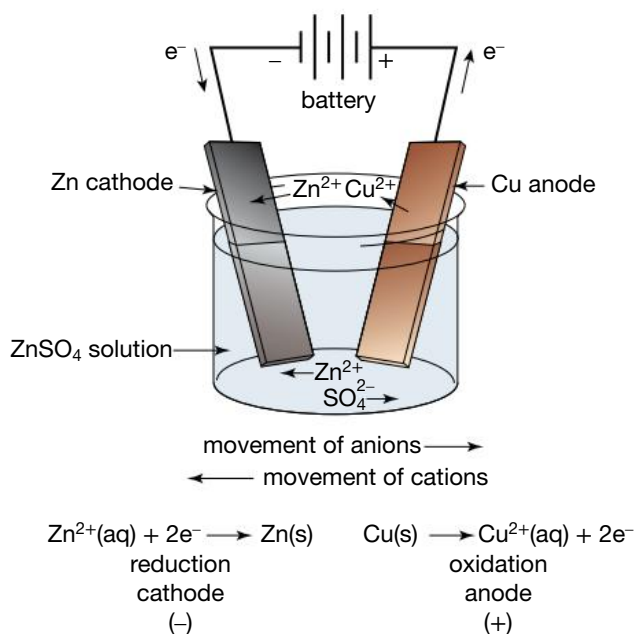
Table 4.1 summarises the major similarities and differences between galvanic and electrolytic cells.

TABLE 4.1 Comparison of galvanic and electrolytic cells

Feature	Galvanic cell	Electrolytic cell
type of redox reaction	spontaneous	non-spontaneous
energy produced or required	produced	required
where oxidation occurs	anode	anode
where reduction occurs	cathode	cathode
anode polarity	negative	positive
cathode polarity	positive	negative
how cell polarity is determined	depends on reactions occurring within cell	external power source



Comparison of zinc–copper half-cells in electrochemical and electrolytic reactions (a) Daniell cell showing fully labelled components, half-equations and overall equation (b) Electrolytic cell showing fully labelled components, half-equations and overall equation

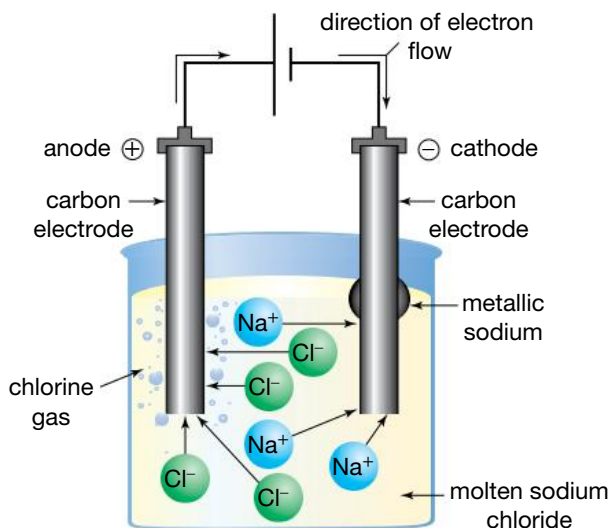


A one-celled electrolytic cell. In an electrolytic cell, the two electrodes are usually immersed in a common electrolyte. In this example, the same reactions would occur if the electrolysis was carried out with copper and zinc electrodes immersed in a zinc sulfate solution.

Electrolysis of molten ionic compounds

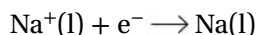
The simplest cases of electrolysis involve the electrolysis of molten ionic substances that are pure, using inert electrodes. As an example, let us consider the electrolysis of molten sodium chloride.

Solid sodium chloride does not conduct electricity. However, when an electric current is passed through molten sodium chloride, a chemical reaction may be clearly observed. A shiny bead of sodium is produced at the cathode and chlorine gas is evolved at the anode.

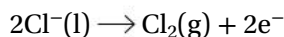


Electrolysis of molten sodium chloride

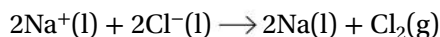
In solid sodium chloride, the oppositely charged sodium ions, Na^+ , and chloride ions, Cl^- , are held tightly together. Heating the solid causes the ions in the crystal to separate so they are then free to move. The molten liquid is called a melt. In an electrolytic cell, the sodium ions are attracted to the negative cathode where they are reduced:



The chloride ions are attracted to the positive anode where they undergo oxidation:

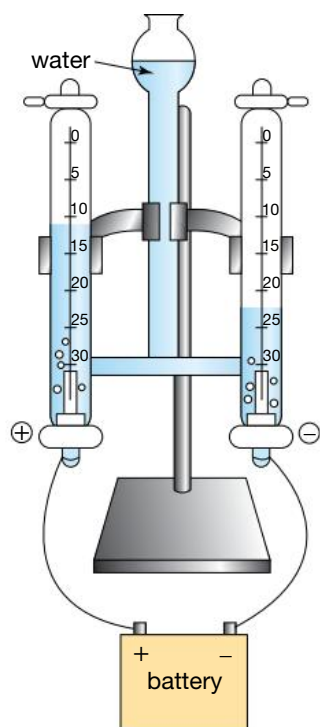


Since, in a redox reaction, the same number of electrons are consumed as are produced, the overall equation is:



Revision questions

1. Draw and label the apparatus you could use in the laboratory for the electrolysis of molten potassium chloride.
2. Explain why the reactants in a galvanic cell must be kept separated whereas the reactants in an electrolytic cell are usually contained within a single compartment.



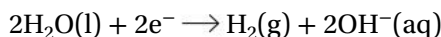
Electrolysis of water using a Hofmann voltameter. When an electric current is passed through water, it decomposes into oxygen and hydrogen. By considering the equation for this decomposition, suggest which tube contains hydrogen gas and which contains oxygen gas.

When aqueous solutions are electrolysed, water may react at one or both electrodes.

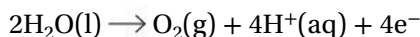
Electrolysis of water

When a current is applied via two electrodes in pure water, nothing happens. There is no current flow and no electrolysis. If, however, an electrolyte such as H_2SO_4 or KNO_3 is added in *low* concentration, the resulting solution conducts electricity and electrolysis occurs. The products of the electrolysis of water, in this case, are hydrogen and oxygen.

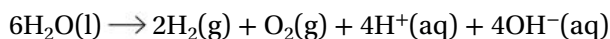
At the cathode, water is reduced to form hydrogen:



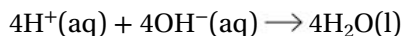
At the anode, water is oxidised to form oxygen:



The region around the cathode becomes basic owing to an increase in OH^- ions, whereas the region around the anode becomes acidic, owing to an increase in H^+ ions. The overall cell reaction may be obtained by adding the half-equations:



However, some of the ions produced re-form into reactants:



and so do not need to be included in the final overall equation:



Electrolysis of aqueous solutions of ionic compounds

When a molten salt is electrolysed, the products are predictable. However, as seen previously, when an aqueous solution of an ionic compound is electrolysed, water may react at one or both of the electrodes in preference to the ions from the salt. Hydrogen sometimes appears at the cathode, rather than a metal, and oxygen sometimes appears at the anode, rather than a metal cation or a halogen. For this reason, we need to be able to predict the products of electrolysis when there is more than one possible reaction around an electrode.

Predicting reactions during electrolysis of aqueous solutions

In aqueous solutions, there is a mixture of at least two oxidising agents and two reducing agents. If non-inert electrodes are used, then even more possibilities may exist. Which oxidising agent and which reducing agent react?

Although electrolytic products depend on a number of factors, the following procedure is useful.

1. List the species present, including all metals that are used as electrodes.
2. Write half-equations involving these species in descending order of E° .
3. Circle the species present in the electrolytic cell that could participate.
4. Select the oxidising agent with the highest E° (the strongest oxidising agent). This will be reduced at the cathode, since it requires less energy for reduction than an oxidising agent with a lower E° .
5. Select the reducing agent with the lowest E° (the strongest reducing agent). This will be oxidised at the anode, since it requires less energy for oxidation than a reducing agent with a higher E° .

study on

Unit 3

AOS 2

Topic 3

Concept 2



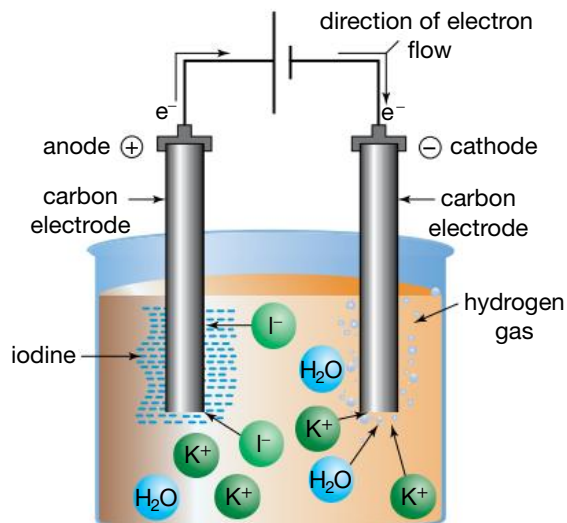
See more
Predicting the
products of
electrolysis

6. Write the overall equation.
7. Determine the minimum voltage required to achieve the reaction by using the formula:

$$\text{minimum voltage required} = E^{\circ}_{\text{oxidising agent}} - E^{\circ}_{\text{reducing agent}}$$



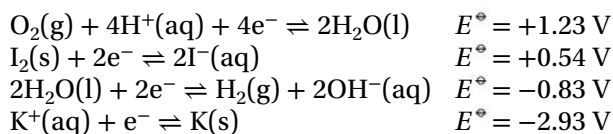
Competing reactions are like wrestlers; the strongest challengers (strongest oxidising agent and strongest reducing agent) make it to the final round.



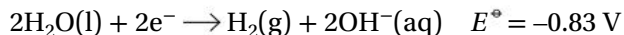
Electrolysis of dilute potassium iodide

The electrolysis of dilute potassium iodide is shown above.

With potassium ions, iodide ions and water present in the cell, the possible half-cell reactions are:

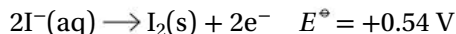


Reduction occurs at the cathode, so there are two possible reactions in this cell. The species that requires the least energy for reduction (the oxidising agent with the highest E° value — the strongest oxidising agent) reacts at the cathode. So, water reacts in preference to potassium ions at the cathode:



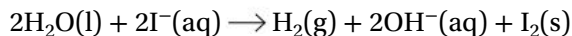
Hydrogen gas is evolved at this electrode and the solution around the cathode becomes alkaline, owing to an increase in hydroxide ion concentration.

Oxidation occurs at the anode, so there are two possible reactions. The species that requires the least energy for oxidation (the reducing agent with the lowest E° value) reacts at the anode. Thus, iodide ions react in preference to water molecules at the anode:



The solution around the anode appears yellow-brown, owing to the formation of iodine.

The overall electrolytic cell reaction would be:



To achieve this reaction, a potential difference greater than the spontaneous reverse reaction would need to be applied. So more than $+0.54 - (-0.83) = 1.37$ volts should be delivered to this electrolytic cell.

The products formed from the electrolysis of some electrolytes are shown in table 4.2.

TABLE 4.2 Products of electrolysis

(a) Using inert electrodes (platinum or graphite)

Electrolyte	Product formed at cathode	Product formed at anode
PbBr ₂ (l) — a melt	Pb(s)	Br ₂ (g)
NaCl(l) — a melt	Na(s)	Cl ₂ (g)
CuCl ₂ (aq)	Cu(s)	Cl ₂ (g), O ₂ *
NaCl(aq)	H ₂ (g)	Cl ₂ (g), O ₂ *
KNO ₃ (aq)	H ₂ (g)	O ₂ (g)
CuSO ₄ (aq)	Cu(s)	O ₂ (g)
H ₂ SO ₄ (aq)	H ₂ (g)	O ₂ (g)
NaOH(aq)	H ₂ (g)	O ₂ (g)

*depending on concentration

(b) When the electrodes take part in the reaction

Electrolyte	Copper cathode	Copper anode
CuSO ₄ (aq)	Cu(s) deposited	Cu(s) dissolves to form Cu ²⁺ ions

Factors affecting electrolysis of aqueous solutions

The products formed during electrolysis depend on the concentration and nature of the electrolyte and the type of electrode used.

What happens during electrolysis depends on a number of factors, including:

- the concentration of the electrolyte
- the nature of the electrolyte
- the nature of the electrodes.

In any electrolysis reaction, alteration of any of these factors may change the nature of the products. The identity of products of an electrolysis reaction under fixed conditions is found by experiment. When the products are known, the reactions occurring at the electrodes may be written.

The effect of concentration

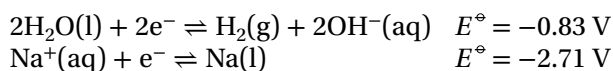
The electrochemical series (see table 3.1 on page 80) is a very useful tool for predicting the products of an electrolysis reaction. It must be remembered, however, that it is based on standard conditions, in particular, where the concentrations of dissolved species are 1 M. If the concentrations of potential reactants are different from this, the observed results might be different from

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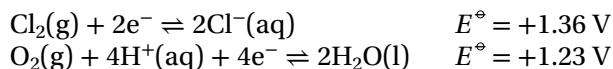
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Experiment 4.1 Electrolysis of aqueous solutions of electrolytes
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those predicted. In the electrolysis of dilute sodium chloride, for example, reduction occurs at the cathode. The possible reactions are:

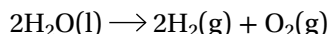


As predicted from a table of standard redox potentials, water, rather than sodium ions, is reduced at the cathode. At the anode, chloride ions or water molecules may be oxidised:



As predicted from a table of standard redox potentials, oxygen gas is evolved in preference to chlorine gas at the anode.

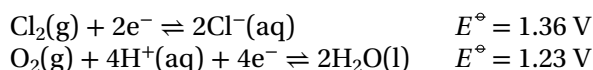
The overall equation is:



(see electrolysis of water on page 113).

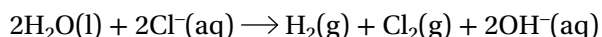
However, at higher concentrations (>6 M) of chloride ions, the discharge of chlorine becomes more favourable. The reduction of water, rather than sodium ions, still occurs at the cathode at higher concentrations of sodium ions. The electrolysis of dilute sodium chloride, therefore, produces hydrogen gas at the cathode and oxygen gas at the anode, but electrolysis of 6 M sodium chloride produces hydrogen gas at the cathode and chlorine gas at the anode.

This can be understood when the E° values for the following reactions are examined:



These values change when conditions are non-standard. In fact, they change enough to swap the order around, thus making the oxidation of chloride ions to chlorine gas the preferred reaction at the anode. Such a reversal at the cathode does not occur because the difference between H_2O and Na^+ ions is too large.

Thus, when concentrated (>6 M) sodium chloride is electrolysed, the overall reaction becomes:

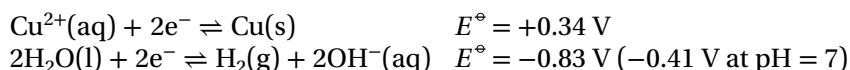


The nature of the electrolyte

If concentrated copper(II) chloride solution, instead of concentrated sodium chloride solution, is electrolysed, the results are different.

At the anode, chlorine gas is evolved in both cells, since the solution is concentrated and the only species present initially are chloride ions and water molecules.

At the cathode, hydrogen gas is evolved in the sodium chloride cell, as discussed earlier. In the copper chloride cell, two reactions are possible at the cathode:



As may be predicted from a consideration of the standard electrode potentials, copper is deposited in preference to the evolution of hydrogen gas.

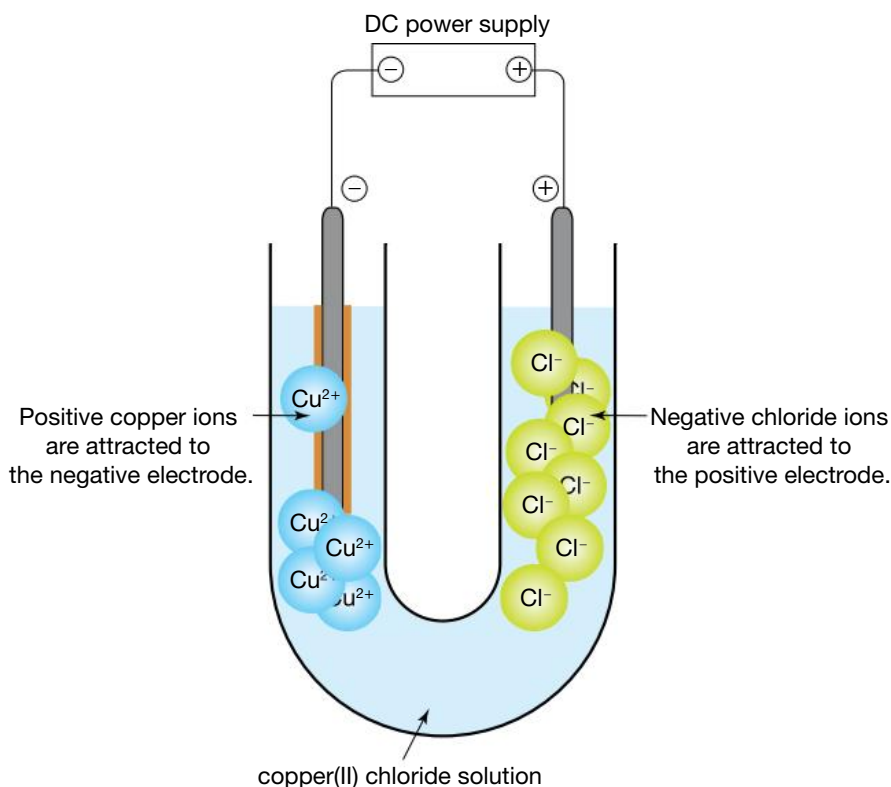
So, the products in an electrolytic reaction depend on the nature of the electrolyte.

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Experiment 4.2 Factors affecting electrolysis

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Electrolysis of a concentrated copper(II) chloride solution produces copper (in solid form) and chlorine gas.

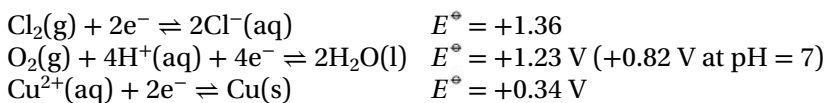
When some metals are used as anodes, they may be oxidised in preference to water or the ions in solution.

The nature of the electrodes

If the anode is made of a metal such as silver, copper or iron, electrons may be removed preferentially from the metal atoms in the electrode rather than from the ionic species in solution or the water molecules themselves.

There is no corresponding effect at the cathode because metals have no tendency to gain electrons.

The electrolysis of copper(II) chloride solution using inert electrodes, for example, results in the production of oxygen gas or chlorine gas (depending on the concentration of the solution; see table 4.2 on page 115) at the anode. However, if copper electrodes are used, copper(II) ions are produced at the anode, since the electrode itself acts as a stronger reducing agent than either water molecules or chloride ions:



The copper anode dissolves to form Cu^{2+} ions.

In many electrolysis reactions, inert electrodes are used. Inert electrodes conduct a current but do not tend to go into solution as ions. Platinum metal and graphite are commonly used as inert electrodes.

Platinum and graphite electrodes do not react.

Revision questions

3. Magnesium may be obtained commercially from sea water. During the last stage of this process, molten magnesium chloride undergoes electrolysis in a cell that contains an iron cathode and a graphite anode.
 - (a) Why may iron be used to form the cathode but not the anode?
 - (b) Draw a fully labelled diagram of an electrolytic cell that could be used to produce magnesium. Include equations.

4. A solution containing lead, magnesium and copper ions is electrolysed for a long time.
- (a) What will be the first product formed at the cathode?
 - (b) If the electrolysis is continued until all the ions responsible for the product in (a) are used up, what will be the next product observed at the cathode?
 - (c) If the electrolysis is continued further until the product from (b) is observed to stop forming, what will be the third product formed at the cathode?
5. Predict the products formed from the electrolysis, using inert electrodes, of:
- (a) molten lead (II) chloride
 - (b) a 1 M solution of lead (II) chloride.

Commercial applications of electrolysis

The principles discussed so far for electrolytic cells can be applied in industry to many important and familiar processes. Electrolysis provides the only practical way to prepare many metals, such as aluminium and metals from groups 1 and 2. Reactive gases such as fluorine and chlorine are also prepared by this method, along with the industrially important chemical sodium hydroxide. The process of electroplating objects is no doubt familiar where a thin coating of metal is applied to a more common 'base' metal, and today's need for ultra-pure copper in the electronics industry is provided by electrorefining.

Producing aluminium

Although aluminium is the most abundant metallic element in the Earth's crust, its extraction before 1886 proved very difficult. The most common process involved its extraction from the ore and conversion into AlCl_3 . This was then chemically reduced using either sodium or potassium, metals that were also difficult to produce. Compared with today's methods, this process was on a small scale and very expensive. In fact, aluminium metal was considered more expensive than gold!

The breakthrough came in 1886 with the development of what we now call the Hall-Héroult cell.

Hall-Héroult cell

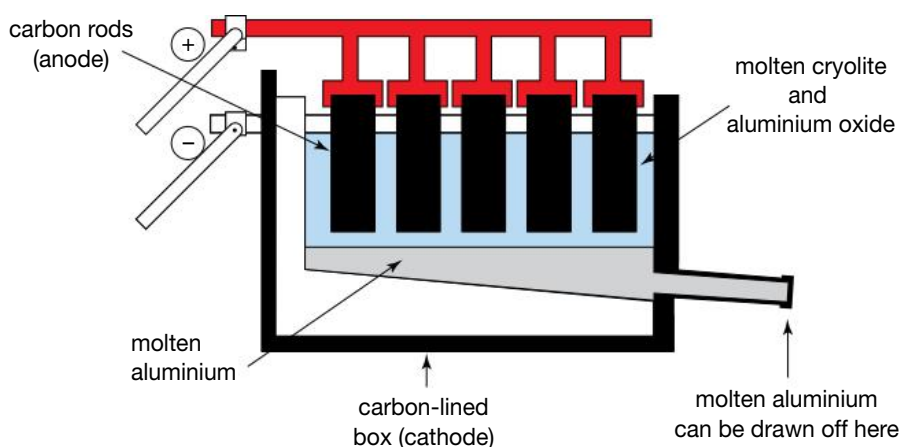
Working independently of each other, Paul Héroult in France and Charles Hall in the USA almost simultaneously filed patent applications for the industrial electrolytic production of aluminium. Today, the **Hall-Héroult** method of aluminium production is used in primary aluminium smelters throughout the world. It has resulted in an enormous growth in aluminium production from 13 tonnes per year in 1885 to more than 25 million tonnes per year today.

The industrial production of aluminium occurs in a Hall-Héroult cell (shown on the next page) and involves electrolysis of alumina that is dissolved in molten cryolite. The electrolysis takes place in a steel vessel called a cell. The cell is lined with carbon and contains the molten cryolite and dissolved alumina mixture maintained at a temperature of about 980°C . Carbon blocks that are suspended above the cell and are partially immersed in the electrolyte act as anodes, while the carbon lining of the cell acts as the cathode.

Today, aluminium is produced by electrolysis in a Hall-Héroult cell.



One hundred and twenty years ago, only the wealthy could afford aluminium. Napoleon III of France was famous for serving food to special guests at banquets on aluminium plates. Ordinary guests were served food on plates made from gold! Today, aluminium products, such as this aluminium scooter, are common.



Schematic diagram of a cross-section of a Hall-Héroult cell for the electrolytic production of aluminium

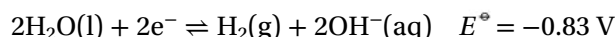
Aluminium cannot be reduced by electrolysis of an aqueous aluminium salt because water would be preferentially reduced.

Cryolite acts as a solvent and an electrolyte. Its use allows the cell to operate at a lower temperature than using alumina alone.

The carbon anodes are consumed in the process.

Aluminium settles at the bottom of the cell and is siphoned out.

Aluminium cannot be reduced by electrolysis of an aqueous solution of a soluble aluminium salt because water, a stronger oxidising agent than aluminium ions, is preferentially reduced.



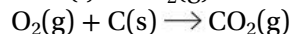
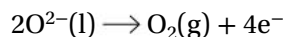
Cryolite, Na_3AlF_6 , acts as a solvent and an electrolyte. Its role is due to its unique combination of properties; it has a melting point less than half that of alumina (960°C compared with alumina's 2020°C), a low vapour pressure and a density lower than molten aluminium's (2.05 g cm^{-3} compared with aluminium's 2.30 g cm^{-3}). Cryolite can dissolve sufficient alumina to allow deposition of aluminium at about 980°C . Less energy is used, saving the industry fuel costs.

The carbon anode and cathode are both made from petroleum coke with pitch as a binder. The anode takes part in the chemical reactions in the cell.

Alumina is fed into the electrolyte at regular intervals where it dissolves, forming aluminium ions, Al^{3+} , and oxide ions, O^{2-} . The direct current applied across each cell moves the ions in opposite directions.

At the anode, the oxide ions are oxidised to form oxygen gas. The oxygen then immediately reacts with the carbon anode to form carbon dioxide.

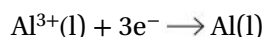
Anode reactions:



As the carbon anodes are gradually consumed during the process, they are lowered to maintain the optimum distance between the anode and cathode surfaces, until they are burned away and replaced. The anodes are generally replaced every 3 weeks so that the process is continuous.

The positively charged aluminium ions that are dissolved in the cryolite are drawn to the negatively charged cathode where they form aluminium.

Cathode reaction:



The density difference between cryolite and newly formed molten aluminium allows the aluminium to settle at the bottom of the cell where it is regularly siphoned out. After siphoning, the molten aluminium may be cast.



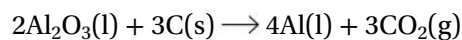
Sapphire is a gemstone composed of aluminium oxide, also known as the mineral corundum. Corundum is colourless, but the inclusion of very small amounts of impurities gives sapphires their characteristic blue colouring. Compounds of aluminium, such as aluminium oxide, are often found in nature. Pure elemental aluminium is very reactive; it reacts with other substances to form compounds. Another compound formed by aluminium found in nature is bauxite (aluminium ore).

Chlorine, hydrogen and sodium hydroxide are produced by the electrolysis of concentrated sodium chloride solution.

In the manufacture of paper, wood pulp is broken down by soaking it in concentrated sodium hydroxide solution. Sodium hydroxide has many other industrial applications and may be produced in large quantities by electrolysis.

A membrane cell uses a plastic semipermeable membrane that allows only sodium ions to pass through.

The overall reaction for the electrolytic production of aluminium by electrolysis can be represented as:



The gases produced in this process are mainly carbon dioxide. Other gases include fluorides that are initially confined by gas hoods, then continuously removed and treated.

The amount of alumina added to a cell must be strictly controlled. If too little alumina is added, maximum yields and productivity rates of aluminium production become economically unfavourable. If too much alumina is added, it does not dissolve. Instead it falls to the bottom of the cell (since it is denser than molten aluminium) where it settles below the aluminium and interferes with the flow of current.

Hall-Héroult cells operate continuously at low voltage of about 4–5 V but require a high current of 50 000–280 000 A. The excess voltage and the heat of combustion of carbon are used to keep the electrolyte in a liquid state.

Industrial electrolysis of brine

Chlorine gas, hydrogen gas and sodium hydroxide are three important industrial chemicals. They may be produced simultaneously by electrolysis of a concentrated aqueous sodium chloride solution (brine). Recently, a new type of electrolytic cell, the **membrane cell**, was developed for this reaction.

Although chloride ions are weaker reducing agents than water molecules, chlorine may be produced electrolytically from aqueous solutions of sodium chloride by altering the operating conditions of electrolytic cells to favour the reduction of chloride ions rather than water molecules.



Membrane cells

Early cells for the electrolysis of brine used either mercury or asbestos in their design. Membrane cells were developed in response to the potential health hazards involved with such cells. Industrial membrane cells can be very large.

A membrane cell is characterised by its plastic, semipermeable membrane that separates the anode half-cell from the cathode half-cell of the electrolytic cell. This semipermeable membrane allows sodium ions and electricity to pass from one electrode half-cell to another but does not allow chloride

study on

Unit 3

AOS 2

Topic 3

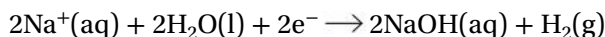
Concept 5

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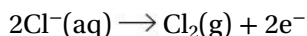
Using the membrane cell to manufacture sodium hydroxide

ions or water to pass through. As a result, sodium ions and hydroxide ions are trapped in the cathode compartment, thus producing pure sodium hydroxide along with hydrogen gas, which is evolved at the cathode itself. Chlorine gas is produced at the anode. The relevant equations are as follows.

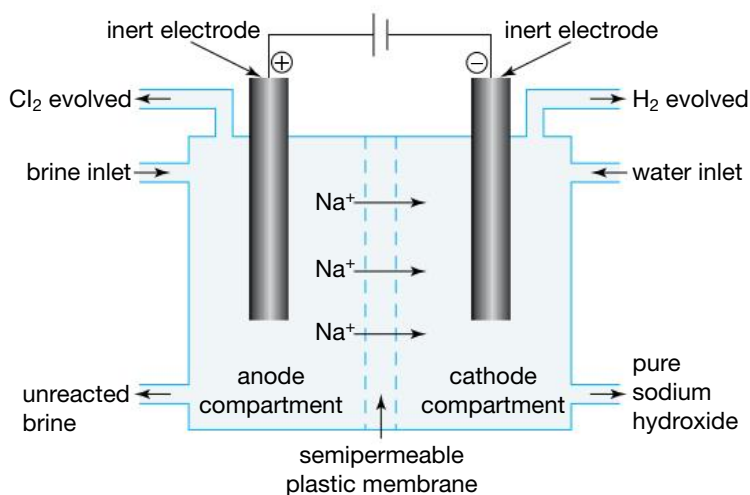
Cathode:



Anode:



As with all electrolytic cells, the products are prevented from coming into contact with each other (this would result in a spontaneous redox reaction, which would re-form the reactants!). The overall reaction for the production of chlorine via the membrane cell process is:



A membrane cell

Revision questions

- The addition of cryolite, Na_3AlF_6 , in the Hall-Héroult process introduces $\text{Na}^+(\text{l})$ and $\text{F}^-(\text{l})$ into the mixture. Why is there no issue with contamination?
- Cryolite is added to lower the melting temperature of alumina and, therefore, use less energy for the process of obtaining aluminium. Why does alumina, Al_2O_3 , have such a high melting point (2020°C)?

Electroplating

Electroplating is coating an object with a thin layer of metal deposited by an electrolytic solution during electrolysis.

Electroplating is the coating of an object with a thin film of metal deposited by an electrolytic solution during electrolysis. Electroplating is often used to produce an attractive and durable finish on articles such as knives and forks (silver plate). It is also used to protect corrosion-prone metals. Relatively unreactive cadmium metal, for example, is often plated onto steel parts to inhibit rusting. Electroplating is a very valuable industrial process but its use requires costly and consistently effective treatment of the wastes it produces.

Inexpensive silver-plated jewellery may be produced through electroplating. 'Gold' rings, which cause fingers to turn green, are actually copper rings that have been electroplated with gold.

In the electroplating process, the article to be plated is used as the cathode and the metal being plated onto the article is used as the anode. The electrolytic solution or 'bath' contains a salt of the metal being plated. A low-voltage

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Experiment 4.3 Electroplating

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electric current causes metal ions from the bath to gain electrons at the cathode and to deposit as a metal coating on the cathode (the object). It also causes metal atoms in the anode to lose electrons and go into the bath as ions. As the plating proceeds, the anode gradually disappears and maintains the metal ion's concentration in the bath.

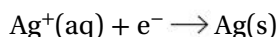
Electroplating operations involve the use of many toxic solutions. Objects to be plated are thoroughly cleaned of all grease and dirt using concentrated acidic or basic solutions. The cleaning solutions eventually become ineffective, owing to contamination, and must be disposed of.

A number of factors contribute to the quality of the metal coating formed in electroplating:

- In the plating solution, the concentration of the cations to be reduced is carefully controlled. Unwanted side reactions must be avoided.
- The type and concentration of electrolyte needs careful consideration.
- The solution must contain compounds to control the acidity and increase the conductivity.
- Some compounds make the metal coating brighter or smoother.
- In many electroplating cells, the anode must be shaped like the object at the cathode to achieve an even metal coating.

Silver-plating

In silver-plating, objects such as cutlery are made the cathode. The plating solution contains silver ions, $\text{Ag}^+(\text{aq})$. The anode is pure silver. When current flows, silver is deposited on the metal object:



At the same time, silver atoms at the anode form silver ions:



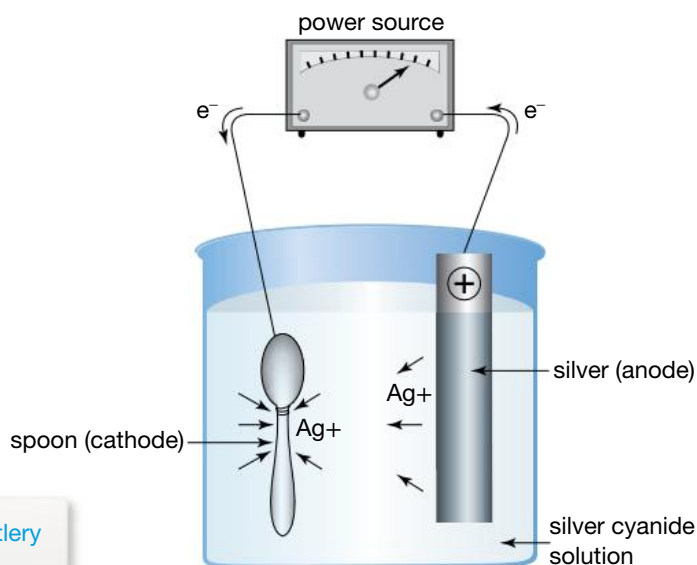
You will notice that the above reactions are possible due to their positions on the electrochemical series relative to water. At the cathode, silver ions are a stronger oxidising agent than water and so they are preferentially reduced. At the anode, silver metal is a stronger reducing agent than water. The silver metal, therefore, reacts in preference to water and is oxidised to silver ions.

The plating is only a few hundredths of a centimetre thick. If the experimental conditions are right, the metal coating adheres strongly and may be polished. However, if conditions are not satisfactory, the metal becomes powder-like and drops off.



A silver-plated trophy for the winner

Silver-plating mechanism for cutlery



Calculations in electrolysis — Faraday's laws

Michael Faraday

Michael Faraday (1791–1867) was a bookbinder by trade who became an assistant to the English chemist Sir Humphrey Davy. Although the job was menial, he advanced quickly, gaining a reputation for dedication and thoroughness.

Faraday first learned about the phenomenon of electricity from an article in an encyclopedia that was brought to his employer for rebinding. His interest in science was kindled and he became an avid reader of scientific papers, in addition to attending lectures on science. Furthermore, he wrote complete notes on every book he read and every lecture he attended.

Faraday began working as an assistant at the Royal Institution and, after 10 years of hard work, began his own research in analytical chemistry. He discovered benzene in 1825 and was the first person to produce compounds of carbon and chlorine in the laboratory. However, he is most famous for his work on electricity and, in 1833, he published the results of his studies of electrolysis. Faraday had made careful measurements of the amount of electricity involved during electrolysis and related it to the amount of substances produced. His work established two 'laws' of electrochemistry. The amount of charge carried by 1 mole of electrons is called a faraday in honour of Michael Faraday's contribution to science.



Michael Faraday.

Michael Faraday

Michael Faraday showed that the amount of electricity used during electrolysis could be related to the amount of substance formed.

The electric charge, $Q = I \times t$.
 Q is measured in coulombs (C).
One coulomb is equal to 6.24×10^{18} electrons.

Faraday's first law of electrolysis

Faraday's first law of electrolysis may be stated as follows:

The amount of any substance deposited, evolved or dissolved at an electrode during electrolysis is directly proportional to the quantity of electric charge passed through the cell.

The quantity of electric charge transferred by an electric current depends on the magnitude of the

current used and the time for which it flows. The electric charge can be calculated using the formula:

$$Q = It$$

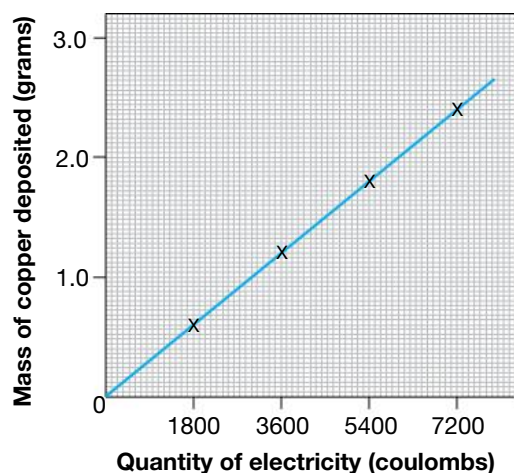
where Q is the electrical charge in coulombs (C)

I is the current in amperes (A)

t is the time in seconds (s).

In an experimental circuit, there is no meter that measures the charge in coulombs. However, an ammeter could be used to measure the rate at which charge flows in a circuit. A current of 1 ampere (1 A) indicates that 1 coulomb (6.24×10^{18} electrons) of charge flows every second. (*Note: Current is symbolised by the letter I .*)

If, for example, a current of 3.00 amperes flows for 10.0 minutes, the quantity of electricity is $(3.00 \times 10.0 \times 60) = 1.80 \times 10^3$ coulombs. The charge flowing through an electrolytic cell can be increased by either increasing the magnitude of the current or by increasing the time.



Graph of copper deposited versus quantity of electricity in electrolysis

TABLE 4.3

Current (A)	Time (s)	Quantity of electricity (C)	Mass of copper (g)
3.00	600	1800	0.59
3.00	1200	3600	1.19
3.00	1800	5400	1.78
3.00	2400	7200	2.38

1 faraday
= charge carried by 1 mole of electrons
= 96 500 coulombs.

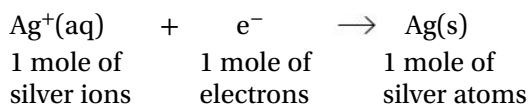
The charge on one electron is 1.602×10^{-19} C. One mole of electrons, therefore, has a charge of $(6.023 \times 10^{23} \times 1.602 \times 10^{-19}) = 9.649 \times 10^4$ C. This quantity of charge carried by a mole of electrons is referred to as the faraday (F), or **Faraday constant**, and is usually given the value of $96\,500 \text{ C mol}^{-1}$.

Faraday's second law of electrolysis

Faraday's second law of electrolysis may be stated as follows:

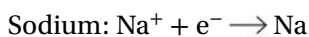
In order to produce 1 mole of a substance by electrolysis, 1, 2, 3 or another whole number of moles of electrons (faradays) must be consumed, according to the relevant half-cell equation.

In the half-cell equation:

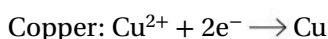


1 mole of electrons is needed to discharge 1 mole of $\text{Ag}^+(\text{aq})$ ions. This liberates 1 mole of silver atoms. Thus, 1 faraday, or 96 500 coulombs, is needed to discharge 1 mole of silver atoms.

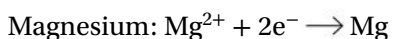
The number of faradays (moles of electrons) needed to liberate 1 mole of an element during electrolysis is found from the equation for the electrode reaction. Some examples are given below.



1 faraday must be passed to liberate 1 mole of sodium atoms (23.0 g).



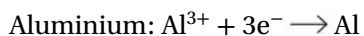
2 faradays must be passed to liberate 1 mole of copper atoms (63.5 g).



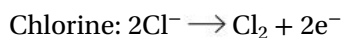
2 faradays must be passed to liberate 1 mole of magnesium atoms (24.3 g).

The number of moles of electrons required in a reaction is proportional to the charge, Q , in coulombs.

$$n(\text{electrons}) = \frac{Q}{F}$$



3 faradays must be passed to liberate
1 mole of aluminium atoms (27.0 g).



2 faradays must be passed to liberate
1 mole of chlorine molecules (71.0 g).



This gold has been refined by electrolysis to 99.999% purity. It has been deposited on a thin gold electrode. High purity gold is used in high-quality electronics.

So, the number of moles of electrons, $n(\text{electrons})$, corresponding to a given charge may be determined as follows:

$$n(\text{electrons}) = \frac{Q}{F}$$

Applying Faraday's laws of electrolysis

Most calculations in electrolysis involve finding the mass of a metal deposited on an electrode, the mass or volume of a gas produced, or the charge of an ion in the electrolytic reaction. Such problems may be solved by using the following formulas:

$$Q = It$$

$$n(\text{electrons}) = \frac{Q}{F}$$

where Q is the electrical charge (C), I is the current (A), t is the time (s) and $F = 96\,500 \text{ C mol}^{-1}$.

These relationships summarise Faraday's two laws of electrolysis.

Sample problem 4.1

A solution of copper(II) sulfate is electrolysed for 30.0 minutes using a current of 0.500 A. Calculate:

- the mass of copper deposited on the cathode
- the volume (at SLC) of oxygen gas evolved at the anode.

Solution: The amount of electricity (Q) used = $I(A) \times t(s)$
 $= 0.500 \times 30.0 \times 60$
 $= 900 \text{ coulombs}$

- (a) At the cathode:



$$\begin{aligned} \text{The number of moles of electrons, } n(\text{electrons}) &= \frac{Q}{F} \\ &= \frac{900 \text{ C}}{96\,500 \text{ C mol}^{-1}} \\ &= 0.009\,32 \text{ mol} \end{aligned}$$

But, from the equation, the number of moles of copper formed equals half the number of electrons used, thus:

$$\begin{aligned} n(\text{Cu}) &= \frac{1}{2} \times 0.009\,32 \text{ mol} \\ &= 0.004\,66 \text{ mol} \end{aligned}$$

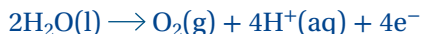
$$\begin{aligned} \text{Therefore, mass of copper} &= 0.004\,66 \text{ mol} \times 63.5 \text{ g mol}^{-1} \\ &= 0.296 \text{ g} \end{aligned}$$

Hence, the mass of copper deposited is 0.296 g.

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(b) At the anode:



$$n(\text{electrons}) = \frac{900 \text{ C}}{96500 \text{ C mol}^{-1}}$$

$$= 0.0093 \text{ mol}$$

But, from the equation: $n(\text{O}_2) = \frac{1}{4} n(\text{electrons})$

$$= \frac{1}{4} \times 0.0093 \text{ mol}$$

$$= 0.0012 \text{ mol}$$

Therefore, the volume of oxygen at SLC $= n \times V_{\text{M}}$

$$= 0.0012 \text{ mol} \times 24.8 \text{ L mol}^{-1}$$
$$= 0.0578 \text{ L}$$

Hence, 57.8 mL of oxygen is produced at SLC.

Revision questions

8. Calculate the mass of iron deposited at the cathode when a solution of iron(II) nitrate undergoes electrolysis for 1 hour 20 minutes using a current of 0.75 A.
9. Calculate the volume (at SLC) of oxygen gas evolved at the anode when a dilute solution of nickel(II) sulfate undergoes electrolysis for 3 hours 25 minutes using a current of 0.40 A.
10. What mass of each of the following substances can be produced in 2.00 hours with a current of 12.0 A?
 - (a) Co from aqueous Co^{2+}
 - (b) I_2 from aqueous I^-
 - (c) Cr from molten CrO_3
11. How long will it take to produce each of the following by electrolysis with a current of 80.0 A?
 - (a) 1.00 kg of Ni(s) from Ni^{2+}
 - (b) 2.50 g of Al(s) from Al^{3+} in a melt
 - (c) 5.25 mol of Ag(s) from Ag^+

Sample problem 4.2

When molten calcium chloride is electrolysed by a current of 0.200 A flowing for 965 seconds, 0.0401 g of calcium is formed. What is the charge on a calcium ion?

Solution: The amount of electricity (Q) used is:

$$\begin{aligned} Q &= It \\ &= 0.200 \text{ C s}^{-1} \times 965 \text{ s} \\ &= 193 \text{ C} \end{aligned}$$

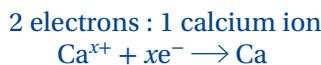
The number of moles of electrons used is:

$$\begin{aligned} n(\text{electrons}) &= \frac{Q}{F} \\ &= \frac{193 \text{ C}}{96500 \text{ C mol}^{-1}} \\ &= 0.00200 \text{ mol} \end{aligned}$$

The number of moles of calcium formed is:

$$\begin{aligned}n(\text{Ca}) &= \frac{0.0401}{40.1 \text{ g mol}^{-1}} \\&= 0.00100 \text{ mol}\end{aligned}$$

Therefore, 0.00200 mol of electrons are needed to liberate 0.00100 mol of calcium. The ratio is:



So, the charge on a calcium ion is 2+.

Revision questions

12. When molten manganese nitrate was electrolysed by a current of 5.00 A for 884 seconds, the mass of the cathode increased from 2.428 g to 3.267 g. Calculate the charge on the manganese ion in the nitrate salt.
13. When a current of 0.0600 A flowed through an electrolytic cell for 1 hour and 6.00 minutes, the mass of the cathode increased by 0.254 g due to the deposition of a metal with a relative atomic mass of 207. Calculate the charge on a cation of this metal.

Faraday's laws in industry

Calculations based on Faraday's laws are critical to industrial electrolytic processes. Due to their large scale, small variations and inefficiencies may result in the loss of many thousands of dollars. In order to determine the efficiency of a particular process, knowledge of the theoretical maximum amount is required.

Sample problem 4.3

A typical Hall-Hérout cell in an aluminium plant operates at an average current of 1.70×10^4 A. Calculate the theoretical mass of aluminium produced in a Hall-Hérout cell over 24 hours.

Solution: The amount of electricity can be calculated according to:

$$\begin{aligned}\text{charge } (Q) &= \text{current } (I) \times \text{time } (t) \text{ in seconds} \\&= 1.70 \times 10^4 \times 60 \times 60 \times 24 \\&= 1.47 \times 10^9 \text{ coulombs}\end{aligned}$$

At the cathode: $\text{Al}^{3+}(\text{l}) + 3\text{e}^{-} \longrightarrow \text{Al}(\text{l})$

$$\begin{aligned}\text{So, } n(\text{electrons}) &= \frac{Q}{F} \\&= \frac{1.47 \times 10^9}{96500} \\&= 1.52 \times 10^4 \text{ mol}\end{aligned}$$

From the equation, the amount of aluminium formed corresponds to one-third of the number of electrons generated, so:

$$\begin{aligned}n(\text{Al}) &= \frac{1}{3} \times 1.52 \times 10^4 \\&= 5.07 \times 10^3 \text{ moles of Al}\end{aligned}$$

The theoretical mass of aluminium produced is therefore:

$$\begin{aligned}\text{mass(Al)} &= n(\text{Al}) \times A_r(\text{Al}) \\ &= 5.07 \times 10^3 \times 27.0 \\ &= 1.37 \times 10^5 \text{ g} \\ &= 1.37 \times 10^2 \text{ kg}\end{aligned}$$

Revision question

14. For a Hall-Héroult cell in an aluminium plant operating at an average of 180 000 A, calculate:
- (a) the theoretical mass of aluminium produced in a Hall-Héroult cell per hour
 - (b) how long it would take for the cell to produce 10.0 kilograms of aluminium
 - (c) the volume of carbon dioxide, measured at SLC, produced per day by the cell.

Secondary cells — rechargeable batteries

Secondary cells, often referred to simply as rechargeable batteries, are devices that can be recharged after they become 'flat'. They are essentially galvanic cells using spontaneous redox reactions to produce electricity during discharge, but they become electrolytic cells converting electrical energy back into chemical energy when they are recharged. To enable this to happen, they are designed so that the discharge products remain in contact with the electrodes at which they are produced. The process of recharging simply involves connecting the negative terminal of the charger to the negative terminal of the battery or cell, and the positive to the positive. This forces the electrons to travel in the reverse direction and, because the discharge products are still in contact with the electrodes, the original reactions are reversed. The cell or battery is, therefore, recharged.

The lead-acid accumulator is a common example of a secondary cell that has been widely used for many years. Other smaller more portable designs are now familiar to us. Although initially more expensive than the primary cells they are designed to replace, their ability to be recharged many hundreds of times makes them a cheaper alternative in the long run.

Lead-acid accumulator

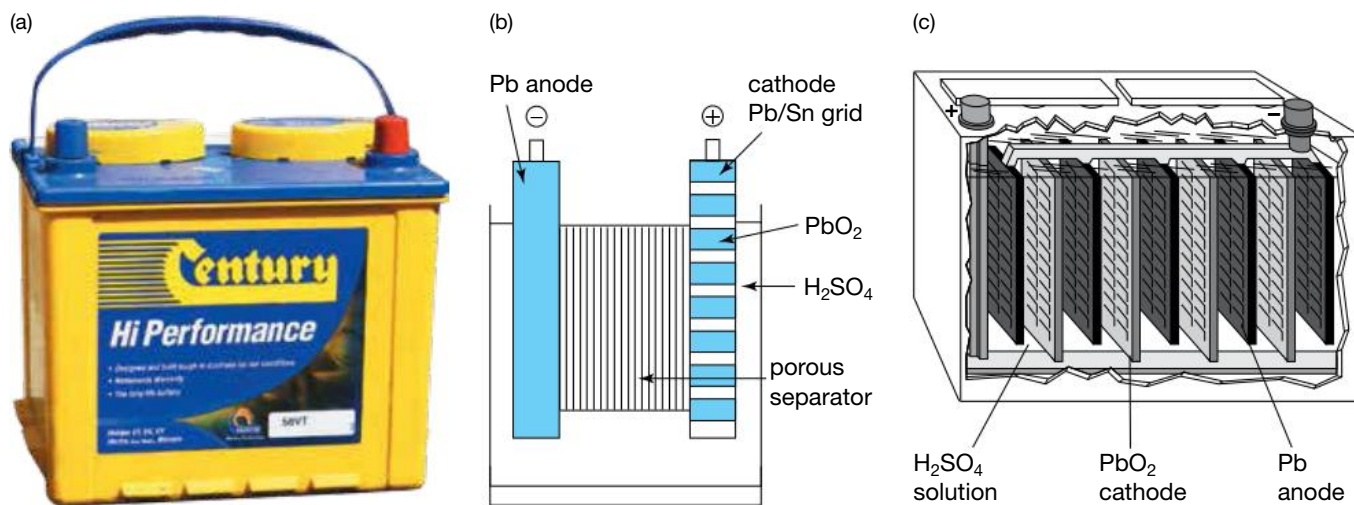
Developed in the late nineteenth century, the **lead-acid accumulator**, an example of a secondary cell, has remained the most common and durable of battery technologies. Lead-acid accumulators are secondary cells. They have a relatively long lifetime and high current, and they are cheap to produce. Largely used in transport applications, they rely on a direct current generator or alternator in the vehicle to apply enough voltage to reverse the spontaneous electrochemical reaction that helps to 'drive' the car.

A 12-volt lead-acid storage battery consists of six 2-volt cells connected in series. The cells do not need to be in separate compartments, although this improves performance.

Each cell consists of two lead electrodes or grids. The grid structure provides a larger surface area for electrode reactions. The grid that forms the anode

The lead-acid battery is the most common secondary cell.

(negative terminal) of the cell is packed with spongy lead. The other grid, the cathode (positive terminal), is packed with lead(IV) oxide, PbO_2 . The electrodes are both immersed in approximately 4 M sulfuric acid and are separated by a porous plate.



(a) A motor vehicle battery (b) A lead-acid storage cell (c) A simplified cross-section of a lead-acid battery

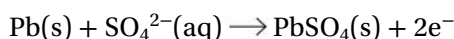
Chemical energy is converted to electrical energy when the battery discharges.

The discharging process in a lead-acid accumulator

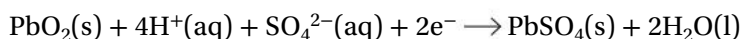
When a lead-acid accumulator discharges, it produces electric power to start the car. Discharge results from a spontaneous redox reaction.

The half-equations at each electrode may be written as follows.

Anode (oxidation):



Cathode (reduction):



At the anode (negative electrode), lead is oxidised to Pb^{2+} ions. These react immediately with the sulfuric acid solution to produce insoluble lead(II) sulfate, which deposits on the grid.

At the cathode (positive electrode), lead(IV) oxide is reduced to Pb^{2+} ions, which again react with the sulfuric acid to form a lead(II) sulfate deposit on the grid. The overall equation for the discharging reaction is:



Note: The pH of the cell increases during the discharge cycle.

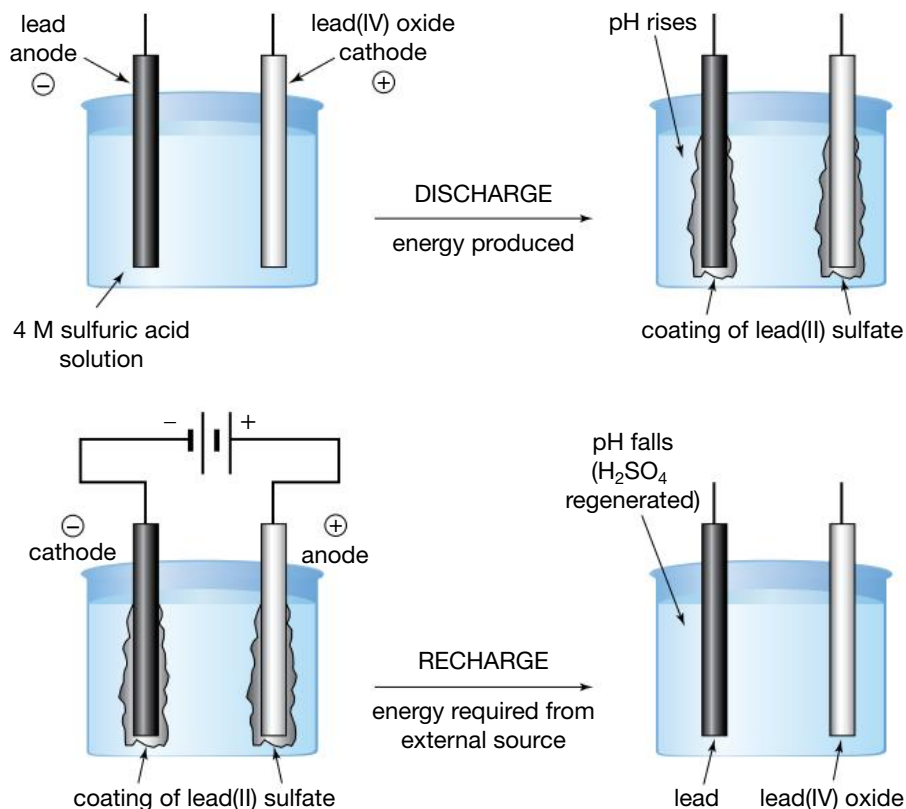
The recharging process in a lead-acid accumulator

Since the products of the discharge process remain as a deposit on the electrodes, the reactions at these electrodes may be reversed by passing a current through the cell in the opposite direction. The battery is then said to be **recharging**. When the battery is recharged, the electrode reactions are reversed by connecting the terminals to another electrical source of higher voltage and reversing the direction of the electric current through the circuit. Recharging occurs while the car is in motion.

Electrical energy is converted to chemical energy when the battery recharges.



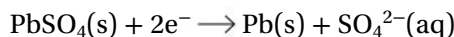
During the operation of a lead–acid accumulator, sulfuric acid is consumed and water is formed. Since sulfuric acid is 1.84 times more dense than water, as the battery operates (discharges), the density of the electrolyte decreases. Although most batteries are sealed, older batteries may be unsealed, so the condition of the battery can be checked by measuring the density (specific gravity) of the fluid in the battery, using an instrument called a hydrometer. Some of the electrolyte is sucked into the hydrometer. The position of the float indicates the specific gravity. If it is much below 1.25, the battery should be recharged.



Discharge/recharge effect on electrodes

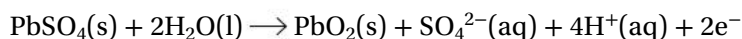
During recharging, the flow of e^- is reversed and the electrode forming the negatively charged anode in the discharging process becomes the negatively charged cathode, where reduction occurs.

Cathode (reduction):

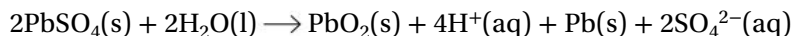


The electrode previously forming the positively charged cathode in the discharging process now becomes the positively charged anode, where oxidation occurs, in the recharging process.

Anode (oxidation):



The overall reaction for the recharging process is therefore the reverse of the discharging process.



Note: The pH of the cell decreases during the recharge cycle.

Since this reaction is not spontaneous, a direct current must be applied in order for it to proceed. This is achieved by the alternator (a motor-driven electrical source of higher voltage than the battery), which has a potential difference of 14 V. The recharging process converts electrical energy into chemical energy and is an example of an electrolytic reaction.

Although, in theory, a lead storage battery can be recharged indefinitely, in practice it may last for only about four years. This is because small amounts of lead(II) sulfate continually fall from the electrodes and drop to the bottom

of the cell. Eventually, the electrodes lose so much lead(II) sulfate that the recharging process is ineffective.

The disposal of lead–acid batteries poses many environmental problems. Lead is poisonous when introduced into most ecosystems, and the impact of acid rain is distinct and measurable. Once disposed of in landfill or illegally dumped, lead–acid batteries may corrode and release lead and lead-contaminated sulfuric acid into the environment. This can pollute drinking water sources such as lakes, rivers, streams and ground water. Responsible lead–acid battery reclaiming and recycling projects now allow for safe disposal of used batteries.

The nickel metal hydride rechargeable cell is lightweight and suitable for cordless appliances.

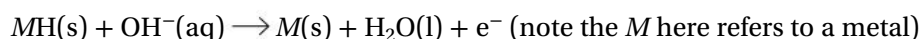
NiMH cells store 50% more power than NiCd cells, recharge faster and do not use toxic metals.

Nickel metal hydride rechargeable cell

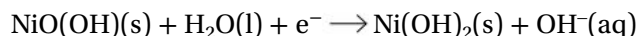
Although the nickel cadmium (NiCd) cell was the first rechargeable cell to find widespread use in many common household devices, it has largely been replaced today by the nickel metal hydride (NiMH) cell. This shares a number of features with the NiCd cell but is environmentally safer due to the absence of cadmium. A problem with NiCd cells was the so-called memory effect. If the cell was only partially discharged before recharging occurred, it would not receive a full charge. NiMH cells show much less of this effect. They also have nearly 50% more charge per gram, can recharge faster and can run longer on each charge.

The reactions involved during discharge to produce an electric current are as follows.

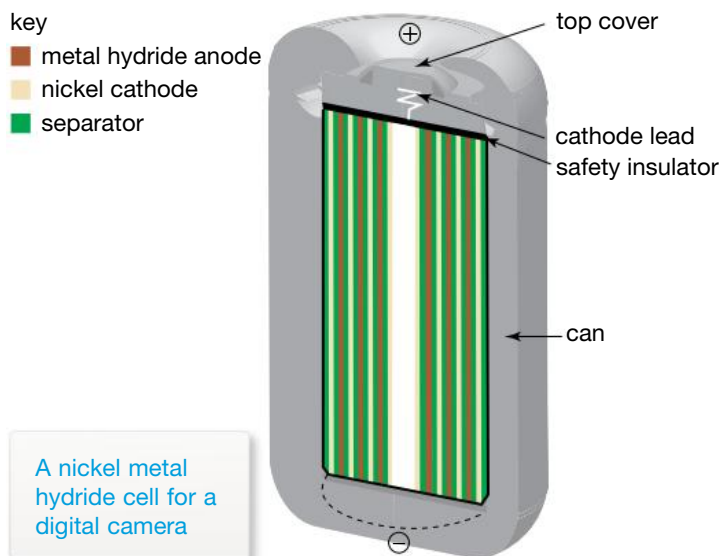
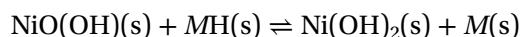
Oxidation takes place at the negative electrode (anode):



Reduction takes place at the positive electrode (cathode).



Overall equation:



Nickel metal hydride batteries are similar to nickel–cadmium batteries except that a hydrogen-absorbing metal is used as the anode. These metals (*M*) can be alloys of lanthanum and rare earths. The electrolyte is potassium hydroxide and the voltage produced is 1.2 volts.

Nickel metal hydride batteries have many advantages but also some disadvantages. They suffer from self-discharge — a problem that is worse at higher temperatures — and require more complicated charging devices to prevent overcharging.

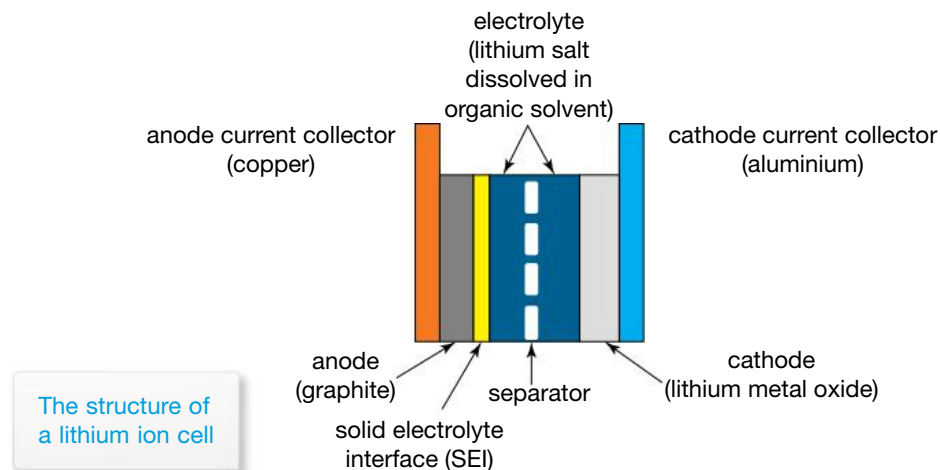
They are used in laptops, electric shavers, toothbrushes, cameras, camcorders, mobile phones and medical instruments, and are being developed for car batteries.

Rechargeable lithium ion cell

The **lithium ion cell**, which uses lithium compounds rather than lithium metal, is rapidly becoming the most popular choice of battery for portable devices. It consists of a porous graphite anode and a porous metal oxide cathode in an electrolyte of lithium salt held in an organic solvent. Lithium is interspersed between the layers of graphite. At the cathode, a commonly used material is cobalt(IV) oxide containing some lithium ions stored in the gaps of its lattice structure. As a result of this, cobalt is present in both the +4 and +3 oxidation states. When the cell is discharging, lithium atoms readily release electrons into the graphite

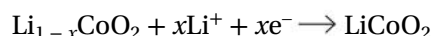
Lithium ion cells are lighter and smaller and provide more power than NiCd or NiMH cells.

anode because lithium is such a good reducing agent. The lithium ions produced travel internally to the cathode where they insert into the cobalt oxide lattice. At the same time, electrons arrive from the external circuit, and further reduction of cobalt from the +4 to +3 oxidation state takes place.

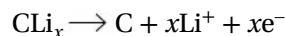


The equations are as follows.

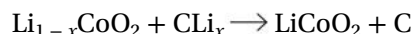
Cathode (reduction):



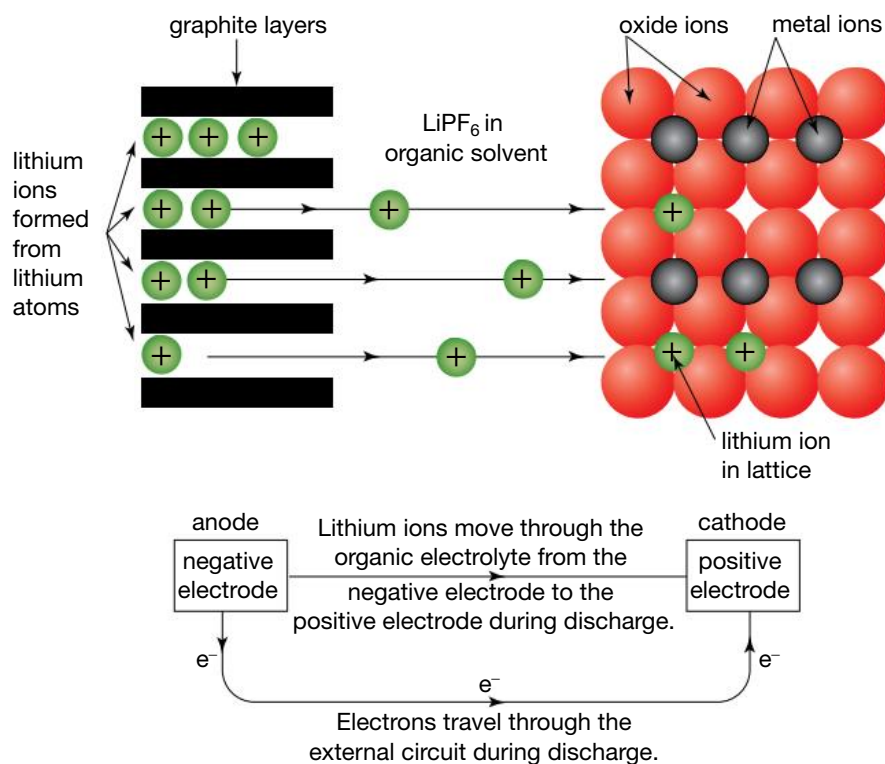
Anode (oxidation):



Overall equation:



These cells are expensive to produce but now are extensively used in mobile phones, laptops, cameras, heart defibrillators, mobile radios, power tools and vehicles.



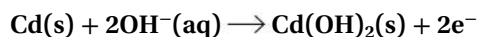
Lithium ion cells have a good shelf life and a very high energy density; they supply a voltage of about 3.7 volts, which is more than double that of most other cells. However, their state of charge needs to be monitored carefully. If they are overdischarged, they cannot be recharged. On the other hand, if they are overcharged, serious safety concerns may arise. To prevent both of these extremes, they are nearly always produced with a protection circuit that prevents both of these situations from arising. This, however, adds to their cost.

The Mars Exploration Rovers *Spirit* and *Opportunity* are powered by lithium ion batteries, which are light and reliable.



Revision questions

15. What feature of a lead–acid accumulator allows it to be recharged?
16. Would the pH of the electrolyte in a lead–acid accumulator increase or decrease during recharge?
17. Why is a porous graphite electrode used in a lithium ion cell?
18. Examine the power cell in a mobile phone or other small electronic device. What type of cell is it? Make a list of the advantages of this type of cell for this application.
19. Write the overall equation for the recharging process in a nickel metal hydride cell.
20. In the nickel–cadmium cell, the cathode reaction is the same as in the nickel metal hydride cell during discharge. The anode reaction is:



Write the overall equation for the discharge of this cell.

Factors affecting battery life

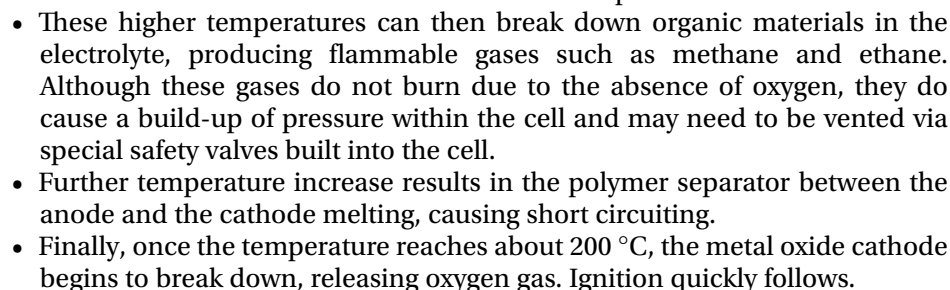
While there are specialist batteries designed to operate at extreme temperatures, the great majority of batteries used today are designed to operate over an optimum range of temperatures that encompass normal room temperature. If they are used outside this range, breakdowns in both the electrochemistry and their physical components may occur, rendering the battery inoperative and even dangerous.

Each battery type also has its own specific problems related to temperature and componentry. In a lead–acid accumulator, for example, overdischarge thickens the layers of lead sulfate that build up on the electrodes. Particles can break off and fall to the base of the cell, thereby lowering the amount remaining for recharge. In extreme cases, due to the closeness of the electrodes, internal

In a lithium ion battery, the situation is even more complex and potentially dangerous, with an internal protective circuit required for consumer safety. To avoid problems, lithium batteries must operate within a narrow window of both temperature and voltage, as shown by the green area in the diagram below.

cause lithium metal to be deposited on the graphite electrode for the same reason, thus lowering the amount of electricity that can be generated by the cell following subsequent recharge cycles.

- As with most chemical reactions, an increase in temperature increases the rate of reactions that produce the electricity. However, due to the internal resistance of the cell, this can generate excessive heat and break down the SEI (solid electrolyte interface) layer. This layer is initially formed by an exothermic reaction between the electrolyte and the graphite electrode under carefully controlled conditions during manufacture. If it is subsequently broken down, this same reaction may recur, but this time in a much more uncontrolled manner, resulting in heat generation and further temperature rise.



Chapter review

Summary

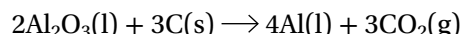
- Electrolysis is the process by which electricity passes through a molten ionic compound or through an electrolyte solution to produce new substances.
- The apparatus in which electrolysis occurs is called an electrolytic cell.
- Solutes that form solutions that can conduct electricity are called electrolytes.
- In electrolysis, positive ions gain electrons at the cathode (negative electrode) and negative ions lose electrons at the anode (positive electrode).
- Electrolytic cells differ from galvanic cells in a number of ways, as summarised in the following table.

Factor	Galvanic cell	Electrolytic cell
type of reaction	spontaneous redox reaction	non-spontaneous redox reaction
energy	produce electricity	require energy
structure	two half-cells connected by a wire (external circuit) and a salt bridge (internal circuit)	one cell, connecting wires and an external power supply (e.g. battery, DC power supply)
anode	negatively charged, oxidation	positively charged, oxidation
cathode	positively charged, reduction	negatively charged, reduction
source of electrons	reducing agent	external power supply

- The products of the electrolysis of molten ionic compounds are predictable whereas the products of the electrolysis of an aqueous solution may be affected by factors including concentration, the nature of the electrolyte and the nature of the electrodes.
- Electrolysis can be used to produce highly reactive elements such as the strong reducing agent metals in groups 1 and 2 in the periodic table as well as chlorine and fluorine, since production by chemical reduction is not practical.
- Cations of reactive metals, including aluminium, cannot be reduced from aqueous solutions since water is a stronger oxidising agent and is preferentially reduced.
- Chlorine, sodium hydroxide and hydrogen gas can be produced industrially in the membrane cell according to the overall reaction:

$$2\text{NaCl(aq)} + 2\text{H}_2\text{O(l)} \longrightarrow 2\text{NaOH(aq)} + \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$$

- Aluminium can be produced industrially by the Hall-Héroult process according to the overall equation:



- Electroplating is the process of coating an object with a thin film of metal deposited from an electrolytic solution by electrolysis.
- In electroplating, the object to be plated is always connected to the cathode.
- Faraday's laws can be used to calculate quantities of products produced in electrolytic cells.
- Faraday's laws can be applied to a range of problems involving quantitative calculations in electrolysis.
- Faraday's first law of electrolysis may be summarised as:

$$Q = It$$

where Q is the electric charge in coulombs

I is the current in amperes

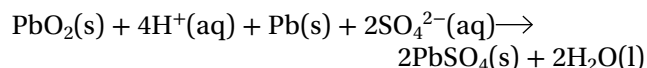
t is the time in seconds.

- Faraday's second law of electrolysis may be summarised as:

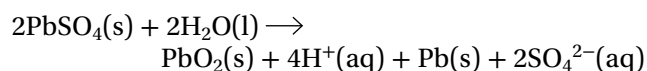
$$\text{number of moles of electrons, } n(\text{electrons}) = \frac{Q}{F}$$

where F is the Faraday constant representing the quantity of charge carried by 1 mole of electrons (96 500 coulombs).

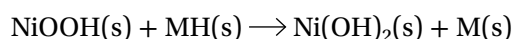
- Secondary cells are electrochemical cells that can be recharged by reversing the spontaneous forward reaction through the application of a DC power source.
- The lead-acid accumulator is a secondary cell that is rechargeable; its largest use is to power transport vehicles. The discharging reaction for the operation of a lead-acid accumulator produces 12 volts and is represented by the overall equation:



The recharging process is the reverse of the discharging process and requires approximately 14 volts of DC power to occur according to the reaction:



- The nickel metal hydride rechargeable cell does not use toxic metals, stores 50% more power than NiCd cells and recharges faster. It takes advantage of the property that some metal alloys have of storing hydrogen atoms. The overall equation representing discharge is:



- The lithium ion cell supplies more than double the voltage of most other cells. Lithium batteries are now used extensively in portable devices because lithium's low density and high reactivity make it an excellent material for use in cells. These batteries involve carbon and cobalt oxide redox reactions.
- Battery life can be affected by temperature, depth of discharge and operating voltage. These can reduce its ability to be fully recharged and affect its safe operation.

Multiple choice questions

- Which one of the following statements about reactions in electrochemical cells and electrolytic cells is correct?
 - Oxidation occurs at the anode of electrochemical cells and at the cathode of electrolytic cells.
 - Electrochemical cell reactions are spontaneous whereas electrolytic cell reactions are driven by external power supplies.
 - Electrochemical cell reactions are redox reactions whereas electrolytic cell reactions are deposition reactions.
 - Oxidation occurs at the positive electrode in both electrochemical and electrolytic cells.
- In an electrolytic cell, electrodes are the:
 - ionic conductors
 - electrical conductors
 - ionic and electrical conductors
 - conductors for negative ions only.
- Which of the following best identifies the cathode in an electrolytic cell?
 - The electrode at which anions are reduced
 - The electrode at which no gas can be produced
 - The electrode at which $\text{OH}^-(\text{aq})$ ions are produced
 - The electrode at which reduction occurs
- Which one of the following occurs in the electrolysis of molten potassium bromide?
 - Potassium is produced at the anode.
 - Potassium ions are oxidised at the cathode.
 - Bromine gas is produced at the cathode.
 - Bromide ions are oxidised at the anode.
- Which one of the following equations represents the reaction at the positive electrode in the electrolysis of molten potassium iodide?
 - $\text{K(l)} \rightarrow \text{K}^+(\text{l}) + \text{e}^-$
 - $\text{K}^+(\text{l}) + \text{e}^- \rightarrow \text{K(l)}$
 - $2\text{I}^-(\text{l}) \rightarrow \text{I}_2(\text{l}) + 2\text{e}^-$
 - $\text{I}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{l})$
- Which of the following reactions occurs at the positive electrode when a solution of sodium sulfate, Na_2SO_4 , is electrolysed using inert electrodes?
 - $\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na(s)}$
 - $2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
 - $2\text{SO}_4^{2-}(\text{aq}) \rightarrow 2\text{SO}_3(\text{g}) + \text{O}_2(\text{g}) + 4\text{e}^-$
 - $2\text{H}_2\text{O(l)} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$
- A very dilute solution of sulfuric acid in water is electrolysed using platinum electrodes. The substances collected at the electrodes are:
 - sulfur dioxide and hydrogen gas
 - hydrogen gas and oxygen gas
 - oxygen gas and nitrogen gas
 - hydrogen gas and sulfur.
- Which one of the statements below is *not* true if a copper(II) sulfate solution is electrolysed using carbon electrodes?
 - $\text{Cu}^{2+}(\text{aq})$ ions gain electrons at the cathode because $\text{Cu}^{2+}(\text{aq})$ ions are more easily reduced than H_2O .
 - Water may be oxidised at the anode.
 - Water is not reduced at the cathode.
 - The mass of the cathode does not change.
- In the electrolysis of molten sodium chloride using inert electrodes, which of the following occurs?
 - Chlorine gas is produced at the cathode and oxygen gas is produced at the anode.
 - Chlorine gas is produced at the anode and oxygen gas is produced at the cathode.
 - Chlorine gas is produced at the cathode and sodium metal is produced at the anode.
 - Chlorine gas is produced at the anode and sodium metal is produced at the cathode.
- An electrolytic cell consists of two carbon electrodes and an electrolyte of aqueous sodium chloride to which phenolphthalein has been added. When an electric current is passed through the cell:
 - bubbles of chlorine appear at the cathode
 - bubbles of hydrogen appear at the anode
 - a pink colour surrounds the cathode
 - sodium metal collects at the cathode.
- A solution contains CuCl_2 , NiCl_2 and ZnCl_2 , each solute being at 1 M concentration. The solution is electrolysed using graphite electrodes. Which of the following reactions takes place first at the cathode?
 - $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$
 - $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni(s)}$
 - $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}$
 - $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
- Which of the following reactions occurs at the anode when a solution of copper(II) sulfate is electrolysed using inert electrodes?
 - $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$
 - $2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
 - $2\text{SO}_4^{2-}(\text{aq}) \rightarrow 2\text{SO}_3(\text{g}) + \text{O}_2(\text{g}) + 4\text{e}^-$
 - $2\text{H}_2\text{O(l)} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$

13. In an electrolytic cell with positive electrode A and negative electrode B, electrons always move towards:
- A, and B attracts negative ions
 - A, and B attracts positive ions
 - B, and A attracts negative ions
 - B, and A attracts positive ions.
14. Consider the following standard reduction potentials:
- $$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Zn}(\text{s}) \quad E^{\circ} = -0.76 \text{ V}$$
- $$2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{H}_2(\text{g}) \quad E^{\circ} = 0.00 \text{ V}$$
- $$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s}) \quad E^{\circ} = +0.80 \text{ V}$$
- $$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^{-} \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^{-}(\text{aq}) \quad E^{\circ} = -0.83 \text{ V}$$
- Which product would be liberated first at the cathode if a solution containing $\text{Zn}(\text{NO}_3)_2$ and AgNO_3 is electrolysed with platinum electrodes?
- $\text{H}_2(\text{g})$
 - $\text{Ag}(\text{s})$
 - $\text{Zn}(\text{s})$
 - $\text{OH}^{-}(\text{aq})$
15. When concentrated brine solution is electrolysed in the membrane cell, the electrode products are:
- $\text{Na}(\text{l})$ and $\text{Cl}_2(\text{g})$
 - $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$
 - $\text{Na}(\text{l})$ and $\text{O}_2(\text{g})$
 - $\text{H}_2(\text{g})$, $\text{Cl}_2(\text{g})$ and $\text{NaOH}^{-}(\text{aq})$.
16. Which of the following does *not* usually occur during the electrolytic extraction of aluminium metal?
- CO_2 is produced at the positive electrode.
 - Alumina is dissolved in molten cryolite, Na_3AlF_6 .
 - The cathode material is consumed and replaced at frequent intervals.
 - Liquid aluminium is drawn off from the bottom of the cell.
17. Which of the following groups of substances would normally be extracted by electrolysis?
- Iron, nickel and chromium
 - Gold, copper, silver and platinum
 - Magnesium, aluminium, sodium and chlorine
 - Oxygen, neon, argon and nitrogen
18. In the electrolytic extraction of aluminium from its oxide, a substance called cryolite is used. Which of the following best describes the function of cryolite in this process?
- It oxidises alumina.
 - It reduces alumina.
 - It acts to absorb ore impurities from the alumina.
 - It acts as a solvent for alumina.
19. Which one of the following materials is *not* used in the production of aluminium metal from its ore?
- Na_3AlF_6
 - Na_2CO_3
 - Bauxite
 - Carbon
20. What volume of chlorine (at SLC) is produced during the electrolysis of 1.00 kg of molten sodium chloride, according to the following equation?
- $$2\text{NaCl}(\text{l}) \longrightarrow 2\text{Na}(\text{l}) + \text{Cl}_2(\text{g})$$
- 0.86 kg
 - 212 L
 - 383 L
 - 383 mL
21. Consider two electrolytic cells connected in series. Cell 1 contained copper(II) sulfate solution with copper electrodes and cell 2 contained copper(II) chloride solution with platinum electrodes. Current was passed for a fixed time, after which the electrodes and electrolytes in each cell were examined. The mass of the cathode in cell 2 was found to have increased in mass by 1.6 g.
- The anode of cell 1 would have:
- increased by 1.6 g
 - remained unchanged in mass
 - given off oxygen gas
 - decreased in mass by 1.6 g.
22. Consider two electrolytic cells connected in series. Cell 1 contained copper(II) sulfate solution with copper electrodes and cell 2 contained copper(II) chloride solution with platinum electrodes. Current was passed for a fixed time, after which the electrodes and electrolytes in each cell were examined. The mass of the cathode in cell 2 was found to have increased in mass by 1.60 g.
- If no oxygen is evolved at the anode of cell 2, the volume of chlorine gas evolved when measured at SLC would be:
- 2480 mL
 - 1250 mL
 - 625 mL
 - 310 mL.
23. Sodium perchlorate can be prepared electrolytically by the reactions:
- $$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^{-} \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^{-}(\text{aq})$$
- $$\text{Cl}^{-}(\text{aq}) + 8\text{OH}^{-}(\text{aq}) \longrightarrow \text{ClO}_4^{-}(\text{aq}) + 4\text{H}_2\text{O} + 8\text{e}^{-}$$
- What mass of sodium perchlorate could be produced in a cell that liberates 3.00 g of hydrogen gas at the cathode?
- 45.9 g
 - 99.5 g
 - 122.5 g
 - 183.8 g
24. What volume of gaseous products is produced at 0 °C and 101.3 kPa when 18.0 g of water undergoes electrolysis?
- 5.6 L
 - 11.2 L
 - 22.4 L
 - 33.6 L

25. If n coulombs of electricity deposits 0.100 moles of silver from a solution of AgNO_3 , how many coulombs are needed to deposit 0.100 moles of aluminium from a solution of $\text{Al}(\text{NO}_3)_3$?
- A $0.25n$
 B $0.33n$
 C $0.75n$
 D $3.00n$
26. In a secondary cell:
- A the negatively charged cathode in the discharging reaction becomes the positively charged anode in the recharging process
 B the negatively charged cathode in the discharging reaction becomes the negatively charged anode in the recharging process
 C the positively charged cathode in the discharging reaction becomes the positively charged anode in the recharging process
 D the positively charged cathode in the discharging reaction becomes the negatively charged anode in the recharging process.
27. What is important about the products in a rechargeable cell?
- A They must be gases.
 B They must be soluble in the electrolyte.
 C They must diffuse away from the electrodes.
 D They must remain in contact with the electrodes.
28. In the lead-acid car battery, the overall discharge reaction is:
- $$\text{Pb(s)} + \text{PbO}_2\text{(s)} + 4\text{H}^+\text{(aq)} + \text{SO}_4^{2-}\text{(aq)} \longrightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$$
- In the recharging process:
- A all $\text{Pb}^{2+}\text{(aq)}$ ions in the battery are oxidised to Pb(s)
 B the lead plates in the battery dissolve as $\text{Pb}^{2+}\text{(aq)}$ ions are produced
 C $\text{Pb}^{2+}\text{(aq)}$ ions are either oxidised or reduced, depending on which electrode they are near
 D the $\text{H}^+\text{(aq)}$ ion concentration decreases.
29. During the discharging process in a lead-acid accumulator:
- A the concentration of hydrogen ions, H^+ , increases, resulting in an increase in pH
 B the concentration of hydrogen ions, H^+ , decreases, resulting in a decrease in pH
 C the concentration of hydrogen ions, H^+ , increases, resulting in a decrease in pH
 D the concentration of hydrogen ions, H^+ , decreases, resulting in an increase in pH.
30. The cathode reaction during discharge in a nickel metal hydride cell is:
- $$\text{NiO(OH)(s)} + \text{H}_2\text{O(l)} + \text{e}^- \longrightarrow \text{Ni(OH)}_2\text{(s)} + \text{OH}^-\text{(aq)}$$

During recharging, which of the following statements is correct?

- A Nickel is reduced from the +3 to +2 oxidation state.
 B Oxidation of nickel occurs from the +2 to the +3 oxidation state.
 C The reverse of the above reaction occurs at the negative electrode.
 D Oxidation occurs at the surface of the negative electrode.

Review questions

Electrolysis — the process

- In what ways are galvanic and electrolytic cells:
 - similar
 - different?
- Why is a direct current, rather than an alternating current, used in electrolytic reactions?
- In the electrolysis of molten sodium chloride, explain:
 - why electricity is conducted in the molten state but not in the solid state
 - why the products are formed only around the electrodes and not throughout the liquid
 - what causes the electric current to flow in the liquid and in the connecting wires.
- Copy and complete the following table to summarise what happens at each electrode during electrolysis of NaCl in different forms.

Electrolyte type	Electrodes	Reaction at	
		Anode (+)	Cathode (-)
molten salt	inert		
1 M aqueous salt solution	inert		
1 M aqueous salt solution	copper		

- Predict the products at the anode and cathode, write an overall equation and determine the minimum cell voltage required for the electrolysis (using carbon electrodes) of each of the following molten components.

(a) sodium bromide	(c) lead(II) chloride
(b) aluminium hydroxide	(d) magnesium chloride
- Predict the products at the anode and cathode, write an overall equation and determine the minimum cell voltage required for the electrolysis (using carbon electrodes) of 1.0 M aqueous solutions of each of the following.
 - potassium hydroxide
 - potassium sulfate

- (c) magnesium chloride
- (d) zinc bromide
- (e) sodium iodide
- (f) hydrochloric acid
- (g) sulfuric acid

7. Predict the products at the anode and cathode, write an overall equation and determine the minimum cell voltage required for the electrolysis of 1.0 M aqueous solutions of:
- (a) copper(II) chloride
 - (b) copper(II) sulfate
- using: (i) carbon electrodes
(ii) copper electrodes.

Electrolysis in industry

8. Sodium chloride can be electrolysed to produce a number of important products. These are hydrogen, chlorine, sodium hydroxide and sodium metal.
- (a) Describe and explain how the products of electrolysis of molten sodium chloride are obtained. Include the relevant equations.
 - (b) Describe and explain how the products of electrolysis of concentrated sodium chloride are obtained. Include the relevant equations.
9. In the production of aluminium in a Hall-Héroult cell, the anode and the cathode are made of carbon. It is found that the anode needs to be replaced every 3 weeks whereas the cathode may last up to 5 years. Explain this difference using an appropriate equation.
10. Explain, using a fully labelled diagram, how you would plate a piece of steel with nickel by electroplating.
11. In electroplating, why is the object being electroplated made the cathode?
12. In nickel-plating, what substance would you choose for:
- (a) the anode
 - (b) the electrolyte?
13. Sketch an electrolytic cell that could be used to plate copper onto a tin keyring. On your sketch, label the:
- (a) anode and cathode
 - (b) direction of electron flow
 - (c) nature of each electrode
 - (d) electrode polarity
 - (e) equations occurring at each electrode.
- ### Calculations in electrolysis — Faraday's laws
14. How many faradays are needed to produce:
- (a) 1.0 mole of copper
 - (b) 2.5 moles of hydrogen gas from water
 - (c) 15 g of aluminium
 - (d) 5.3 g of sodium
 - (e) 87 mL of oxygen gas from water at SLC?
15. Calculate:
- (a) the mass of copper deposited
 - (b) the volume of oxygen formed at SLC during the electrolysis of aqueous copper(II) sulfate using carbon electrodes when:
 - (i) a current of 1.2 A flows for 8.0 minutes
 - (ii) a current of 0.75 A flows for 3.0 hours
 - (iii) a current of 3.5 A flows for 2.0 hours 25 minutes
 - (iv) a current of 2.4 A flows for 1.0 day.
16. Calculate the amount of time (in days) required to produce 2.00 kg of magnesium metal by the electrolysis of molten magnesium chloride, MgCl_2 , using a current of 45.0 A.
17. A metal M forms a chloride with the formula MCl_2 . Crystals of MCl_2 were placed in a crucible and heated. The molten chloride was then electrolysed using carbon electrodes. The ammeter in the circuit read 0.250 A and the current was passed for 4 hours 56.0 minutes. The mass of M deposited was 1.28 g.
- (a) Write an equation for the reaction at the cathode.
 - (b) Calculate the number of moles of M produced.
 - (c) Determine the atomic mass of M .
 - (d) Use your periodic table to suggest a metal that M could be.
 - (e) Draw a diagram of the apparatus suitable for this experiment.
18. Chromium chloride is electrolysed using chromium electrodes. A current of 0.200 A flows for 1447 seconds. The increase in the mass of the cathode is 0.0520 g.
- (a) How many coulombs of electricity are used?
 - (b) How many moles of electrons are transferred?
 - (c) How many moles of chromium are liberated?
 - (d) What is the charge on the chromium ion?
19. When a current of 10.0 A was passed through a concentrated solution of sodium chloride using carbon electrodes, 2.80 L of chlorine (at SLC) was collected. How long (in minutes) did the electrolysis take?
20. A current of 4.25 A is passed through molten Al_2O_3 for 13.5 hours.
- (a) How many grams of aluminium would be produced?
 - (b) What volume of oxygen, at 152 kPa (1.50 atm) and 29.0 °C, would be evolved?
21. Calculate the time taken to deposit gold from a solution of gold(I) cyanide to a thickness of 0.0100 mm onto a copper disc that has a diameter of 10.0 mm and a thickness of 5.00 mm if a current of 0.750 A is used. (The density of gold is 19.3 g cm^{-3} .)

22. (a) What volumes of hydrogen gas, H_2 , and oxygen gas, O_2 , are produced from the electrolysis of water by a current of 2.50 A in 15.0 minutes at SLC?
 (b) Identify the reactions occurring at the electrodes in the reaction in (a).
23. A solution containing a 3^+ metal ion is electrolysed by a current of 2.00 A for 25.0 minutes. What is the identity of the metal if 1.19 g of the metal was deposited on the cathode?
24. How many electrons are required to deposit 1.00 g of copper from copper(II) sulfate solution?
25. Sir Humphry Davy discovered sodium by electrolysing molten sodium hydroxide. How long (in minutes) must a current of 1.5 A flow to produce 1.0 gram of sodium?
26. A Hall-Heroult cell is an electrolytic cell in which molten alumina, Al_2O_3 , is electrolysed to produce aluminium. The overall reaction may be written:
- $$4\text{Al}^{3+}(\text{l}) + 6\text{O}^{2-}(\text{l}) + 3\text{C}(\text{s}) \longrightarrow 4\text{Al}(\text{l}) + 3\text{CO}_2(\text{g})$$
- A typical Hall-Heroult cell uses a current of 1.70×10^5 A. Assuming 98% efficiency, calculate the following for a 24-hour period:
- the mass of aluminium produced
 - the volume of carbon dioxide formed at SLC.
27. A given quantity of electricity is passed through two cells containing solutions of silver nitrate and tin(II) chloride respectively. What mass of tin is deposited in one cell if 2.00 g of silver is deposited in the other cell?
28. What current is needed to deposit 0.65 g of silver onto a metal spoon in 1.0 hour?
29. A home renovator wants to chrome-plate her kitchen tap so that a layer of chromium 0.150 mm thick is evenly plated over the tap. The total surface area of the tap is 35.0 cm^2 . Given that the density of chromium is 7.20 g cm^{-3} , calculate the time (in hours) that the tap should be left in the electrolytic bath of chromium(III) nitrate if the bath has a current of 4.55 A passing through it.

Secondary cells

30. Why are lead-acid accumulators often referred to as storage batteries?
31. For a lead-acid storage cell:
- What is the standard cell potential?
 - What is the battery potential, assuming it is composed of six lead-acid storage cells?
 - Describe the composition of the anode, cathode and electrolyte when it is fully discharged.
32. The Edison cell is a 1.3-volt storage battery that can be recharged, even after long periods of being left uncharged. Its electrolyte is 21% potassium hydroxide solution and the reaction on discharge is:
- $$\text{Fe}(\text{s}) + 2\text{NiO}(\text{OH})(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Fe}(\text{OH})_2(\text{s}) + 2\text{Ni}(\text{OH})_2(\text{s})$$
- Outline two uses for which this type of cell would be ideal.
 - Give electrode reactions during:
 - discharging
 - recharging.
 - What materials would be used for the electrodes?
 - In the discharge process, which electrode is the anode and which is the cathode?
 - In the recharge process, which electrode is the anode and which is the cathode?
33. The market for lithium batteries is continually increasing in our energy-hungry society. Applications of this technology extend from tiny cells used in medical implants, to laptops, mobile phones and military devices.
- What properties of lithium make it so useful for cells?
 - Discuss the chemistry involved in the operation of a lithium cell compared with the operation of a nickel metal hydride cell.

**Exam practice questions**

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

1. An aqueous solution of NiBr_2 is electrolysed using inert electrodes.
 - (a) Sketch the cell showing:
 - (i) the direction of current flow in the external circuit and through the electrolyte
 - (ii) the cathode and anode, and their polarity.**2 marks**
 - (b) Write half-equations for the expected reactions at each electrode, and then write the overall equation. **2 marks**
 - (c) Calculate the minimum voltage needed to electrolyse the solution under standard conditions (SLC). **1 mark**
 - (d) Explain how the products of electrolysis would differ if nickel electrodes were used. **2 marks**
2. After Millikan showed that the charge on an electron was 1.6×10^{-19} coulomb, electrolytic reactions were used to obtain accurate estimates of the Avogadro constant. Consider a current of 0.10 A flowing through an electrolytic solution to produce a deposit of 0.10 g of copper.
 - (a) Find the charge passing through the cell if the time taken for the deposit was 50 minutes and 40 seconds. **1 mark**
 - (b) Calculate the amount of copper produced. **1 mark**
 - (c) Write the equation for the reaction and hence calculate the number of moles of electrons consumed. **2 marks**
 - (d) Calculate the charge on 1 mole of electrons. **2 marks**
 - (e) Calculate the Avogadro constant, given that the charge on an electron is 1.6×10^{-19} coulombs. **1 mark**
3. What mass (in kg) of chlorine gas is produced in 1.00 hours in an electrolytic cell using a concentrated NaCl electrolyte, given that the current is 1.40×10^3 A and the cell's efficiency is 90%? **5 marks**

Rates of reactions

Collisions cause change. Car accidents, tenpin bowling, hitting a golf ball, hurricanes and striking a match; all of these collisions affect their surroundings. The more energy a collision has, the more dramatic are the changes produced. On a much smaller scale, collisions between atoms, molecules and ions are at the heart of all chemical reactions. The same ideas about energy and collisions causing change explain much about how chemical reactions occur.

YOU WILL EXAMINE:

- the concept of rate of a reaction
- the use of collision theory to explain reaction rates
- energy profile diagrams for exothermic and endothermic reactions and the concept of activation energy
- factors that affect the rate of a reaction
- how catalysts affect the rate of a reaction
- Maxwell–Boltzmann distribution curves and their use in explaining reaction rates.



Blasting is an important step in open-cut mining. It frees up the ore for collection and subsequent transport. The explosions that release the ore are chemical reactions designed to happen almost instantaneously, and they release huge volumes of gases and vast amounts of energy. The energy shockwave fractures the rock and ore into smaller, more convenient pieces. Not all chemical reactions happen so quickly, however. Chemists can control the rates of reactions using knowledge of various factors.

study on

Unit 3

AOS 2

Topic 1

Concept 4

Do moreEnergy profiles
for endothermic
reactions**study on**

Unit 3

AOS 2

Topic 1

Concept 6

Do more

Activation energy

Chemical reactions involve breaking old bonds and forming new bonds. New substances form after the atoms rearrange themselves. The energy required to initiate this process is called the activation energy.

Energy profile diagrams are a convenient way of representing the energy changes during a chemical reaction. Depending on these changes, reactions may be classified as exothermic or endothermic. A **negative ΔH** value indicates an exothermic reaction, while a **positive ΔH** value indicates an endothermic reaction.

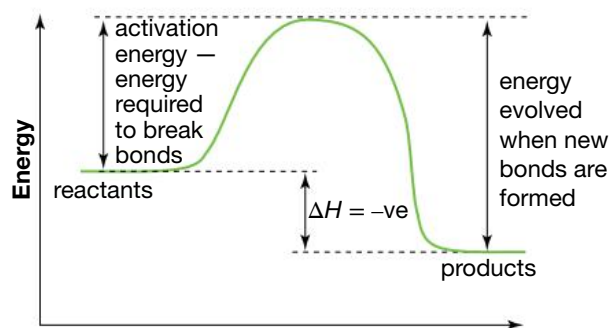
How does a chemical reaction occur?

All chemical reactions involve the rearrangement of atoms that are already present. For such an arrangement to occur, existing (or old) bonds need to be broken and 'new' bonds allowed to form. This means that there is always an energy requirement before a chemical reaction can take place; this corresponds to breaking the 'old' bonds. This energy required to break these bonds is called the **activation energy** and comes from either or both:

- thermal energy (heating)
- the kinetic energy of colliding particles.

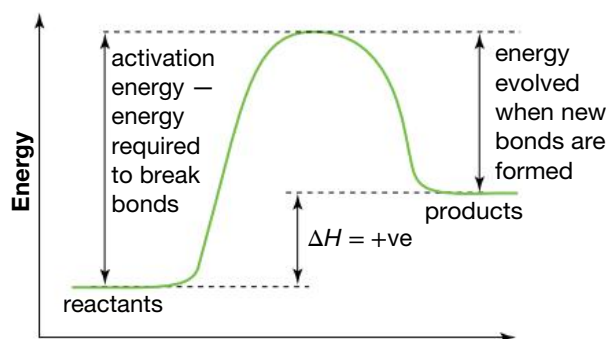
When new bonds form, energy is released as the particles involved organise themselves into stable arrangements that form the products. The total energy stored in a substance is called the **enthalpy**, or **heat content**, of the substance and is given the symbol H . It is not possible to measure H directly but the **change in enthalpy** (ΔH) can be measured when a substance undergoes a chemical reaction. Change in enthalpy was discussed in chapter 2. Energy changes can be conveniently summarised using the following energy profile diagrams.

Energy diagram for an exothermic reaction



Energy profile diagrams showing activation energies. A chemical reaction can be recognised as either exothermic or endothermic by its ΔH value. If the ΔH value is negative, the reaction is exothermic. If the ΔH value is positive, the reaction is endothermic.

Energy diagram for an endothermic reaction



From these diagrams we can note a number of points:

- The energy required to break the old bonds is called the activation energy.
- For an **exothermic** reaction, the activation energy is less than the energy released when new bonds form. Consequently, there is a net release of energy (usually as heat released to the surroundings).
- In an **endothermic** reaction, the activation energy is greater than the energy released when new bonds form. Consequently, there is a net input of energy (in most cases, heat is absorbed from the surroundings).
- In both cases, however, the activation energy represents a requirement for the progress of the chemical reaction. This must be overcome before a reaction proceeds.

Bond breaking > bond forming $+\Delta H$

Bond breaking < bond forming $-\Delta H$

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Unit 3

AOS 2

Topic 1

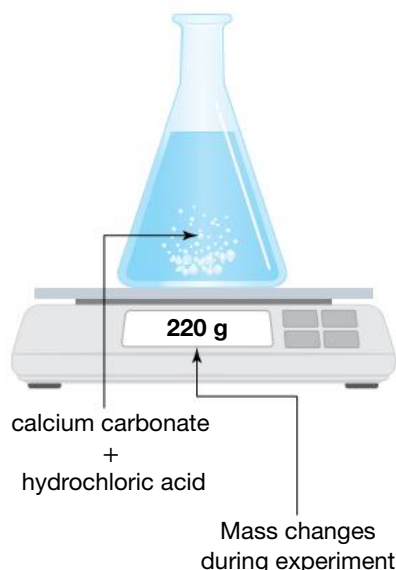
Concept 2



See more

Endothermic and exothermic reactions

The rate of a chemical reaction can be affected by the concentrations of reactants, the temperature, the presence of a catalyst and, in heterogeneous reactions, the surface area. Heterogeneous reactions have reactants in different phases, such as a powder and a gas.



Apparatus used to measure rate

Collision theory

A chemical reaction involves particles that are moving around in constant random motion and sometimes colliding with each other. The greater the number of successful collisions there are the faster the rate. Not all collisions result in a reaction; the particles may simply bounce off each other. In summary, in order for a reaction to take place the reactants must:

- collide
- have the correct orientation for bond breaking to occur
- have sufficient energy for the reaction to occur. The reactant particles must contain enough energy to overcome the activation energy requirement, allowing the particles present to break their bonds and then rearrange themselves, forming new bonds, into the products.

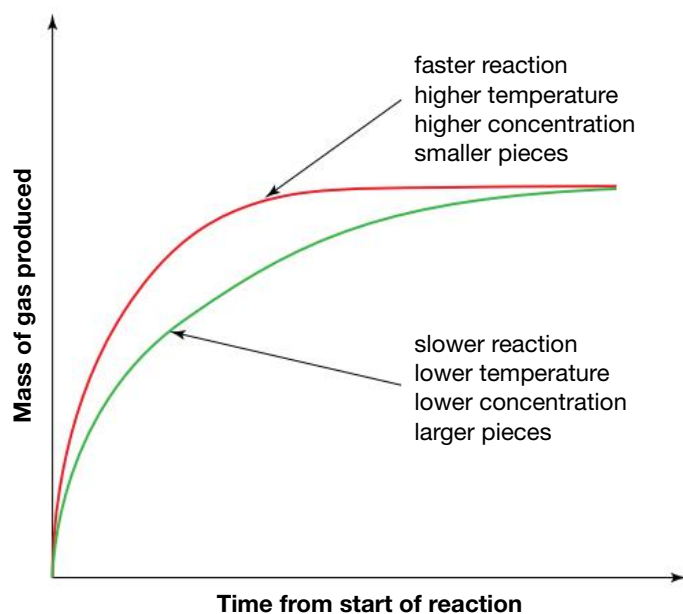
Measuring reaction rates

The progress of a reaction may be conveniently monitored by following either the decrease in the amount of a reactant or the formation of a product. Methods used to observe reaction rates include measuring the change over a period of time of:

- the volume of a gas evolved
- the mass of a solid formed
- the decrease in mass due to gas evolving
- the intensity of colour of a solution
- the formation of a precipitate
- pH
- temperature.

A typical example of apparatus used to measure rates is illustrated below left. The rate of the reaction can be observed by measuring the change in mass over fixed intervals of time, such as grams per 10 seconds. As the reaction proceeds, the mass of the flask and contents decreases.

The variables that might be tested are temperature, concentration of the hydrochloric acid or the size of the particles of calcium carbonate (surface area).



Graph displaying mass of gas lost from apparatus

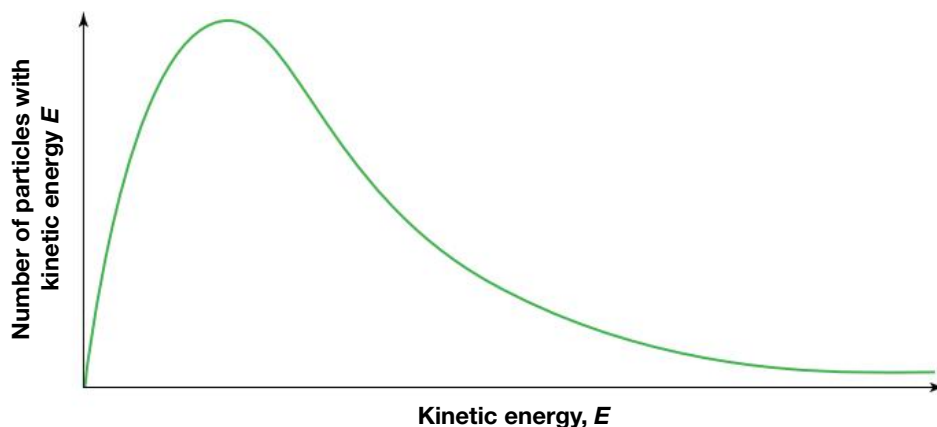
The graph displays the mass of gas lost and is found by subtracting the mass at each time interval from the initial mass of the apparatus. The gradient (steepness) of the red line is greater, indicating a faster rate than the green line. The graph flattens when the limiting reactant is consumed.

Maxwell-Boltzmann distribution curves

During the second half of the seventeenth century, work by scientists such as James Clerk Maxwell and Ludwig Boltzmann led to what is now known as the Maxwell-Boltzmann distribution. This is a statistical analysis of the range of energies present in the particles of a gas sample. It has proven to be very useful in explaining some of the factors that influence chemical reactions and their rates. Although originally developed for gases, many of its ideas can also be applied to liquids and reactions in solution as well.

A Maxwell-Boltzmann distribution curve, such as that shown below, shows the number of particles with a particular energy graphed against the value of that energy.

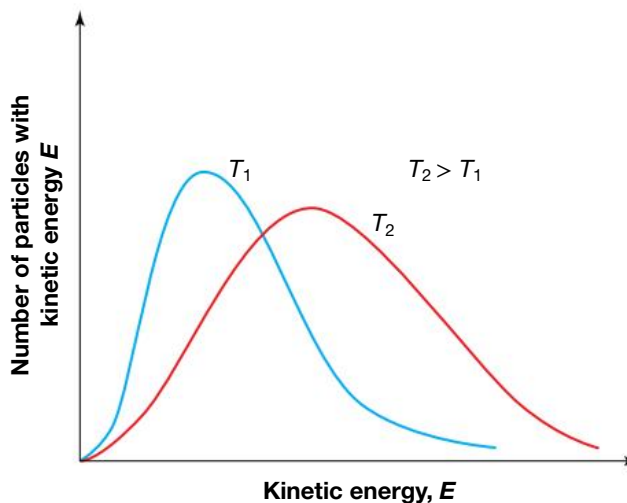
The Maxwell-Boltzmann curve shows the number of particles with a particular energy graphed against the value of that particular energy.



Some points to note about this graph include:

- The particles in a sample have a wide range of kinetic energies. As kinetic energy is given by the formula $\frac{1}{2}mv^2$, this means that there is also a range of velocities. This is due to the collisions that the particles are constantly undergoing.
- It is not symmetrical.
- The highest point represents the most probable velocity; however, this is not the same as the average velocity.
- The area under the graph represents the total number of particles in the sample.

If the temperature of a sample is increased, the graph changes in a very predictable manner as shown below.



Increasing the temperature of a gas sample stretches the Maxwell-Boltzmann curve to the right.

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Experiment 5.1 Reaction rates
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Square brackets denote concentration in mol L⁻¹ (M).

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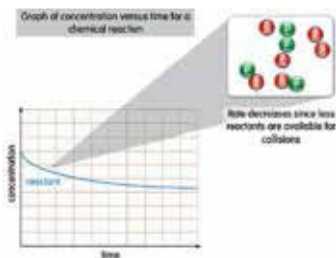
Unit 3

AOS 2

Topic 2

Concept 1

See more
Increasing reaction rate



Increasing concentration and increasing temperature both increase the number of collisions each second and also increase the rate of a reaction. Temperature also affects the energy of a collision.

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Temperature and reaction rate
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The effect of increasing the temperature is to 'stretch' the graph to the right. As a result, there are more particles with higher kinetic energies. Although the area under the graph is the same (the total number of particles has not been altered), on average they all move faster and the average kinetic energy is higher.

Note: At the higher temperature, the graph is *stretched* to the right, rather than *moved* to the right. The graph is always 'anchored' to the origin, as there are always a few particles with very low or zero velocity.

Factors that affect the rate of a reaction

Concentration

Table 5.1 shows some results from an experiment involving the reaction:

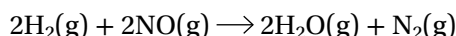


TABLE 5.1 Rate of reaction between H₂ and NO (at 800 °C)

Experiment	Initial concentrations (M)		Initial rate of H ₂ O production (M s ⁻¹)
	[NO]	[H ₂]	
1	6.0 × 10 ⁻³	1.0 × 10 ⁻³	0.64 × 10 ⁻²
2	6.0 × 10 ⁻³	2.0 × 10 ⁻³	1.28 × 10 ⁻²
3	1.0 × 10 ⁻³	6.0 × 10 ⁻³	1.00 × 10 ⁻³
4	2.0 × 10 ⁻³	6.0 × 10 ⁻³	3.90 × 10 ⁻³

In experiments 1 and 2, [NO] is the same but [H₂] is different. In experiments 3 and 4, [H₂] is the same but [NO] is different. Therefore, each pair of experiments allows us to analyse the effect of changing the concentration of one of the two substances. Compare experiment 1 with experiment 2, and then compare experiment 3 with experiment 4. Increasing the concentration of either reactant causes an increase in the rate of the reaction. In terms of our model of a chemical reaction, we can explain this by the crowding together of the reacting particles as the concentration is increased. This results in an increased frequency of successful collisions during any given period of time and hence a higher rate of reaction.

Pressure

For reactions involving gases, the effect of increasing pressure is the same as increasing concentration. Both effects result in more crowding together of the particles and hence more successful collisions within a certain time.

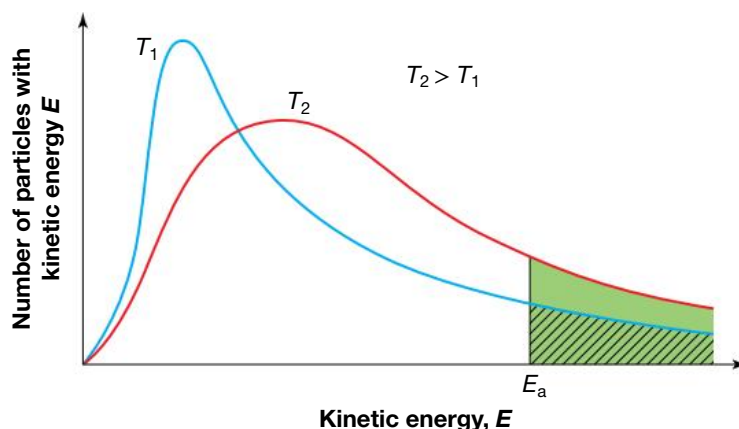
This can be verified using the universal gas equation. For a given temperature, it can easily be shown that pressure is proportional to concentration by manipulating the equation to produce $P = \frac{n}{V}RT$.

Temperature

Most chemical reactions are observed to proceed more quickly as the temperature is increased. Examples from everyday life that demonstrate this are the cooking of food and setting of glues such as Araldite.

An examination of the following Maxwell-Boltzmann curves at different temperatures reveals why this is so.

Increasing the temperature means that there are more particles with enough energy to overcome the activation energy barrier.



For the given activation energy (E_a), the shape of the graph clearly shows that there is more area under the graph (and hence more particles) to the right of E_a at the higher temperature than at the lower one. More collisions will therefore be 'successful' in overcoming the activation energy barrier.

Another effect of increasing the temperature is that there is an increased frequency of collisions due to the particles moving faster. However, a more sophisticated analysis of the situation reveals that this is secondary to the effect of the energy distributions mentioned above.

Revision question

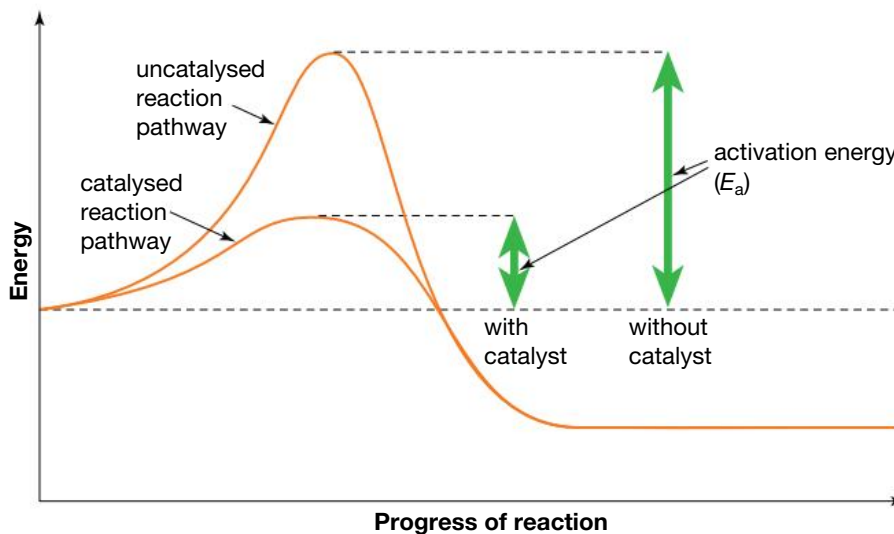
- The evolution of bubbles when a soft drink is opened is due to dissolved carbonic acid decomposing to carbon dioxide and water. The equation for this process is:



- This evolution is initially fast, but gradually slows down with time. Why does the rate of carbon dioxide evolution decrease?
- How would the rate of reaction be affected if the soft drink was warm?

Catalysts

A **catalyst** is a substance that alters the rate of a chemical reaction without itself being consumed. It provides an alternative reaction pathway with a lower activation energy. This increases the proportion of collisions with energy greater than the activation energy.



A catalyst acts by providing an alternative pathway with a lower activation energy for reactants to form products.

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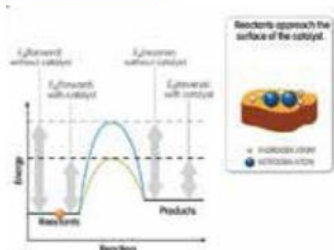
Unit 3

AOS 2

Topic 1

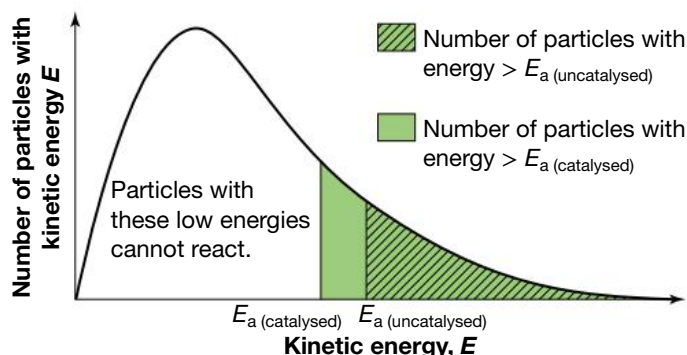
Concept 7

See more
Catalysts



Catalysts are usually used to speed up a reaction. Sometimes, however, they are added to slow a reaction down, in which case they are called negative catalysts or inhibitors.

Adding a catalyst does not alter the value of ΔH .



A catalyst provides an alternative pathway with a lower activation energy. Therefore, more particles have enough energy to overcome the new activation energy requirement.

Appropriate catalysts lie at the heart of many industrial processes, especially in green chemistry industries. Much money is spent by companies on research into new and improved catalysts, and the results of such research are often among a company's most closely guarded secrets. Biological catalysts, or enzymes, are also responsible for the management of thousands of biological reactions important in maintaining life.

In terms of the particle model of chemical reactions, particles must not only collide, but also do so with sufficient energy to break bonds. The presence of a catalyst provides an alternative pathway for the reaction. This pathway has a lower activation energy, as shown on the energy profile diagram at the bottom of the previous page. This means that the value of E_a on the Maxwell-Boltzmann curve shown above is shifted to the left. Therefore, there are now more particles under the curve to the right of this new E_a value. These are the particles that have enough energy to overcome the activation energy requirement, so the reaction occurs at a faster rate as there are more 'successful' collisions within a certain time.

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Experiment 5.2 Catalytic oxidation of ammonia

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Catalysts reduce the energy required for a reaction to occur.

Catalytic converters — catalysts in car exhausts

Catalytic converters are used in the exhaust systems of cars to reduce the amount of gaseous pollutants emitted into the atmosphere. The essential feature of these converters is a rare metal catalyst made from platinum and rhodium. This is finely dispersed over an internal structure that provides a very large surface area over which the exhaust gases are forced to pass. Table 5.2 shows the effect that these catalysts have on the exhaust gases that pass over them.

TABLE 5.2 The changes in exhaust gas composition caused by catalytic converters

Before reaction	After reaction
$\text{CO} + \text{O}_2$	CO_2
hydrocarbons + O_2	$\text{H}_2\text{O} + \text{CO}_2$
nitrogen oxides	$\text{N}_2 + \text{O}_2$

The effect of surface area

Catalysts increase the rate of a reaction by reducing its activation energy. Increasing the surface area of a reactant allows more reactant particles to come into contact with each other.

This is an important factor in heterogeneous reactions — reactions where the reactants are in different phases, such as a solid and a liquid. Its effect is due simply to the fact that, by increasing the surface area, more of a substance is brought into contact with other substances with which it might react. The same mass of wood on a fire burns much faster if, for example, it is cut into small pieces than if it is left as a log. Powdered calcium carbonate reacts faster in acid solution than a block of calcium carbonate of the same mass.

In terms of collision theory, an increase in surface area means that more reactant particles can collide with one another and, therefore, there are more successful collisions between them in a given period of time. This leads to an increased rate of reaction.

Both beakers contain 25 mL of hydrochloric acid and 1 g of calcium carbonate (marble). The marble in the beaker on the left has been ground into a powder; in the beaker on the right, it is in large chunks. The powder has a much higher surface area than the acid, resulting in a much higher reaction rate, which is shown by the faster release of carbon dioxide bubbles.



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Experiment 5.3 Rate of hydrogen production — a problem-solving exercise

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Exploding custard factories

The effect of increasing surface area on the rate of combustion reactions can lead to unexpected, and sometimes catastrophic, results.

A well-documented case in Banbury, Oxfordshire, England, in November 1981, involved a custard powder factory that exploded. Eight people were seriously burned as a result.

Like other solids such as coal and wheat, custard powder does not normally burn very fast. As a dust, however, all of these solids present a huge surface

area to the oxygen in air. All that is needed is an errant spark (from a machine or from static electricity) and the resulting reaction is so fast that it causes an explosion.

Wheat silos have been destroyed and many tragedies have occurred in underground mines from this effect.

Sample problem 5.1

The use of powdered coal is being investigated in experimental railway locomotives as an alternative to oil.

Powdered coal can be introduced in smaller 'doses' that burn much faster than the traditional 'lump' coal once used in steam locomotives.

Why does the powdered coal have a much faster rate of combustion?

Solution: The larger surface area of powdered coal means that it can combust at a much faster rate than lump coal due to the increased frequency of collisions between O_2 and coal.

Sample problem 5.2

Gas leaks in confined spaces can be very dangerous. A single spark can lead to an explosion. Explain, in terms of reaction rates, why this is so.

Solution: Initially the gas and oxygen mixture is non-reactive due to the reaction having a high activation energy. Although the molecules are constantly colliding, there is not enough energy in these collisions to break bonds. This prevents a reaction in the absence of an external energy source.

A spark, however, supplies energy to the molecules in its immediate vicinity and increases their kinetic energy. Some collisions between these molecules now have energy in excess of the activation energy, and bond breaking followed by the formation of new bonds to make products can occur. As this reaction is exothermic, the energy released increases the energy of more reactant molecules, leading to further reactions.

The reaction, therefore, proceeds very quickly with respect to temperature and rate.

Revision questions

- In an investigation of the rate of reaction of gas produced from magnesium and hydrochloric acid, HCl , a student has available three forms of magnesium: powder, small turnings and a strip. Also available are reagent bottles of 0.5 M HCl , 1 M HCl and 2 M HCl . The student could also use a hot water bath and a cool water bath.
 - Which combination of reactants and conditions would produce the fastest rate of reaction?
 - Which combination would produce the slowest rate of reaction?
- The reaction between two gases occurs at a measurable rate at 700 °C. If the temperature is held constant at 700 °C and the reacting mixture is compressed, predict and explain what will happen to the rate of this reaction.

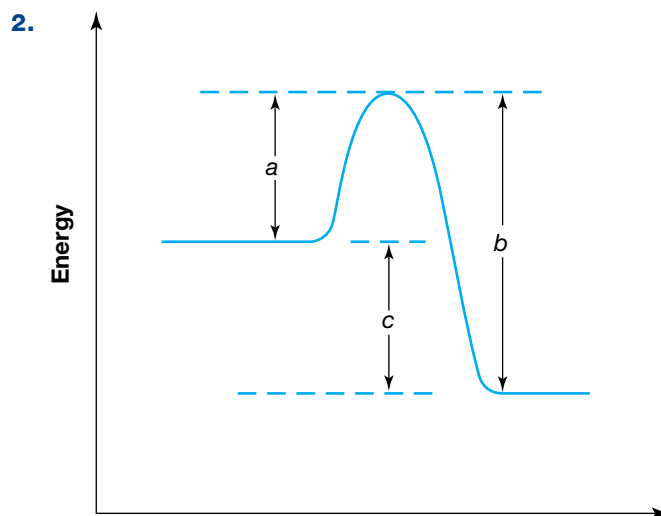
Chapter review

Summary

- Chemical reactions show a wide range of reaction rates.
- Chemical reaction rates may be explained in terms of collisions between the particles involved. The rate depends on factors such as the kinetic energy involved in the collision, the activation energy, the number of collisions per unit time and whether a catalyst is present.
- The activation energy is the energy required to break the original bonds, before new bonds can form.
- A catalyst is a substance that provides an alternative pathway for a reaction — one that has a lower activation energy. Although a catalyst plays an important role in a reaction, it is not used up and does not affect the nature of the actual products formed.
- A chemical reaction is exothermic (and has a negative ΔH value) if the energy released as new bonds form is greater than the energy required to break the old bonds.
- A chemical reaction is endothermic (and has a positive ΔH value) if the energy released as new bonds form is less than the energy required to break the old bonds.
- The rate of a chemical reaction is affected by factors such as the concentration of the particles, the pressure, the temperature, the presence of a catalyst and surface area. Each of these can be explained using collision theory.
- A Maxwell-Boltzmann distribution curve is a graph that shows the number of particles with a particular energy graphed against kinetic energy.
- Maxwell-Boltzmann curves are useful in explaining how factors such as temperature increase and catalysts affect the rate of a chemical reaction.

Multiple choice questions

1. Most chemical reactions display a rate increase with increasing temperature. This can be explained by:
 - A the temperature lowering the activation energy
 - B the particles having more collisions involving higher energies
 - C the temperature making the reactant's bonds weaker
 - D the temperature making the collisions between the particles more elastic.



An energy profile diagram for a chemical reaction is shown above. On this graph:

- A a represents the activation energy for the forward reaction and c represents the activation energy for the backward reaction
 - B a represents the activation energy for both the forward and the reverse reactions
 - C b represents the activation energy for both the forward and the reverse reactions
 - D a represents the activation energy for the forward reaction and b represents the activation energy for the backward reaction.
3. The following reaction has an activation energy of 183 kJ mol^{-1} .
$$2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$$
The reverse reaction:
$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$$
has an activation energy of 157 kJ mol^{-1} . The ΔH value for the first equation above is:
 - A -340 kJ mol^{-1}
 - B $+340 \text{ kJ mol}^{-1}$
 - C -26 kJ mol^{-1}
 - D $+26 \text{ kJ mol}^{-1}$.
 4. Which of the following statements about activation energies is correct?
 - A Activation energies are always positive.
 - B Activation energies are always negative.
 - C Activation energies are positive only for endothermic reactions.
 - D Activation energies are negative only for exothermic reactions.
 5. When zinc is added to hydrochloric acid, the rate at which hydrogen gas is evolved can be used as a measure of reaction rate. Which of the following

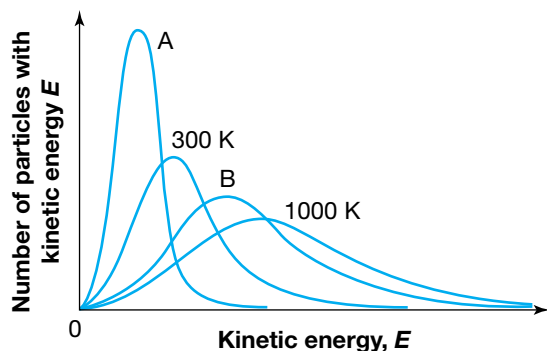
combinations produces the fastest rate of hydrogen gas evolution?

- A Powdered zinc added to 2 M HCl at 20 °C
- B Powdered zinc added to 2 M HCl at 40 °C
- C Granular zinc added to 2 M HCl at 20 °C
- D Granular zinc added to 2 M HCl at 40 °C

6. A sample of gas is heated. Which of the following statements is *incorrect*?

- A The most common speed for its molecules increases.
- B The average speed of its molecules increases.
- C The number of collisions between molecules, per unit time, increases.
- D The area under the Maxwell-Boltzmann distribution curve increases.

7. The Maxwell-Boltzmann distribution graphs for a sample of gas at four different temperatures is shown below.



Which of the following statements is true?

- A Graph A represents the highest temperature.
- B The area under graph A is greater than the area under graph B.
- C A possible temperature for graph B could be 600 K.
- D Graph A contains more fast-moving molecules than graph B.

8. When a reaction occurs at a higher temperature, two important things happen.

Effect 1: More collisions between particles occur each second.

Effect 2: More energy is involved in these collisions.

Which of the following is a true statement?

- A Effect 1 is more important than effect 2 for increasing the rate of a reaction.
- B Effect 2 is more important than effect 1 for increasing the rate of a reaction.
- C Effects 1 and 2 are both equally significant for any increase in reaction rate.
- D Neither 1 nor 2 affects the rate of the reaction.

9. An industrial process involving an exothermic reaction requires that the reaction be slowed down so that the heat evolved can be collected safely. In order to achieve this:

- A the ΔH value of the reaction needs to be decreased

B the ΔH value of the reaction needs to be increased

C the activation energy of the reaction needs to be increased

D the activation energy of the reaction needs to be decreased.

Review questions

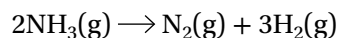
Using energy profile diagrams

- Using the concepts of activation energy and reaction pathways, explain how a catalyst can speed up the rate of a chemical reaction.
- Enzymes are a very important class of biochemical molecules that are often described as biological catalysts. The enzyme lipase, for example, is an important digestive enzyme that assists in the breakdown of fats according to the following generalised equation.

lipase

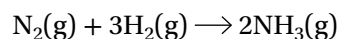


- Using the concept of activation energy, explain why the rates of reactions such as this are very much greater in the presence of lipase.
 - How does the amount of lipase present at the start of a reaction such as this compare with the amount present at its completion?
- The decomposition of ammonia to produce nitrogen and hydrogen according to:



has an activation energy of 330 kJ mol⁻¹ and a ΔH value of +92 kJ mol⁻¹. If tungsten is used as a catalyst, the activation energy is 163 kJ mol⁻¹.

- Give a definition for the term 'catalyst'.
 - Show all of the information above on an energy profile diagram for this reaction.
- The reverse reaction to this as shown by the equation:



is a very important reaction in industry.

- Calculate the activation energy for the uncatalysed version of this reaction.
 - Calculate the activation energy when tungsten is used as a catalyst.
- Sometimes, a catalyst is described as a substance that *lowers the activation energy*. Why is it more correct to describe it as *a substance that provides an alternative pathway with a lower activation energy*?

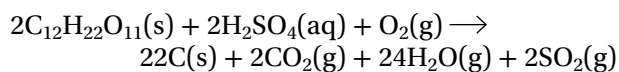
Explaining reaction rates

- Comment on the rates observed for each of the following situations. For each one, use the

particle theory for chemical reactions to explain the rate behaviour observed.

- (a) Ten mL of spilt petrol evaporates faster than 10 mL of petrol in a narrow container.
 - (b) A piece of steel wool burns in a Bunsen flame, but the same mass of solid steel does not.
 - (c) A pinch of manganese dioxide added to hydrogen peroxide continues to produce oxygen for as long as fresh hydrogen peroxide is added.
 - (d) The chemicals mixed by a panelbeater to make body filler harden faster on a hot day than on a cold day.
 - (e) Nail polish remover evaporates faster if you shake your fingers than if you don't.
 - (f) The addition of vinegar to some 'bicarbonate of soda' causes an evolution of gas that is quick at first but then slows down.
 - (g) Photographers using infrared-sensitive film store it in a refrigerator before use.
6. The reaction between hydrogen gas and nitrogen(IV) oxide is represented by the equation:
- $$2\text{H}_2(\text{g}) + 2\text{NO}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$$
- (a) Explain why the rate of this reaction decreases with time.
 - (b) Explain why the progress of this reaction can be monitored by measuring the drop in pressure.
7. The dehydration properties of concentrated sulfuric acid are often demonstrated using sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Black carbon and steam, along with

sulfur dioxide and considerable heat, are produced. The equation for this reaction is:



Explain why this reaction occurs much faster when castor sugar, rather than granulated sugar, is used as a source of sucrose.

8. Maxwell-Boltzmann curves show that particles have a wide range of velocities (and hence energies). Using collision theory, explain why this is so.
9. The rate of a chemical reaction is a very important consideration in industrial chemistry where chemicals are made on a large scale. Reactions need an acceptable rate to be economical. A number of important industrial reactions have rates that are too slow at even moderate temperatures and, therefore, need to be sped up. Further increasing the temperature is a common means of achieving this; however, sometimes this is an inappropriate strategy. Suggest two other methods by which an increase in reaction rate may be produced in these situations.
10. (a) Use a Maxwell-Boltzmann curve to clearly explain why:
- (i) a catalyst can alter the rate of a reaction
 - (ii) increasing temperature usually increases the rate of a reaction.
- (b) Mark an X on the graph showing the average energy of particles in your sample.

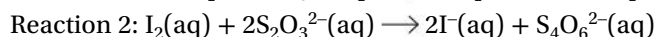
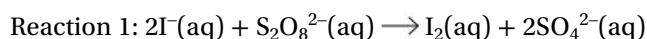


Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response question

1. In chemistry, a number of reactions are collectively referred to as 'clock reactions'. These reactions produce a sudden colour change after a period of time. One of the better known examples of such reactions is that between iodide ions and persulfate ions in the presence of thiosulfate ions and starch. Two reactions are involved:



The iodine produced by reaction 1 is immediately removed by reaction 2. However, $\text{S}_2\text{O}_3^{2-}(\text{aq})$ ions are also removed and are eventually all used up. After this time, iodine builds up and is detected by the starch present, which forms an intensely coloured dark blue complex. This occurs at iodine concentrations as low as 10^{-5} M, making starch an excellent indicator for this reaction.

If the amount of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ is kept constant, the appearance of the dark blue colour may be used to measure the rate of reaction 1.

In one such experiment using 0.2 M KI(aq) solution, 0.2 M $\text{Na}_2\text{S}_2\text{O}_8(\text{aq})$ and 0.1 M $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ solutions, the following results were obtained.

Trial number	$V(\text{I}^-(\text{aq}))$ solution (mL)	$V(\text{S}_2\text{O}_8^{2-}(\text{aq}))$ solution (mL)	$V(\text{S}_2\text{O}_3^{2-}(\text{aq}))$ solution (mL)	$V(\text{water})$ (mL)	$V(\text{starch})$ solution (mL)	Time for blue colour to appear (s)
1	20	20	20	40	10	220
2	20	40	20	20	10	150
3	40	20	20	20	10	142

- (a) Explain how these results show that increasing $\text{S}_2\text{O}_8^{2-}(\text{aq})$ concentration produces a faster rate in reaction 1. Compare two appropriate trials from the data above as part of your explanation. **2 marks**
- (b) Use the results above to explain how the rate of reaction is affected by the concentration of iodide ions. Select two appropriate trials to support your explanation. **2 marks**
- (c) The experiment is repeated using solutions that were stored in a refrigerator for 24 hours. These solutions were used immediately after being removed. How would the reaction times in the table above be affected? **1 mark**
- (d) What is the purpose of the two different amounts of water used in the above trials? **2 marks**
- (e) Explain why the amount of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ solution is kept constant in each trial. **1 mark**

6 Equilibrium systems



The look on this girl's face says it all! Certain substances have been recognised for their sour taste for hundreds of years. We know today that many foods contain chemicals that are weak acids. In fact, the word 'acid' comes from the Latin word meaning sour. Weak acids are examples of substances that produce equilibrium reactions when dissolved in water and are a good illustration of common equilibrium systems. Citrus fruits, such as this lemon, contain acids including citric acid and ascorbic acid. The latter is also known as vitamin C — a substance essential to human life.

Many chemical reactions appear not to use up all their reactants. While this might seem strange at first, such reactions are very common. These are called equilibrium reactions. Chemical reactions involving equilibria are all around us. Many even occur inside our bodies and play a vital role in keeping us alive and healthy. Equilibrium reactions respond to changes and this is an important feature in how they function to keep us healthy. How do they respond to such changes? Knowledge of the equilibrium law and the ability to predict the response to change is vital to the understanding of these reactions. Additionally, equilibrium reactions are at the heart of processes that manufacture some of our most widely used chemicals. Therefore, thorough knowledge of equilibrium reactions is essential to their manufacture.

YOU WILL EXAMINE:

- the concept of a chemical equilibrium
- the equilibrium law and equilibrium calculations
- the use of graphs to represent equilibrium situations in chemical reactions
- the distinction between the rate of a reaction and the extent of a reaction
- Le Châtelier's principle and its use to make predictions about changes to equilibrium reactions
- how rate and equilibrium factors affect the production of certain chemicals
- oxygen transport as a biological application of equilibrium
- carbon monoxide poisoning as an example of competing equilibria.

Chemical equilibrium

In all the stoichiometric calculations you have done so far, an important assumption has been that the reaction ‘proceeds to completion’. In other words, you have assumed, subject to mole ratios and amounts present, that all reactants are converted into products. This allowed the amount of expected product to be calculated. While many reactions follow this pattern, many do not go to completion. The following two examples illustrate this point.

Reaction 1: The decomposition of hydrogen bromide

If some hydrogen bromide is placed in a suitable container and heated, it decomposes according to the following equation:

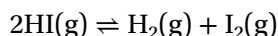


If the products are analysed after some time, it is found that the amounts of hydrogen and bromine are as predicted from a normal stoichiometric calculation. If the concentration of the hydrogen bromide is monitored against time, a graph similar to that shown on the left is obtained.

Another way to describe this reaction is that it ‘goes completely to the right’. The ‘right’, of course, means the product side of the chemical equation.

Reaction 2: The decomposition of hydrogen iodide

The equation for the decomposition of hydrogen iodide is:



At first glance, you might expect this decomposition to be very similar to that shown for hydrogen bromide. However, when this decomposition is attempted under similar conditions to the hydrogen bromide reaction, the yield of hydrogen and iodine is always less than the stoichiometric prediction. This occurs no matter how long you wait. Furthermore, it appears that the concentrations of all species reach certain values and thereafter remain constant. The graph on the left shows this effect for hydrogen iodide.

This second example illustrates what we call an **equilibrium reaction**. Because such reactions are quite common, a method using them to make predictions would be a decided advantage. The profitability or otherwise of an important industrial process costing millions of dollars to research and develop could depend on such calculations.

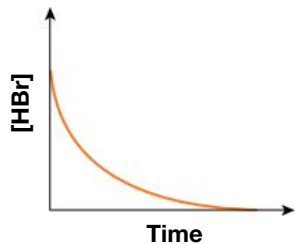
Strictly speaking, all chemical reactions are equilibrium reactions. However, in many cases the degree of backward reaction (that is, products re-forming reactants) is so small that it can effectively be ignored.

Equilibrium reactions are also called reversible reactions, as opposed to irreversible reactions. Their equations show a double arrow ($\rightleftharpoons$) rather than a single arrow ($\longrightarrow$).

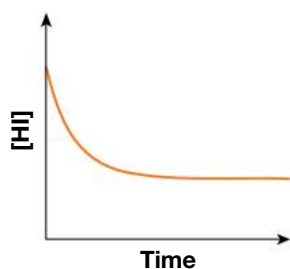
Equilibrium reactions can be classified as homogeneous or heterogeneous, depending on the physical states of the substances involved. If these states are all the same, it is called a homogeneous equilibrium. If they are different, it is heterogeneous. Note that knowledge of heterogeneous equilibria is currently not required for VCE.

The equilibrium law

If a large number of experiments are done, it soon becomes apparent that every reaction, given enough time, comes to a stage at which the composition of the reaction mixture no longer changes. From this stage onwards, the system is said to be at equilibrium. If the concentrations of the substances present are measured at this stage, a large amount of seemingly unrelated data may be obtained. However, on closer analysis, a surprising result emerges.



A typical concentration versus time graph for the decomposition of hydrogen bromide



A typical concentration versus time graph for the decomposition of hydrogen iodide

Many reactions do not completely convert all the reactants into products. Some reactants always remain, mixed with the products of the reaction. These are called equilibrium reactions.

study on

Unit 3

AOS 2

Topic 2

Concept 2

Do more
Homogeneous
equilibria and the
equilibrium law



The equilibrium law and the equilibrium constant that results from it allow us to deal with equilibrium mixtures in a quantitative way.

Table 6.1 shows the results of some experiments in which the hydrogen iodide reaction mentioned on the previous page was studied. In each experiment, different initial amounts of the three substances involved were mixed and heated, and enough time allowed for equilibrium to be reached. The resulting equilibrium concentrations were then measured. Table 6.2 shows a similar set of results for the synthesis of ammonia from nitrogen and hydrogen (the industrially important Haber process).

As can be seen from the last column in tables 6.1 and 6.2, it is possible to write a concentration fraction involving the equilibrium concentrations that has a constant value. A closer inspection of this fraction reveals that its form is closely related to the equation for the reaction. The top line of the fraction contains the products and the bottom line contains the reactants. The coefficients from the chemical equation become indices to their respective concentrations in this fraction. This is the **equilibrium law**. The value of this fraction at equilibrium is called the **equilibrium constant**, which is often assigned the symbol K_c .

TABLE 6.1 Data for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ (at 458 °C)

$[\text{H}_2]$ (M)	$[\text{I}_2]$ (M)	$[\text{HI}]$ (M)	$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$
0.002 484	0.002 514	0.01695	46.0
0.002 636	0.002 305	0.01664	45.7
0.004 173	0.001 185	0.01494	45.1
0.003 716	0.001 478	0.01576	45.2
(i)			
0.002 594	0.002 597	0.01763	46.3
0.001 894	0.001 896	0.01283	45.9
0.001 971	0.001 981	0.01342	46.1
0.002 413	0.002 424	0.01641	46.0
(ii)			

(i) Equilibrium established by combination of hydrogen and iodine

(ii) Equilibrium established by decomposition of hydrogen iodide

Note that square brackets are used to denote concentration measured in M (or mol L⁻¹).

TABLE 6.2 Data for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Run	Equilibrium amounts			$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
	$[\text{N}_2]$ (M)	$[\text{H}_2]$ (M)	$[\text{NH}_3]$ (M)	
1	0.0011	0.0011	2.73×10^{-7}	0.051
2	0.0025	0.0055	4.58×10^{-6}	0.050
3	0.55	0.65	0.0886	0.052
4	0.25	0.75	0.074	0.052

In general, we can say that, for the reaction



the equilibrium constant is denoted by:

$$K_c = \frac{[\text{Z}]^z [\text{Y}]^y [\text{X}]^x \dots}{[\text{A}]^a [\text{B}]^b [\text{C}]^c [\text{D}]^d \dots}$$

The value of the equilibrium constant can be used to indicate the extent of the reaction. If the value is high ($>10^4$), we can predict that there has been a significant conversion of reactants into products by the time that equilibrium was reached. On the other hand, a small value ($<10^{-4}$) indicates that not much conversion has occurred, and the position of equilibrium favours the back reaction.

When describing an equilibrium qualitatively, the phrase ‘position of equilibrium’ is often used. If the value of the equilibrium constant is *small*, the equilibrium is said to lie to the *left*. If the value of the equilibrium constant is *large*, the equilibrium is said to lie to the *right*. Left and right, of course, refer to the equation as it has been written and used to evaluate K_c .

A closer look at equilibrium constants

The equilibrium constant is not necessarily constant!

This statement appears contradictory at first, but a closer examination will help. The equilibrium constant is affected by temperature, and its value may depend on how the reaction equation is written. This will also determine the units of the equilibrium constant. Putting it another way, a particular chemical reaction may have an equilibrium constant with different values and different units, depending on how its equation is written and the temperature at which the reaction occurs.

To illustrate these points, consider the data in table 6.3 for the dissociation of dinitrogen tetroxide gas, N_2O_4 , into nitrogen dioxide gas, NO_2 , at a constant temperature.

TABLE 6.3 Equilibrium data for the reaction between N_2O_4 and NO_2

Experiment number	$[\text{N}_2\text{O}_4]$ (M)	$[\text{NO}_2]$ (M)
1	0.127	0.150
2	0.253	0.216
3	0.364	0.255
4	0.492	0.293
5	0.645	0.338

Case 1:

The equation is written as $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

$$\begin{aligned}\text{Using data from experiment 1: } K_c &= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \\ &= \frac{(0.150)^2}{0.127} \\ &= 0.177\end{aligned}$$

$$\text{Units for } K_c: \frac{\text{M}^2}{\text{M}} = \text{M}$$

Case 2:

The equation is written as $\frac{1}{2}\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons \text{NO}_2(\text{g})$.

$$\begin{aligned}\text{Using data from experiment 1: } K_c &= \frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]^{\frac{1}{2}}} \\ &= \frac{0.150}{(0.127)^{\frac{1}{2}}} \\ &= 0.421\end{aligned}$$

$$\text{Units for } K_c: \frac{\text{M}}{\text{M}^{\frac{1}{2}}} = \text{M}^{\frac{1}{2}}$$

Case 3:

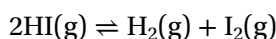
Because there are two reactions involved in every equilibrium reaction, the equation can just as correctly be written as the reverse reaction: in other words, $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$.

$$\begin{aligned}\text{Using data from experiment 1: } K_c &= \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \\ &= \frac{0.127}{(0.150)^2} \\ &= 5.64\end{aligned}$$

$$\text{Units for } K_c: \frac{\text{M}}{\text{M}^2} = \text{M}^{-1}$$

As can be seen with the three cases above, the same reaction can have different equilibrium constants and different units. Therefore, when discussing equilibrium constants, it is important to be clear about the equation being used to represent the reaction.

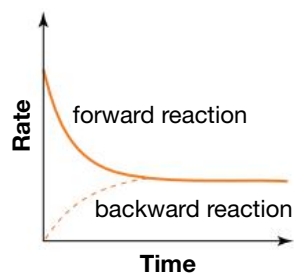
A special situation that also needs to be mentioned is when an equation has the same number of total moles on each side, such as in the hydrogen iodide reaction mentioned earlier:



If we analyse the equilibrium expression for this reaction, all concentrations cancel out. The equilibrium constant (K_c) is therefore *without* units.

Equilibrium constants are also affected by temperature. However, in many situations, such as the $\text{N}_2\text{O}_4(\text{g})/\text{NO}_2(\text{g})$ equilibrium discussed previously, we deal with a situation at a particular temperature. Therefore, when the equation is clearly written or understood, K_c is always constant. The effect of temperature on the value of K_c is discussed later in this chapter.

In summary, when dealing with equilibrium reactions and equilibrium constants, it is important that the equation being used to represent the reaction is clearly understood. It is also assumed that, in the absence of information to the contrary, temperature is constant.



A typical rate versus time graph for an equilibrium system. Once the two rates become equal, no further net change occurs to the amounts or concentrations of the substances involved, and the reaction is said to have reached equilibrium.

At equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction. This means that there is no overall change to the system, even though chemical reactions are still taking place in both directions.

The dynamic nature of equilibrium

The equilibrium state is obviously a significant stage in a reaction. Just what is happening when a reaction reaches equilibrium? Although it is tempting to think that the reaction has stopped, further investigation reveals that this is not so. Instead, *the forward and reverse reactions are still occurring, but at the same rate*. The reagents in the reaction are thus being formed and used at the same rate, their concentrations showing no overall change.

Experiments involving the use of radioactive tracers may be used to verify the dynamic nature of the equilibrium state. If the hydrogen iodide system (on page 157), for example, is heated and allowed to come to equilibrium, it is possible to remove some of the iodine and replace it with the same amount of radioactive iodine — iodine containing the ^{131}I isotope. As isotopes are chemically identical, such a change would have no effect on the chemical nature of the equilibrium. If the system is examined again some time later, the radioactive iodine is found to be distributed between the hydrogen iodide and the iodine molecules. This can be explained only if the forward and reverse reactions are still proceeding.

We should also note that, because equilibrium reactions involve a forward and a reverse reaction, it is possible that a starting mixture of chemicals would

produce a backward reaction that is initially faster than the forward reaction. With time, however, the stage would once again be reached where both forward and reverse reactions have the same rate, and equilibrium is established.

Dynamic equilibrium and collision theory

Collision theory further supports the idea that equilibrium is dynamic.

As a reaction proceeds towards equilibrium, there are collisions between reactant particles and also collisions between product particles. Some of these collisions have enough energy to overcome their respective activation energies and so form either more products or re-form more reactants. As the concentrations of the reactants and products rise and fall because of this, there will come a point where the number of successful collisions going in one direction is balanced by the number of successful collisions in the opposite direction. In other words, the rates of these opposing reactions will be equal and the reaction will be at equilibrium.

The distinction between rate and extent

These terms are related but it is important that they are not confused. The extent of a reaction describes the degree to which reactants are converted into products. The value of the equilibrium constant gives an indication of this. As mentioned earlier, a high value for K_c indicates a significant conversion of reactants into products, and such a reaction would be described as having occurred to a significant extent. A low value indicates the opposite — that the reaction has occurred only to a small extent and there has been only a small amount of conversion of reactants into products.

The rate of a reaction is simply an indication of how fast it occurs. The rate shows how long it takes to establish the position of equilibrium.

We should note also that a catalyst has no effect on the position of equilibrium or the value of the equilibrium constant. A catalyst affects the rate of the forward reaction and the rate of the backward reaction equally. It merely alters the time taken to get to equilibrium, not the position of it.

It is, therefore, possible to have slow reactions occur to a great extent as well as other combinations between rate and extent. An explosion, for example, can be described as a fast reaction that occurs to a large extent, whereas it is possible to have equilibrium reactions that occur at moderate rates and to moderate extents.

study on

Unit 3

AOS 2

Topic 2

Concept 5

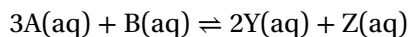
Do more

Calculations involving equilibrium constants and related equations

Calculations involving the equilibrium constant

Sample problem 6.1

Consider an equilibrium reaction that is represented by the equation:



In a particular experiment, random amounts of the above substances were mixed and allowed to come to equilibrium in 500 mL of solution. The amounts present at equilibrium were:



Use this information to calculate the value of the equilibrium constant.

Solution: $[A] \text{ at equilibrium} = \frac{0.351}{0.500} = 0.702 \text{ M}$

$$[B] \text{ at equilibrium} = \frac{0.18}{0.500} = 0.36 \text{ M}$$

$$[Y] \text{ at equilibrium} = \frac{0.632}{0.500} = 1.264 \text{ M}$$

$$[Z] \text{ at equilibrium} = \frac{1.21}{0.500} = 2.42 \text{ M}$$

$$K_c = \frac{[Y]^2[Z]}{[A]^3[B]}$$

$$= \frac{(1.264)^2(2.42)}{(0.702)^3(0.36)}$$

$$= 31$$

$$\text{Units for } K_c = \frac{\text{M}^2 \times \text{M}}{\text{M}^3 \times \text{M}}$$

$$= \text{M}^{-1}$$

$$\therefore K_c = 31 \text{ M}^{-1}$$

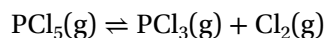
$\therefore$ The position of equilibrium favours the forward reaction.

Note that the above answer can be quoted to only 2 significant figures.

Note also the unit of K_c . As you will notice from other examples, the unit of K_c may vary from one reaction to another, depending on the specific form of the equilibrium expression. In some cases, K_c may even be without a unit.

Sample problem 6.2

At 250 °C, phosphorus(V) chloride decomposes to phosphorus(III) chloride plus chlorine, according to the following equation:



In a particular investigation, a quantity of PCl_5 was heated in a 12.0-litre reaction vessel to 250 °C and allowed to reach equilibrium. Subsequent analysis revealed that 0.210 mol of PCl_5 , 0.320 mol of PCl_3 and 0.320 mol of Cl_2 were present. Calculate the value of the equilibrium constant.

Solution: $[\text{PCl}_5] = \frac{0.210}{12.0} = 0.0175 \text{ M}$

$$[\text{PCl}_3] = \frac{0.320}{12.0} = 0.0267 \text{ M}$$

$$[\text{Cl}_2] = \frac{0.320}{12.0} = 0.0267 \text{ M}$$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$= \frac{(0.0267)(0.0267)}{(0.0175)}$$

$$= 0.0407$$

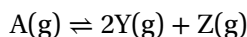
$$\text{Units for } K_c = \frac{\text{M} \times \text{M}}{\text{M}}$$

$$= \text{M}$$

$$\therefore K_c = 0.0407 \text{ M}$$

Sample problem 6.3

In studying the reaction represented by the equation:



a small amount of substance A was added to a reaction vessel, such that its initial concentration was 1.0 M. When equilibrium was subsequently attained, the concentration of product Z was measured and found to be 0.3 M.

Use this information to determine the value of the equilibrium constant for this reaction.

Solution:

study on

Unit 3

AOS 2

Topic 2

Concept 6



See more

Calculations involving initial and equilibrium concentrations



We must be careful to distinguish between initial concentrations and equilibrium concentrations. In a situation such as this, we can use the mole ratios of the equation (its stoichiometry) to determine the remaining necessary equilibrium concentrations.

[A] at equilibrium = 1.0 – 0.3 = 0.7 M

(For every 1 mol of Z produced, 1 mol of A is consumed.)

[Y] at equilibrium = 2 × 0.3 = 0.6 M

(For every 1 mol of Z formed, 2 mol of Y are formed.)

Hence:

$$\begin{aligned} K_c &= \frac{[\text{Y}]^2 [\text{Z}]}{[\text{A}]} \\ &= \frac{(0.6)^2 (0.3)}{(0.7)} \\ &= 0.2 \text{ M}^2 \end{aligned}$$

Alternative solution:

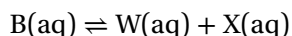
Another way to organise the determination of the equilibrium concentrations for problems such as this is to use what is frequently called ‘icebox’ setting out. This involves setting up a table with row headings ‘I’ (initial), ‘C’ (change) and ‘E’ (equilibrium) as shown below. This can be used for moles (which are then converted to concentrations) or directly with concentrations.

	A	⇌	2Y	+	Z
Initial amount	1		0		0
Change in amount	–0.3		+0.6		+0.3
Equilibrium amount	0.7		0.6		0.3

The calculation of K_c then proceeds as shown previously.

Sample problem 6.4

For the reaction represented by:



initial concentrations of 2.0 M and 3.0 M were recorded for substances B and X respectively. After allowing sufficient time for the reaction to reach equilibrium, the concentration of X had increased to 3.5 M.

Calculate the value of the equilibrium constant.

Solution: The concentration of X has obviously increased by 0.50 M. The stoichiometry of this reaction, therefore, tells us that the concentration of W has also increased by this amount, but the concentration of B has decreased by this amount. In the absence of any information about W, it is reasonable to assume that its initial concentration was zero.

Therefore, at equilibrium we get: $[B] = 2.0 - 0.50 = 1.5 \text{ M}$

$$[W] = 0 + 0.50 = 0.50 \text{ M}$$

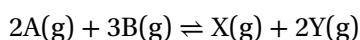
$$[X] = 3.5 \text{ M (as measured)}$$

$$\begin{aligned} K_c &= \frac{[W][X]}{[B]} \\ &= \frac{(0.50)(3.5)}{(1.5)} \\ &= 1.2 \text{ M} \end{aligned}$$

'Icebox' setting out, as shown in sample problem 6.3, is another way to solve this problem.

Sample problem 6.5

The equilibrium constant for the reaction represented by the equation:



is 300 M^{-2} . In a vessel of volume 4.00 L, equilibrium is established and the following concentrations are determined:

$$\begin{aligned} [A] &= 0.326 \text{ M} & [B] &= 1.537 \text{ M} \\ [X] &= 2.541 \text{ M} \end{aligned}$$

Calculate the number of moles of substance Y that were present at equilibrium.

Solution:

$$K_c = \frac{[X][Y]^2}{[A]^2[B]^3}$$

Therefore:

$$300 = \frac{(2.541)[Y]^2}{(0.326)^2(1.537)^3}$$

$$\begin{aligned} [Y]^2 &= \frac{300 \times (0.326)^2 \times (1.537)^3}{(2.541)} \\ &= 45.6 \end{aligned}$$

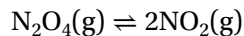
$$[Y] = 6.75 \text{ M}$$

$$\text{Since } n = c \times V$$

Therefore: $n(Y) = 6.75 \times 4.00 = 27.0 \text{ mol.}$

Sample problem 6.6

Equilibrium between dinitrogen tetroxide and nitrogen dioxide is represented by the equation:



At a particular temperature, the value of the equilibrium constant for this reaction is 0.11 M.

In a particular study, 0.12 mol of NO_2 is present at equilibrium in a 2.0 L vessel. Calculate the number of moles of N_2O_4 that are present.

Solution:

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$[\text{NO}_2] = \frac{0.12}{2.0} = 0.060 \text{ M}$$

$$\therefore 0.11 = \frac{(0.060)^2}{[\text{N}_2\text{O}_4]}$$

$$\therefore [\text{N}_2\text{O}_4] = \frac{(0.060)^2}{0.11}$$

$$= \frac{0.0036}{0.11}$$

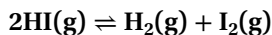
$$= 0.033 \text{ M}$$

$$\therefore n(\text{N}_2\text{O}_4) = 0.033 \times 2.0$$

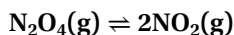
$$= 0.066 \text{ mol}$$

Revision questions

1. An equilibrium mixture contains 1.00 mol of iodine, 0.625 mol of hydrogen and 0.25 mol of hydrogen iodide, all in a 2.00 L vessel. Calculate the value of the equilibrium constant for the reaction represented by the equation:

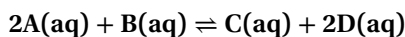


2. Use the data in table 6.3 on page 158 to calculate the value of the equilibrium constant for the reaction:



in each of experiments 2 to 5.

3. Calculate the value and unit of the equilibrium constant for the reverse reaction to the equation in sample problem 6.1, pages 160–161.
4. Consider the reaction represented by the equation:



An initial mixture where all concentrations are 2.0 M is allowed to reach equilibrium. At equilibrium, the concentration of substance C was measured to be 1.5 M. Calculate the value of the equilibrium constant.

5. For the same reaction and the same conditions (the same temperature and the same volume) as described in sample problem 6.6, calculate the number of moles of NO_2 that would be present in equilibrium with 0.056 mol of N_2O_4 .

How can we tell if a reaction is at equilibrium?

If a reaction reaches equilibrium quickly because its rate is fast, then this might not be a problem. It will quickly become apparent that no further concentration changes are occurring and that chemical equilibrium has been attained.

For reactions that are slower, however, the situation may be much more uncertain. If the concentrations are changing only slowly, it may appear that they have become constant. To overcome this problem, we introduce the idea of the **reaction quotient**, Q (also known as the **concentration fraction**).

Reaction quotient, Q , and the equilibrium constant, K_c

If the reaction quotient, Q , or concentration fraction of a reaction is equal to the value of the equilibrium constant, the reaction is at equilibrium.

The equilibrium law generates an expression that can be called a 'concentration fraction'. Because it is just a 'fraction that involves concentrations', it is possible to write a similar fraction at *any other stage* during a reaction. When we do this, we often give it the symbol Q (for reaction quotient). It therefore follows that, if the value of Q is equal to the equilibrium constant, K_c , the reaction is at equilibrium. If the value is *different*, the reaction has *yet to reach equilibrium*.

More specifically, if $Q > K_c$ (the reaction quotient is higher than the equilibrium constant), a net backward reaction is occurring. The rate of the backward reaction is greater than the rate of the forward reaction as this mixture moves towards equilibrium. If $Q < K_c$, the reaction quotient is low, and so a net forward reaction is occurring. The rate of the forward reaction is greater than the rate of the backward reaction as this reaction seeks equilibrium.

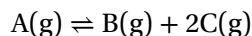
Representing chemical equilibrium graphically

Using graphs of equilibrium situations can be a very informative way to summarise and understand an equilibrium reaction, as well as producing a deeper understanding of what is happening in such situations.

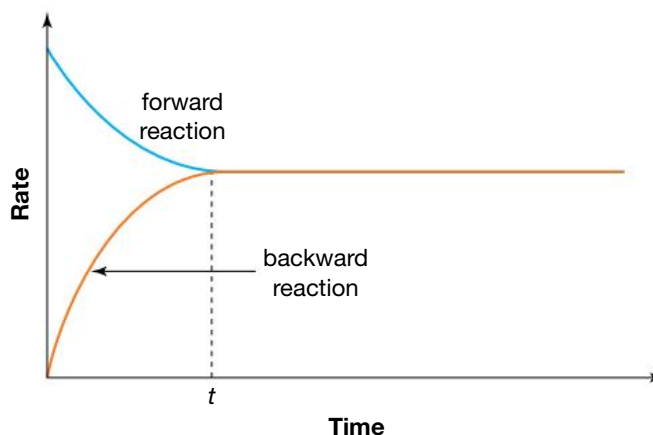
Two types of graphs are frequently used:

- rate versus time graphs
- concentration versus time graphs.

To illustrate these, consider a situation where substance A is added to a container and allowed to come to equilibrium with products B and C at constant temperature, according to the equation:



As discussed in chapter 5, the rate of a reaction depends on concentration. As substance A is used up, its concentration drops and so does the rate of the forward reaction. Conversely, as the concentrations of substances B and C increase, so too does the rate of the backward reaction. A general rate versus time graph, as shown below, illustrates this.



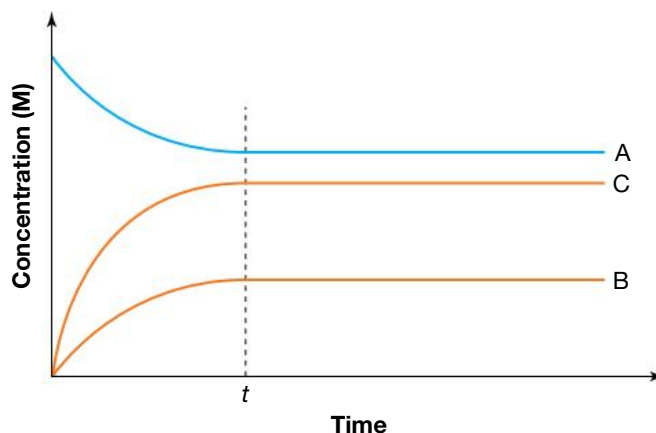
An example of a rate versus time graph

There will therefore be a net forward reaction until time t , when the two rates become equal and equilibrium is established. Thereafter, there will be no change in these rates as the net concentrations of reactants and products remain constant.

It should be noted that this equilibrium could just as easily be produced by mixing substances B and C together and allowing a net backward reaction to produce equilibrium. In this case, the graph would show a decreasing rate for the backward reaction and an increasing rate for the forward reaction until equilibrium is once again established.

It is also possible to represent this scenario using concentration versus time graphs. In the first instance above, such a graph might look like that shown below.

An example of a concentration versus time graph. The final concentrations of substances A, B and C depend on their initial concentrations, the stoichiometry in the equation and the value of the equilibrium constant.



The concentrations of the substances involved increase or decrease depending on whether they are produced or consumed. They also change by amounts that reflect the stoichiometry of the reaction. In this example, substance A decreases by the same amount that substance B increases as there is a 1 : 1 ratio between them in the equation. Substance C increases by twice the amount that substance B does, as there is a 2 : 1 ratio involved. To determine the equilibrium constant, simply substitute the final (equilibrium) concentrations of substances A, B and C into the equilibrium expression.

If this reaction has a catalyst added to it, the only change to this graph would be that time t would be lower. In other words, equilibrium is attained faster. The final concentrations of substances A, B and C, however, are not altered.

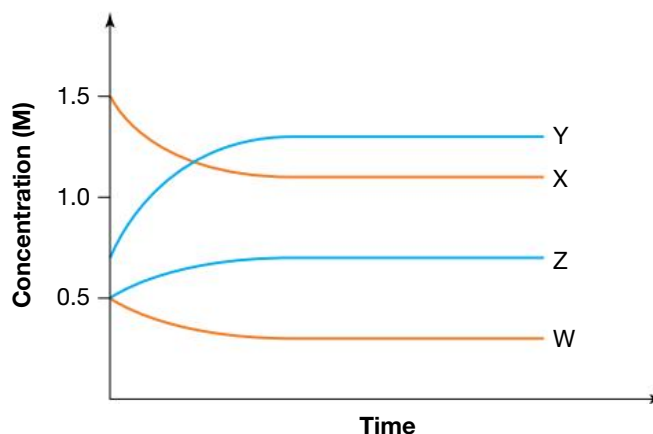
Concentration–time graphs are very useful when considering changes made to a reaction once it has reached equilibrium. This will be discussed later in the chapter.

Sample problem 6.7

The concentration versus time graph for an equilibrium reaction involving four substances (W, X, Y and Z) is shown below.

The general form of this equation is $aW + bX \rightleftharpoons cY + dZ$.

- If $a = 1$, determine the values of b , c and d for the above reaction.
- Calculate the value of the equilibrium constant for this reaction.
- What are the units for this equilibrium constant?



- Solution:** (a) To answer this, it is necessary to use the graph to determine the concentration of each component initially and again when the system reaches equilibrium. This shows a change in concentration for components W, X, Y and Z by 0.2, 0.4, 0.6 and 0.2 M respectively. The ratios of these numbers are 1, 2, 3 and 1. Therefore, the values of a , b , c and d (the coefficients of W, X, Y and Z respectively) are also 1, 2, 3 and 1. The equation is, therefore, $W + 2X \rightleftharpoons 3Y + Z$.
- (b) From the graph, we can ascertain the following equilibrium concentrations.

$$[W] = 0.3 \text{ M}, [X] = 1.1 \text{ M}, [Y] = 1.3 \text{ M}, [Z] = 0.7 \text{ M}$$

$$\begin{aligned} K_c &= \frac{[Y]^3[Z]}{[W][X]^2} \\ &= \frac{(1.3)^3(0.7)}{(0.3)(1.1)^2} \\ &= 4.2 \end{aligned}$$

(c) Units: $\frac{\text{M}^3 \times \text{M}}{\text{M} \times \text{M}^2} = \text{M}$

Revision question

6. Draw the concentration versus time graph for the reaction involved in sample problem 6.3, page 162.

Making changes to equilibrium mixtures — Le Châtelier's principle

An important consequence of the equilibrium law is that it is possible for every equilibrium mixture (belonging to a particular reaction) to be different. (Check tables 6.1 and 6.2 again to see this!) This is due to the fact that it is the whole equilibrium expression that is constant. Individual concentrations within this expression may vary quite considerably from one equilibrium situation to another. However, so long as the value of the whole expression is equal to the value of the equilibrium constant, a mixture will be at equilibrium.

This property can be put to use in the manufacture of some important chemicals. It is often possible to make these economically, despite the fact that the reactions from which they are formed have low equilibrium constants. By altering the concentrations of the other species involved in the equilibrium expression, it is often possible to maximise the production of the desired product, thereby increasing its yield.

To see how changes made to an equilibrium mixture affect its components, we often make use of an important predictive tool — **Le Châtelier's principle**. Essentially, this states:

Any change that affects the position of an equilibrium causes that equilibrium to shift, if possible, in such a way as to partially oppose the effect of that change.

Using this, we can make predictions about what will happen if we disturb a system that is at equilibrium.

There are three common ways in which a system at equilibrium might be disturbed:

- by adding or removing a substance that is involved in the equilibrium
- by changing the volume (at constant temperature)
- by changing the temperature.

We will now consider the effect of each of these in turn.

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Experiment 6.1 Investigating changes to the position of an equilibrium
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Le Châtelier's principle allows predictions to be made about certain changes and how an equilibrium mixture might be affected.

study on

Unit 3

AOS 2

Topic 2

Concept 7

Do more

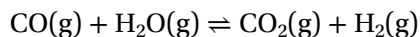
Le Châtelier's principle — adding or removing reactants or products

Adding or removing a substance that is involved in an equilibrium leads to a shift in equilibrium opposing this change.

An example of a concentration versus time graph where a substance has been added to the equilibrium mixture

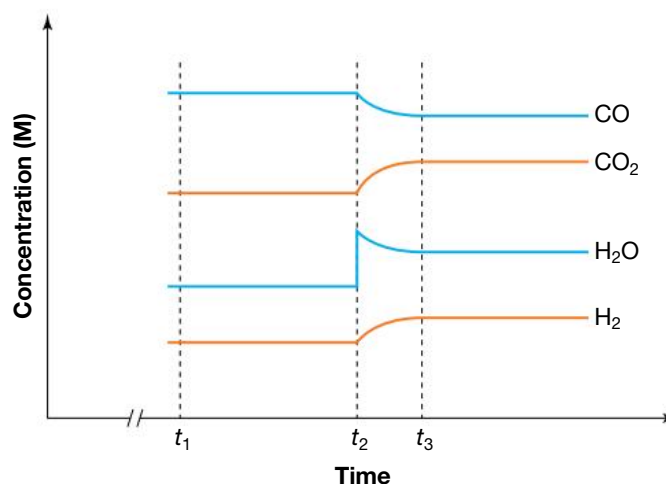
Adding or removing a substance that is involved in the reaction

Consider the reaction between carbon monoxide and water vapour to produce carbon dioxide and hydrogen.



If some extra water vapour is added to this system once it has attained equilibrium, the equilibrium will be disturbed. According to Le Châtelier's principle, the system will then react by trying to use up some of this extra water vapour in its efforts to get back to a new equilibrium position. The only way that this can be done is by causing some of the reactants to be transformed into products. Thus, more CO_2 and H_2 will be made as a result of consuming CO and H_2O . However, although all the amounts, and hence all the concentrations, involved will now be different from their original values, the *value of the equilibrium constant will remain unchanged* (the same value as before the water vapour was added).

A concentration versus time graph for this situation would look like the one below.



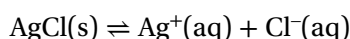
In this graph, time t_1 represents the time when equilibrium was reached for the first time. Time t_2 is when the extra water vapour was added, and time t_3 is when equilibrium is re-established for the second time. The equilibrium may be described as having been 'shifted to the right' (the forward reaction is favoured).

Changes like this, where a substance has been added or removed, can be identified from concentration-time graphs by a sudden spike or dip in only *one* of the substances involved.

A more informative way to describe these changes is in terms of reaction rates. At the first equilibrium, the rates of the forward and reverse reactions are equal. On addition of the water vapour, the forward reaction, for some time, becomes faster than the backward one. However, as more products are made, the two rates eventually become equal again and hence equilibrium is re-established.

When considering these reactions, the method of addition (continuous supply) or removal (ducting gas away) may be physical, or it may be achieved by chemical means. It makes no difference — the system always tries to oppose us in its efforts to re-attain equilibrium!

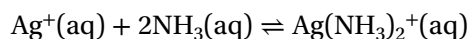
As a further example, this principle may be used to dissolve an otherwise insoluble salt. For example, silver chloride is only sparingly soluble in water. In other words, the equilibrium constant for the reaction:

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Changing the position of an equilibrium — adding reactant
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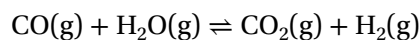
is very low ($K_s = 1.8 \times 10^{-10}$). This is an example of a heterogeneous equilibrium. In these cases, the equilibrium constant is usually denoted by K_s . As such, it is just a special type of K_c value. When writing the equilibrium expression for such reactions, the 'concentration' of any solid substances is always taken to be '1'.

If, however, a chemical is added to remove the Ag^+ ions, this reaction responds by trying to replace them. To do this, more AgCl(s) has to dissolve. If enough of the Ag^+ ions are removed, it is possible that all the silver chloride would dissolve. A suitable chemical for the removal of Ag^+ ions is ammonia, NH_3 . Ammonia achieves this by forming a complex ion according to the reaction:



Sample problem 6.8

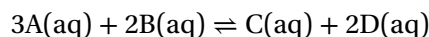
Predict the effect of (a) adding carbon dioxide and (b) removing hydrogen on the position of the equilibrium for the reaction:



- Solution:**
- (a) The reaction would partially oppose the addition of carbon dioxide by using up some of what was added. This is done by the backward reaction becoming temporarily faster than the forward reaction. The 'position' of the equilibrium would, therefore, 'shift to the left'. The back reaction is favoured.
 - (b) The reaction would partially oppose the removal of the hydrogen by attempting to replace some of it. This is achieved by the forward reaction becoming temporarily faster than the backward reaction. The 'position' of the equilibrium would, therefore, 'shift to the right'. The forward reaction is favoured.

Explaining Le Châtelier's principle mathematically

Consider the reaction that is represented by the equation:



Suppose that some extra substance A, is added to the equilibrium mixture, and that we wish to predict the effect on substance D.

For this reaction we can write two expressions:

$$Q = \frac{[\text{C}][\text{D}]^2}{[\text{A}]^3[\text{B}]^2} \text{ and } K_c = \frac{[\text{C}][\text{D}]^2}{[\text{A}]^3[\text{B}]^2}$$

where the concentrations for the equilibrium constant K_c are equilibrium concentrations but the concentrations for the reaction quotient Q can be at *any stage* during the reaction. If $Q = K_c$, equilibrium has been established.

Immediately after the addition of substance A, the value of Q is decreased, and Q is therefore less than K_c . The reaction is, therefore, no longer at equilibrium, and the value of Q must increase for equilibrium to be re-established, and once again $Q = K_c$. There needs to be a higher concentration of products and a lower concentration of reactants. This can be achieved by a net forward reaction — the rate of the forward reaction becomes greater than the rate of the backward reaction, and the equilibrium therefore shifts to the right. Essentially, $K_c = \frac{[\text{products}]}{[\text{reactants}]}$. Thus, if $Q < K_c$, $[\text{reactants}] > [\text{products}]$ and,

to re-establish equilibrium, [products] must increase. Therefore, this means a net forward reaction.

This is exactly what is predicted by Le Châtelier's principle. After the sudden increase in substance A, some of it is used by the net forward reaction predicted above.

The effect of changing volume can be predicted in the same way.

The effect of changing volume

Changing volume affects the total concentration (or pressure) of a reaction system. In re-establishing equilibrium, the consequent change is to alter the total number of particles present. This occurs so that the effect of the original volume change is partially offset.

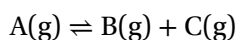
If a reaction has the same number of moles on each side of its equation, it is not displaced from equilibrium when a volume change is made. Therefore, a volume change has no effect.

When considering changes in volume (at constant temperature), it is important to think of the effect on the total concentration of all the species present. Le Châtelier's principle can then be interpreted in terms of how the system changes the total number of particles present to produce an opposing trend in total concentration.

Three situations present themselves:

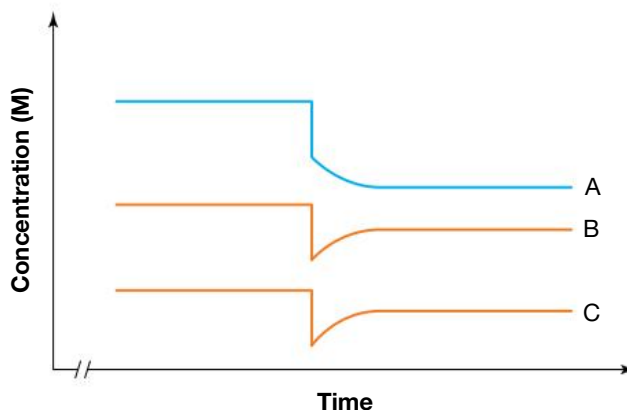
1. The change in volume causes an increase in the total concentration of particles. To decrease this, the system reacts in the direction that produces fewer particles. (Fewer particles, of course, means a lower overall concentration, in line with the opposition predicted by Le Châtelier's principle.)
2. The change in volume causes a decrease in the total concentration of particles. To increase this concentration, the system must react in the direction that produces more particles if it is to re-establish equilibrium.
3. Although the change in volume affects the total concentration, the system cannot change the number of particles present. This situation occurs when the total number of moles on the left-hand side of the equation equals the number of moles on the right-hand side. *Mathematically, it can be shown that a volume change for such a reaction does not disturb the equilibrium.*

As an example of situation 1, consider the reaction represented by:



It might be predicted that an increase in volume, such as by dilution (and therefore a decrease in total concentration or pressure), would lead to an increase in the total number of particles as the reaction attempts to re-build the total concentration. In this case, this can be achieved if the equilibrium shifts to the right (forward reaction).

On a concentration-time graph, this would look like the figure below.



A concentration-time graph illustrating the effect of increasing the volume of the reaction $\text{A(g)} \rightleftharpoons \text{B(g)} + \text{C(g)}$

A change in volume of an equilibrium mixture is identified on these graphs as a sudden spike or dip involving all substances.

eLesson

Changing the position of an equilibrium — gas pressure
eles-1672

A special note about gases

For a change in volume at constant temperature, the universal gas equation allows a 'concentration' interpretation to be replaced by a 'pressure' interpretation. Therefore:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

Since $\frac{n}{V}$ is concentration, and $R \times T$ is constant, we see that pressure is proportional to concentration.

For gaseous reactions, volume changes may also be interpreted in terms of partial pressures, rather than concentrations.

Sample problem 6.9

The following gaseous system is set up and allowed to reach equilibrium.

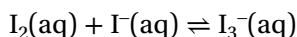


What would be the effect on the amount of bromine present if the volume is then increased?

Solution: An increase in volume immediately decreases the concentration (or pressure) of all substances present, and hence the total concentration (or pressure). The system would then try to offset this effect by making a greater number of moles. This can be achieved by the forward reaction (which turns two moles on the left-hand side into three moles on the right). Therefore, when equilibrium is re-established, more bromine would be present than at the earlier equilibrium.

Sample problem 6.10

Consider the reaction represented by the equation:

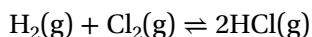


What would be the effect on the amount of I_3^- caused by increasing the volume by adding more water?

Solution: Addition of water immediately lowers the total concentration. The system responds by increasing the number of moles in an effort to compensate. The backward reaction, therefore, is the one that brings the system back to equilibrium with a consequent decrease in the amount of I_3^- present.

Sample problem 6.11

Would a volume change affect the following reaction?



Solution: No. The equation has 1 mole of H_2 and 1 mole of Cl_2 on the left-hand side. The right-hand side has 2 moles of HCl . As the total number of moles on each side is the same, a volume change would not disturb the equilibrium.

Revision question

- The same change in volume may cause one reaction to shift to the right (forward reaction) and another to shift to the left (back reaction). Explain why this is so.

Changing temperature is the only change that alters the actual value of the equilibrium constant. If temperature increases, the value of K_c increases if the reaction is endothermic, but decreases if the reaction is exothermic.

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Experiment 6.2 Temperature and the equilibrium constant
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The effect of changing temperature

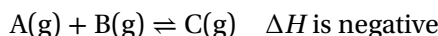
Of all the possible ways that we might change an equilibrium mixture, *this is the only method that actually alters the value of the equilibrium constant*. Temperature is the only factor that changes the value of K_c , because changing the temperature also changes the energy available to the system.

At a particular temperature, the system has a certain amount of energy, which is distributed between all the species present. We use the equilibrium expression to describe the concentrations of all species once they have settled on a way to share that energy, and we interpret the value of K_c (whether large or small) as sharing in favour of reactants or products.

Varying the concentration of a species (n or ν) causes a redistribution of the available energy. A different equilibrium position is reached. However, since the available energy remains the same, the value of K_c is the same.

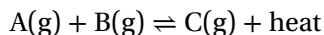
Changing the temperature changes the total amount of energy in the system. Hence, K_c has a different value. How this value responds to temperature change depends on whether the reaction is exothermic or endothermic. Classifying an equilibrium reaction as exothermic or endothermic relates, by convention, to the forward reaction as written in the equation. An endothermic reaction absorbs heat and has a positive ΔH value. An exothermic reaction evolves heat and has a negative ΔH value.

If we consider an exothermic reaction, typified by the thermochemical equation:



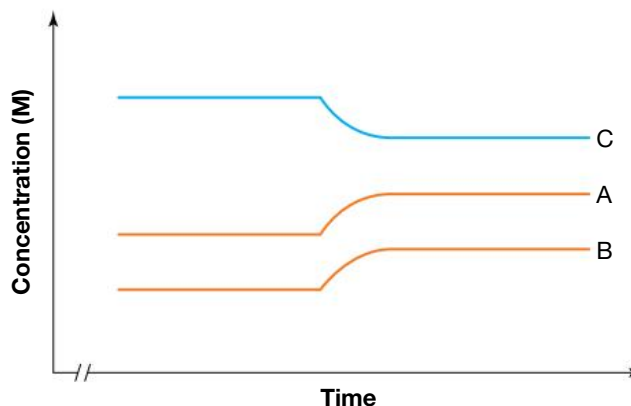
an increase in temperature requires the application of heat. Le Châtelier's principle would, therefore, predict that the system tries to absorb some of this added heat. Hence, the backward reaction is favoured as it is endothermic. A and B are produced at the expense of C, lowering the *value* of the equilibrium constant. Thinking mathematically, when the value of the denominator in K_c increases, the value of K_c decreases.

This equation can also be written as:



where heat can be treated as a product.

For the reaction above, the concentration–time graph might look like that below.



A typical concentration–time graph showing the effect of increasing temperature on the equilibrium $\text{A(g)} + \text{B(g)} \rightleftharpoons \text{C(g)}$, where ΔH is negative

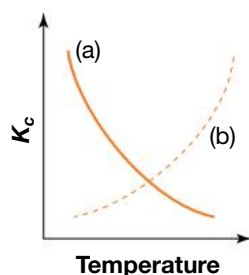
A change in temperature can be identified on concentration–time graphs by its effect on the concentrations without an obvious sudden change to any of the substances involved.

In an endothermic reaction under the same conditions, the forward reaction would oppose the addition of heat. Upon re-establishing equilibrium, the value of the equilibrium constant would, therefore, be higher.



The equilibrium reaction between brown NO_2 and colourless N_2O_4 is affected by temperature. These tubes initially contained equal amounts of gas; the tube on the left is being cooled.

- Thus, in summary:
- If a reaction is exothermic, an increase in temperature decreases the equilibrium constant because more reactants are favoured.
 - If a reaction is endothermic, an increase in temperature increases the equilibrium constant because more products are favoured.

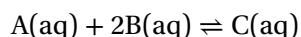


- (a) Exothermic reactions ———
(b) Endothermic reactions - - - - -

The general relationship between K_c and temperature for (a) exothermic reactions and (b) endothermic reactions

Sample problem 6.12

Suppose that, in the reaction:



substance C has an easily detected red colour.

If it is observed that heating the equilibrium mixture causes the red colour to fade, what is the resulting effect on the K_c value? Is this reaction an exothermic or an endothermic reaction?

Solution: The fading of the red colour implies that there has been 'a net backward reaction'. The value of K_c will, therefore, be lower.

As K_c has dropped as a result of an increase in temperature, this means that the reaction (as written above) must be an exothermic reaction.

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Unit 3

AOS 2

Topic 2

Concept 9

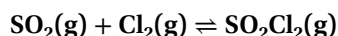


See more

Le Châtelier's principle — change in temperature

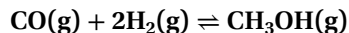
Revision questions

8. For the reaction:



predict the effect on the equilibrium mixture caused by the addition of some extra chlorine gas.

9. A method for making methanol involves the following reaction.



Predict the effect on the amount of methanol produced if the equilibrium mixture is compressed.

10. To increase the product yield in an endothermic reaction, should the temperature be raised or lowered?

The yield of a chemical reaction

There are many situations in chemistry where we want to know how much reactant has been converted into product. Chemists use the concept of reaction **yield** to express this idea in quantitative terms. The yield of a reaction is often quoted as a percentage and is defined as follows.

$$\text{yield (\%)} = \frac{\text{actual mass obtained}}{\text{theoretical maximum mass}} \times 100$$

The yield of a reaction can be calculated using the formula:
yield (%) =

$$\frac{\text{actual mass obtained}}{\text{theoretical maximum mass}} \times 100$$

Equilibrium and rate must be considered when producing chemicals on a large scale.

The equilibrium reactions we have been studying in this chapter are clearly examples of reactions that display yields of less than 100%. It should be remembered, however, that there are often additional reasons why a given reaction does not achieve a 100% yield. Some of these may be practical (to do with the method by which the chemical is made). Another situation might be a very slow reaction that has not been given enough time to either reach equilibrium or go to completion.

In equilibrium work, and in the design of large-scale manufacturing techniques for chemicals produced from equilibrium reactions, the use of Le Châtelier's principle, together with a measurement of yields, is an important consideration.

Le Châtelier's principle and industrial chemicals

As mentioned earlier in this chapter, the manufacture of some important chemicals involves allowing for the fact that, at certain desired temperatures, the values of their equilibrium constants are low. Examples of such chemicals are ammonia, nitric acid, HNO_3 , and sulfuric acid, H_2SO_4 .

To make these chemicals on a large scale, the chemical engineer must have a sound knowledge of equilibrium principles and also of rate principles. In designing a plant, the engineer will ultimately be trying to:

- maximise the *yield* of the desired product by applying Le Châtelier's principle to make as much of the chemical as possible
- produce the desired chemical at an acceptable *rate* — it has to be made quickly enough to satisfy market demand if the plant is to be economical
- balance the above two requirements against other variables, such as plant operating costs, to ensure that the whole process is as economical and safe as possible.

The final design of such a plant is often a compromise between these factors.

Making ammonia — applying equilibrium and rate principles in industry

Ammonia is a widely used and very important chemical. Besides having a number of direct uses, it is also a precursor for the manufacture of nitric acid and many fertilisers. Current world production is close to 150 million tonnes, making it the second most widely produced chemical in the world. From this production, close to 80% is used to make fertilisers. Table 6.4 shows a range of nitrogen-based fertilisers.

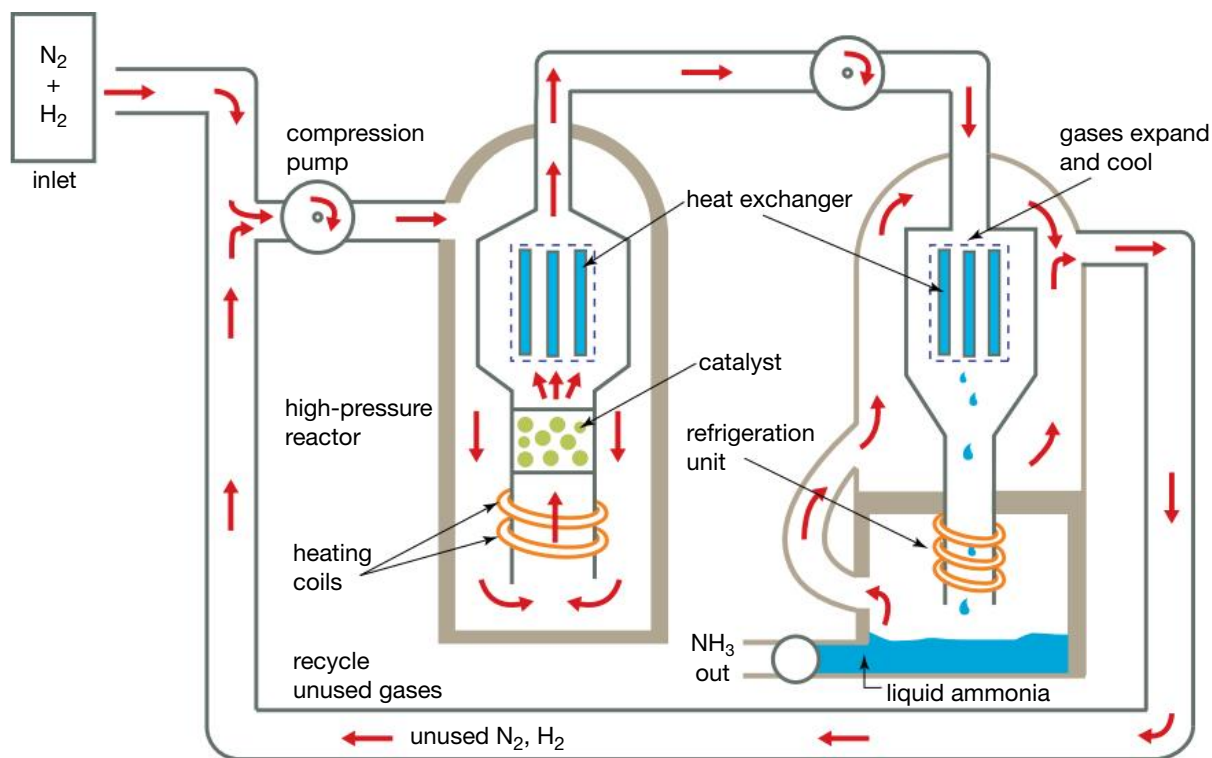
TABLE 6.4 World consumption of nitrogenous fertilisers

Type of fertiliser	Composition	Consumption (% of total)
ammonium sulfate	$(\text{NH})_4\text{SO}_4$	38
'nitro-chalk'	NH_4NO_3 with chalk	16
ammonia	NH_3	14
ammonium nitrate	NH_4NO_3	12
calcium cyanamide	CaCN_2	5
calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	5
sodium nitrate	NaNO_3	5
urea	$\text{CO}(\text{NH}_2)_2$	5

World food production has increased dramatically since the availability of large amounts of nitrogen-based fertilisers. Because of this, ammonia now has a critical role in feeding the world's ever-growing population.

Ammonia is also involved in the manufacture of explosives, fibres, plastics, dyes and pharmaceuticals.

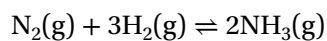
Virtually all the ammonia required in the world today is made by the Haber process.



The Haber process makes ammonia from hydrogen and nitrogen gas. First, the gases are cleaned (top left), and then they are cycled through the reaction tower, heater and catalyst beds. A cooling loop at the base of the reaction tower condenses the ammonia into a liquid that is removed. High-pressure reactors are expensive to run, so many industrial plants use lower pressures to increase the life of the reactor and reduce the chance of equipment failure.

The Haber process

The Haber process is a single-step process in which nitrogen and hydrogen are reacted according to the equation:



In the Haber process, there is a conflict between rate and extent with respect to the temperature required. However, by careful consideration of other factors that affect rate and the position of equilibrium, the Haber process is still able to make ammonia economically.

This reaction is a good example of a dilemma often faced by a chemical engineer. At normal temperatures, the value of the equilibrium constant is quite high. The problem, however, is that the rate of reaction is very slow. In other words, the mixture of nitrogen and hydrogen is metastable. If, however, the temperature is increased to bring about a better rate, the yield of ammonia quickly begins to suffer. This is because the above reaction is exothermic and, as temperature is increased, the value of its equilibrium constant decreases.

Two of the most important industrial considerations (yield and rate) are therefore in conflict. So, the ultimate design of the plant and its operating conditions must reflect a compromise between these factors.

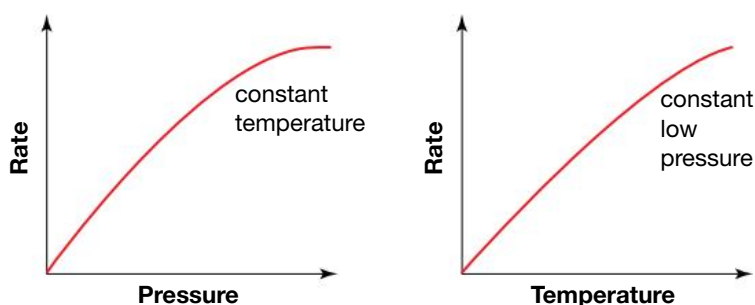
A closer look at these factors, however, reveals that we can lessen the effect of this compromise in a number of ways. These are:

1. Use a suitable catalyst to help obtain the rate required. This means that the temperature needed is lower than that needed without a catalyst. The use of a lower temperature increases the yield by increasing the value of the equilibrium constant. A lower temperature reduces the rate, but this can be compensated for by using a catalyst, which increases the rate.
2. Compress the gases so that the reaction is carried out at high pressure. Le Châtelier's principle predicts that, if a system is pressurised, it tries to reduce that pressure. Consequently, there should be a tendency to reduce the number of particles present. In this case, this means that the reaction proceeds to the right, as the forward reaction converts 4 molecules into 2 molecules, thus favouring the production of ammonia.
3. Separate the ammonia from the unreacted nitrogen and hydrogen in the exit gases from the converter. This nitrogen and hydrogen can then be recycled and may be converted into more ammonia.

In the operation of a typical plant, nitrogen and hydrogen are mixed in the 1 : 3 ratio required by the equation. The gases are then compressed to about 250 atm and heated to about 500 °C. (These precise conditions may vary slightly from one plant to another.) The gases then pass into the converter. This is a huge reinforced steel cylinder containing 7 to 8 tonnes of pea-sized catalyst beads. The catalyst most often used is an iron catalyst made from iron oxide, Fe_3O_4 , with traces of aluminium oxide and potassium oxide.

Typical conditions for making ammonia using the Haber process are a temperature of about 500 °C (at this temperature the rate is fast enough but the exothermic reaction still proceeds forward) and a pressure of around 250 atmospheres (this forces the equilibrium reaction to the product side). A catalyst based on iron oxide is used.

High pressure and temperature result in an increase in the rate of reaction.



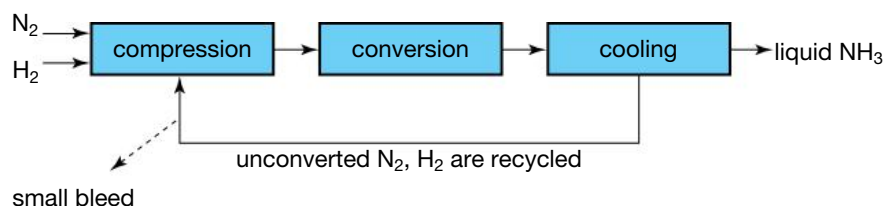
When the gases leave this chamber they contain about 20% ammonia. By cooling the mixture, the ammonia can be liquefied and separated. The unreacted nitrogen and hydrogen can then be recycled so that ultimately they pass through the converter again. This is an example of green chemistry.

The energy costs in the operation of such a plant are one of its most important overheads. With careful planning, energy costs can be minimised. In this case, the actual formation of the ammonia from its elements is an exothermic process. The heat generated from this reaction can be made use of elsewhere in the plant, rather than just being allowed to go to waste. Heat exchangers are therefore used. For example, the incoming cold nitrogen/hydrogen mixture can be passed over pipes containing the hot gases that exit from the converter. The resultant transfer of heat helps to heat the incoming gases and cool the exit gases.

Other considerations

Finally, it is worth noting that there are further compromises in operation here. Better yields of ammonia might be obtained by using higher pressures. However, this necessitates the use of more powerful pumping equipment and stronger reaction vessels to withstand the extra pressure. Economically, it is not worthwhile to do this, because the extra ammonia produced does not offset the extra costs involved in building such a plant.

The diagram below shows a simplified flowchart for the Haber process.



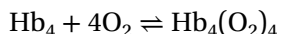
An important biological application of equilibrium

An important concept in biology is that of homeostasis. This is the ability of an organism to maintain a fairly constant internal environment, despite changes to the outside environment. Such systems in the human body are extremely important to our wellbeing and continued survival.

We have many different ways of maintaining homeostasis, most of which include chemical processes at equilibrium. Oxygen transport is one such example.

Transport of oxygen by the blood

Although oxygen is soluble in water, this solubility is not high enough to enable the blood to supply adequate amounts of oxygen to our cells. The blood, therefore, transports oxygen by a different mechanism — the red blood cells. These cells contain a special protein called **haemoglobin**, which can combine with oxygen to form oxyhaemoglobin. This is a reversible reaction that can be represented by the equation:



where the symbol Hb_4 represents the very complex haemoglobin molecule.

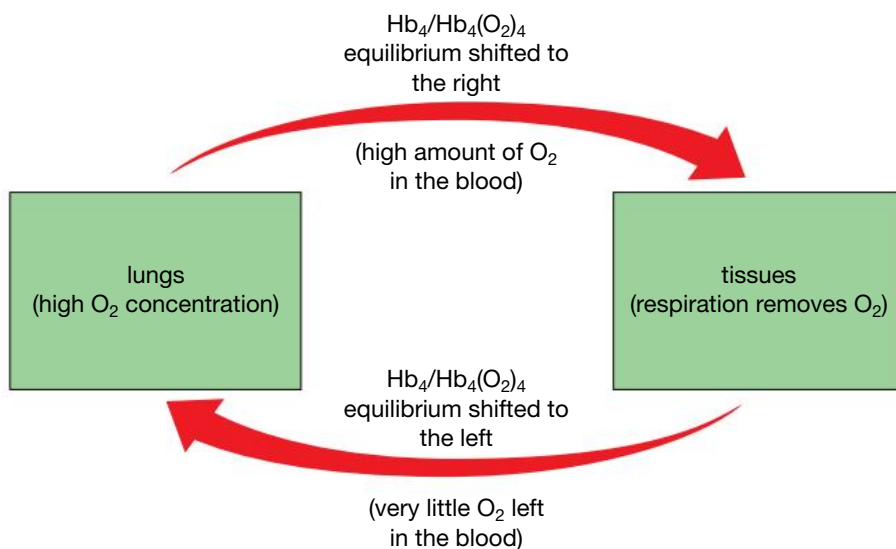
The haemoglobin–oxyhaemoglobin system is an equilibrium that responds to changes in the concentration of oxygen. These changes are necessary to transport oxygen around the body and to recirculate haemoglobin molecules. Le Châtelier's principle may be used to explain the operation of this system.

Red blood cells carry oxygen around our bodies.



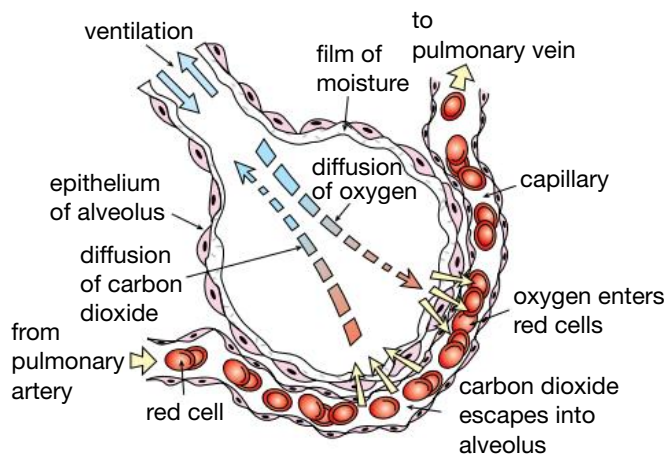
The position of this equilibrium is such that normal bodily variations in oxygen concentration can push it in either direction. When blood enters the lungs, it is exposed to a high concentration of oxygen. As oxygen is a reactant in this equation, Le Châtelier's principle predicts that more oxyhaemoglobin is produced. The red blood cells thus become 'loaded' with oxygen. This

mechanism allows much more oxygen to be transported around the body than by dissolving it in the plasma alone.



The transport of oxygen around the body relies on how the differing conditions in the lungs and in the tissues affect the haemoglobin–oxyhaemoglobin equilibrium.

However, when the blood reaches the cells, there is a much lower oxygen concentration because it is used in cellular respiration. In response to this removal of oxygen by respiration, the reaction on the previous page responds by moving to the left in an effort to replace this oxygen. The oxyhaemoglobin then decomposes back to haemoglobin, its oxygen being unloaded for use by the cells. The haemoglobin molecules then return to the lungs to start the cycle again.



Exchange of gases in an alveolus, part of the lungs. The alveoli are the structures in the lungs that transfer gases into and out of the blood supply.

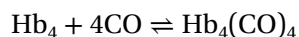
Carbon monoxide poisoning

Carbon monoxide is an odourless and very poisonous gas. As we have seen in chapter 2, it is produced from the incomplete combustion of fossil fuels — typically in situations where the supply of oxygen to the combustion process is limited. This lack of odour makes it particularly dangerous as it can be inhaled

The haemoglobin-carboxyhaemoglobin system is not sensitive to changes that normally occur in the human body because it has a very high equilibrium constant. This means that less and less haemoglobin is available for oxygen transport, resulting in lack of oxygen in blood received by the tissues.

without a person realising it and can quickly lead to unconsciousness. Typical situations in which this may occur include leaking car exhausts, improperly maintained central heating units and the use of outdoor appliances such as camping heaters and barbeques in enclosed spaces.

Carbon monoxide is so poisonous because the reaction between carbon monoxide and haemoglobin:



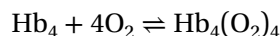
is similar to that between oxygen and haemoglobin. This sets up a competing equilibrium with the oxygen-haemoglobin system. However, an important difference is that the position of this equilibrium lies much further to the right. The equilibrium constant for this reaction is about 20 000 times greater than that for the oxygen-haemoglobin system. If there is carbon monoxide in the lungs, carboxyhaemoglobin will readily form. When these blood cells reach the respiring cells, the reaction cannot be reversed. These blood cells are thus effectively removed from the 'pool' available to carry oxygen. If this happens to enough of them, consequences can be fatal. A person would die of oxygen starvation, even though there might still be a plentiful supply of oxygen in their lungs.

Treating victims of carbon monoxide poisoning

The level of carbon monoxide in the blood that can cause death is surprisingly low. The reason for this is its ability to compete much more effectively than oxygen for the available haemoglobin.

If a victim of carbon monoxide poisoning is discovered soon enough, giving them oxygen-rich air to breathe may reverse the dangerous changes that have taken place in their red blood cells. This treatment once again relies on competing equilibria and Le Châtelier's principle.

The two equations involved are:



and



The extra oxygen has two effects. First, it pushes the first equilibrium further to the right, thus making more efficient use of the few uncombined haemoglobin molecules that remain. The second effect follows from the first. As haemoglobin is used up by this extra oxygen, a reactant is effectively being removed from the second equilibrium. Despite

its higher equilibrium constant, this reaction is forced in the backward direction to replace this haemoglobin. Thus, the carboxyhaemoglobin complex is encouraged to decompose and, in so doing, it frees up the haemoglobin for normal oxygen transport.



Carbon monoxide fumes are a serious problem in traffic-congested cities.

Chapter review

Summary

- Many chemical reactions have lower yields than might otherwise be expected. They do not go to completion. Such reactions are called equilibrium reactions. They can also be called reversible reactions.
- Equilibrium reactions always reach a point at which no further change seems to be occurring. Such reactions have not stopped, however. Rather, the rate of the forward reaction has become equal to the rate of the backward reaction. This is referred to as the dynamic nature of the equilibrium state.
- At equilibrium, it is possible to write a fraction involving the equilibrium concentrations of all species present, which is related to the stoichiometry of the reaction. This fraction always has a constant value (at a particular temperature) and is given the symbol K_c . This is called the equilibrium law.
- It is also possible to write and evaluate this concentration fraction at *any stage* of a reaction, in which case, it is usually given the more general symbol Q . If the value obtained for Q is not equal to K_c , the reaction is not at equilibrium. The changes taking place as the reaction seeks to attain equilibrium can be predicted by comparing the values of K_c and Q .
- The magnitude of the equilibrium constant, K_c , gives us an indication of the extent of an equilibrium reaction.
- The equilibrium constant has units that depend on the equation that it refers to. For some reactions, it is also possible that it has no units.
- Equilibrium reactions may be represented by rate versus time graphs and concentration versus time graphs.
- Quantitative predictions may be made by performing calculations based on the equilibrium law.
- There are a number of ways that changes may be made to a reaction that is at equilibrium. These include the addition or removal of a participating substance, dilution, pressure changes (through compression or expansion) and temperature changes.
- Le Châtelier's principle may be used to predict the effect of a change to a mixture that is at equilibrium.
- The yield of a chemical reaction is usually expressed as a percentage that compares the actual amount obtained with the theoretical maximum amount possible.
- Equilibrium reactions are important in many situations. Many useful chemicals are manufactured industrially using such reactions. They are also

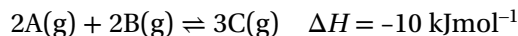
important biologically, as illustrated by the way that oxygen is transported around the body using haemoglobin.

- Carbon monoxide poisoning involves competing equilibrium reactions. Carbon monoxide competes very effectively with oxygen, resulting in a drastic reduction in the amount of haemoglobin available for oxygen transport.

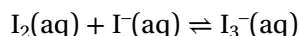
Multiple choice questions

1. A reaction has an equilibrium constant, K_c , of magnitude 2.56×10^{-7} . From this we can say that:
 - A there will be minimal conversion of reactants into products
 - B equilibrium will be established very quickly
 - C equilibrium will be established very slowly
 - D the backward reaction will have a faster rate than the forward reaction.

Use the following information to answer questions 2–4. An equilibrium reaction is represented by the thermochemical equation:



2. The correct expression from which to calculate the equilibrium constant for this reaction is:
 - A $\frac{[A][B]}{[C]}$
 - B $\frac{[A]^2[B]^2}{[C]^3}$
 - C $\frac{[C]^3}{[A]^2[B]^2}$
 - D $\frac{[C]}{[A][B]}$
3. The units for the equilibrium constant for this reaction are:
 - A M
 - B $M^{\frac{1}{2}}$
 - C M^{-1}
 - D $M^{\frac{1}{2}}$
4. If the temperature at which this reaction is carried out is lowered, the value of K_c will:
 - A increase
 - B decrease
 - C remain the same
 - D change in a manner related to the total number of particles on each side of the equation.
5. When molecular iodine is mixed with iodide ions, an equilibrium is set up as triiodide ions are produced. The equation for this process is:

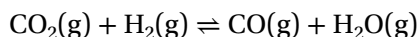


Suppose that, once this equilibrium is established, some iodine is removed and replaced by exactly

the same amount of radioactive iodine. After some time, we would expect that:

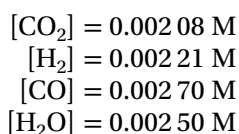
- A** the overall total level of radioactivity would increase
- B** radioactivity would be detected in I_2 , I^- and I_3^-
- C** radioactivity would be detected in I_2 and I_3^- , but not in I^-
- D** radioactivity would be detected only in the I_2 .

Use the following information to answer questions 6–8. The reaction represented by the equation:



has an equilibrium constant, K_c , of 1.58 at 990 °C.

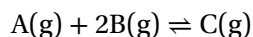
In an experiment, the concentrations of these four substances were measured at a particular time. The values obtained are shown below.



6. Which of the following statements is true of this reaction at this time?
 - A** There is a net forward reaction.
 - B** There is a net backward reaction.
 - C** The rate of the backward reaction is faster than the rate of the forward reaction.
 - D** The reaction is at equilibrium.
7. After equilibrium was established, the volume of the container was increased. Which of the following statements about the effect of this change is true?
 - A** There will be no effect on the concentrations of any of the substances.
 - B** There will be no effect on the amounts of any of the substances.
 - C** The concentration of carbon monoxide will increase.
 - D** The amount of carbon monoxide will increase.
8. In another experiment involving the same reaction (and at the same temperature), a mixture was allowed to reach equilibrium. At this point, the concentrations of CO_2 , H_2 and CO were 0.0046 M, 0.000 67 M and 0.0022 M respectively. The concentration of H_2O would therefore have been:
 - A** 0.0009 M **C** 0.0022 M
 - B** 0.0016 M **D** 0.0044 M.
9. If some product is removed from a system that is at equilibrium:
 - A** the value of the equilibrium constant would decrease
 - B** a net backward reaction would result
 - C** the rate of the backward reaction would increase
 - D** extra product would be produced to re-establish the equilibrium.

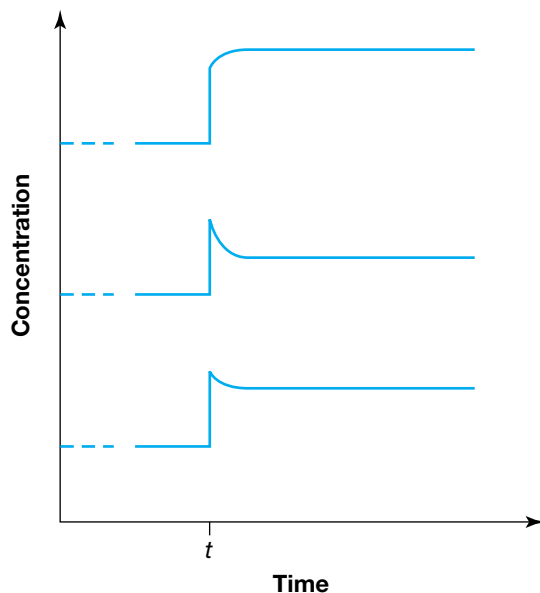
Use the following information to answer questions 10 and 11.

A reaction between the chemicals A, B and C is allowed to reach equilibrium. The equation for this reaction is:



At a certain time, t , a change is made.

The graph below shows the concentration of each of these substances before and after this change.



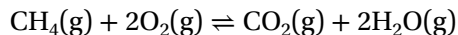
10. What type of change was made at time t ?
 - A** The addition of one of the substances
 - B** The removal of one of the substances
 - C** An increase in volume
 - D** A decrease in volume
11. From top to bottom, the graphs refer to the substances:
 - A** C, B, A
 - B** A, B, C
 - C** B, A, C
 - D** C, A, B.

Review questions

Equilibrium and the equilibrium law

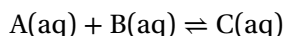
1. What is the difference between a reversible reaction and an irreversible reaction?
2. What is the difference between the rate of a reaction and the extent of a reaction?
3. Using radioactive tracers (small amounts of radioactive isotopes), it is possible to demonstrate the dynamic nature of equilibrium. Describe how such an experiment may be performed, choosing a specific example to illustrate your answer.

4. It has been estimated that the reaction between methane and oxygen represented by the equation:



has an equilibrium constant, at room temperature, of 10^{140} .

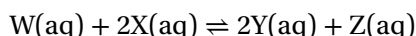
- What does this value suggest about the extent of this reaction?
 - Do you think the use of the $\rightleftharpoons$ arrow is justified in the above equation?
5. Write an expression for the equilibrium constant for each of the following equations.
- $\text{Cl}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightleftharpoons 2\text{ClF}_3(\text{g})$
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
 - $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + 2\text{Cl}_2(\text{g})$
 - $2\text{COF}_2(\text{g}) \rightleftharpoons \text{CF}_4(\text{g}) + \text{CO}_2(\text{g})$
 - $\text{P}_4(\text{g}) + 10\text{F}_2(\text{g}) \rightleftharpoons 4\text{PF}_5(\text{g})$
6. For each of the reactions shown in question 5, state the units for K_c .
7. Two students, Isla and Colin, were discussing the use of M as a unit. Colin stated that K_c can't have these units as M is a unit of concentration. However, Isla maintained that, although it is a unit of concentration, K_c could also sometimes have this unit. Who is correct? Explain.
8. Consider the reaction:



which is being investigated at constant temperature.

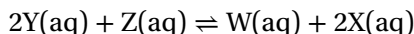
Explain why the concentrations of A, B and C can vary enormously from one investigation to another, yet each time they are at equilibrium.

9. An equilibrium reaction is represented by the following equation:

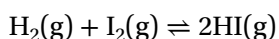


The magnitude of the equilibrium constant at a particular temperature is 6.3.

- What are the units of the equilibrium constant?
- Calculate the value of the equilibrium constant for the reaction:



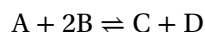
10. An equilibrium mixture consisting of hydrogen, iodine and hydrogen iodide was analysed. It was found that 1.1 mol of hydrogen and 3.3 mol of hydrogen iodide were present in a 3.0 L container at a temperature of 600 K.
- If the value of the equilibrium constant, K_c , is 49 for the reaction:



calculate the concentration of iodine.

- Why is the temperature specified in this question?

11. The reaction represented by the equation:



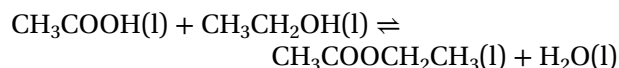
was investigated by mixing various amounts of these four substances. After a period of time, the concentration of each species was measured. This procedure was repeated a number of times to give the results shown in the following table.

Experiment	[A]	[B]	[C]	[D]
1	1.7	1.2	2.5	2.8
2	1.4	0.9	2.3	2.7
3	1.6	1.1	2.3	2.4
4	1.5	0.9	2.6	2.8
5	1.4	1.0	2.5	2.7

At the temperature of this experiment, it is known that the value of the equilibrium constant is 6.0.

In which of the above experiments was the reaction mixture at equilibrium when it was analysed?

12. The formation of ethyl acetate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$, is represented by the equation:



The value of K_c for this reaction is 4.

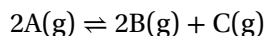
A number of experiments were conducted in which various amounts of these chemicals were mixed and allowed to react for varying periods of time. The results are tabulated below.

Experiment	$[\text{CH}_3\text{COOH}]$	$[\text{CH}_3\text{CH}_2\text{OH}]$	$[\text{CH}_3\text{COOCH}_2\text{CH}_3]$	$[\text{H}_2\text{O}]$
1	1	1	1	1
2	4	0.5	2	4
3	1.5	1	3	1.5
4	0.5	1	1.5	2
5	1	1.5	2	3
6	3	2	1.5	1

- In which experiments had equilibrium been achieved by the time of the analysis?
- For those not at equilibrium, in which direction would the reaction proceed to establish equilibrium?

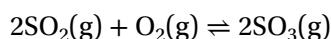
13. Hydrogen and iodine combine at 450 °C to make hydrogen iodide. The value of the equilibrium constant at this temperature is 64. In a particular experiment, 2.5 mol of hydrogen and 1.3 mol of iodine were found to be present at equilibrium in a 2.0 L vessel. Calculate the mass of hydrogen iodide present.

14. In a reaction specified by the equation:



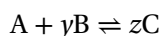
3.5 mol of substance A is initially introduced into a 500 mL reaction vessel and allowed to reach equilibrium. At this stage, its concentration was found to be 2.0 M. Calculate the value of the equilibrium constant for this reaction.

15. In a 10 L vessel, 0.20 mol of SO₂, 0.40 mol of O₂ and 0.70 mol of SO₃ were mixed and allowed to come to equilibrium. Upon establishment of equilibrium, it was found that 0.30 mol of SO₃ remained. Calculate the value of the equilibrium constant for this reaction, given that the equation is:

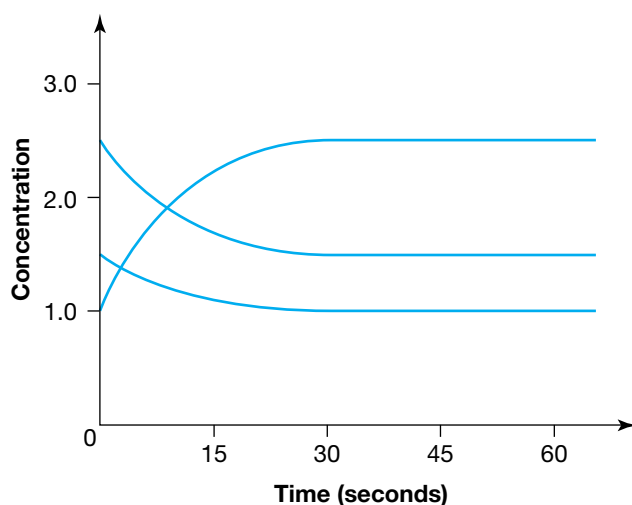


16. Upon dissolving in water, the sugar α-D-glucose undergoes conversion into an isomer called β-D-glucose. This process is called mutarotation and reaches equilibrium when 63.6% of the original α-D-glucose has been converted. Calculate the value of the equilibrium constant for this process.
17. In an experiment, the equilibrium established between substances A, B and C was investigated. Certain initial concentrations of each substance were mixed and then allowed to come to equilibrium.

The reaction between these three substances may be represented by the equation:



The changes in concentration are shown in the graph below.



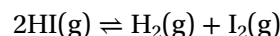
- (a) Identify which line belongs to which substance.
- (b) During the first 30 seconds of the experiment, how does the rate of the forward reaction compare with the rate of the backward reaction?
- (c) After 30 seconds, how does the rate of the forward reaction compare with the rate of the backward reaction?
- (d) From the graph, identify the values of y and z in the equation.
- (e) Calculate the equilibrium constant for this reaction.

Making changes to equilibrium mixtures

18. Predict the effect of the stated change on each of the systems represented by the equations below.

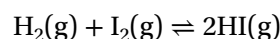
- (a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
(adding methanol)
- (b) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
(increasing the pressure)
- (c) $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$
(increasing temperature, given that the reaction is exothermic)
- (d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(removing chlorine)

19. Pure hydrogen iodide is a gas that partially decomposes when heated according to the equation:

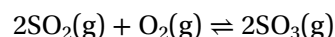


At 500 K, the equilibrium constant for this reaction is 6.25×10^{-3} . At 600 K, the equilibrium constant is 2.04×10^{-2} .

- (a) Is this reaction exothermic or endothermic?
- (b) Calculate the value of the equilibrium constant at 500 K for the reaction:

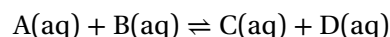


20. A student was asked to explain why the use of increased pressure should favour the formation of sulfur trioxide, SO₃, according to the equation:



As part of her answer, she stated that '... the increased pressure will cause the system to move to the right. The resulting increase in the equilibrium constant means that there will be more SO₃ present.' Criticise the chemical accuracy of her answer.

21. Suppose that compounds A and B react according to the following equation.

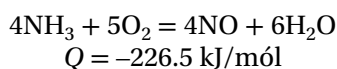


- (a) If 500 mL of an equilibrium mixture from this reaction is analysed and found to contain 0.010 mol of A, 0.020 mol of B, 0.010 mol of C and 0.040 mol of D, calculate the value of the equilibrium constant.

- (b) A second equilibrium mixture at the same temperature and of the same volume is analysed. The concentrations of A, B and C are all found to be equal to 0.020 M. How many moles of D are present?
- (c) What would be the effect, on the amount of D present at equilibrium, of adding a further 500 mL of water to make a total volume of 1 L?

22. It's not very likely that you can understand Hungarian, but the symbols of chemistry form an international language. This is one item from a Hungarian book of chemistry questions.

216. Az ammónia oxidációs folyamatát az alábbi egyenlet fejezi ki:



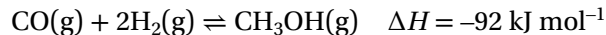
Az egyenletekben szereplő vegyületek közül a NO képződéshője pozitív, az NH_3 és a víz képződéshője negatív. Ennek ismeretében magyarázzuk meg, miért kell a reakciót nagy reakciósebességgel lejártszatni, majd a reakciótermékeket gyorsan lehűteni?

- (a) Describe the reaction referred to in the question.
- (b) Is this reaction an exothermic or an endothermic reaction?
- (c) Would this reaction be best performed at a high or low temperature to obtain a high value for the equilibrium constant?
- (d) Would the formation of products in this reaction be favoured by high or low pressure?
- 23.** The table below shows the percentage formation of a product in equilibrium mixtures at different temperatures and pressures.

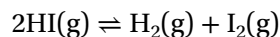
Pressure ($\times 10^5 \text{ Pa}$)	Temperature ($^{\circ}\text{C}$)			
	200	300	400	500
1	10	3.5	1.3	0.5
200	64	30	23	19
300	98	62	43	21

- (a) Is the reaction under study exothermic or endothermic?
- (b) If the equation for this reaction was written, how would the number of particles on the right-hand side compare with the number on the left?

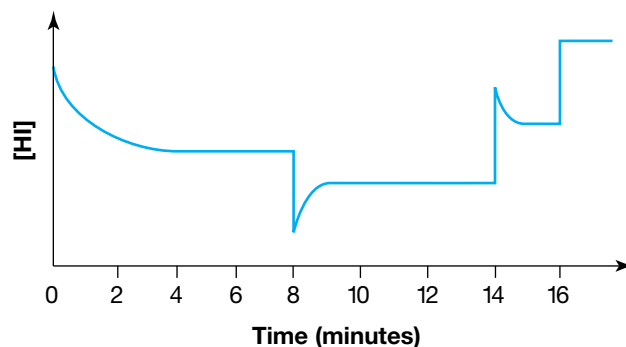
24. Methanol may be prepared commercially from carbon monoxide and hydrogen using a suitable catalyst, according to the equation:



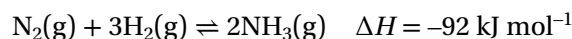
- (a) How could the pressure under which the reaction is performed be adjusted to maximise the yield of methanol?
- (b) How could the temperature at which the process is performed be adjusted to make more methanol?
- (c) If extra carbon monoxide is added, how would this affect the amount of methanol produced?
- (d) Which of the above proposals would actually change the value of the equilibrium constant?
- 25.** In an investigation of the decomposition of hydrogen iodide, represented by the equation:



the concentration versus time graph shown in the figure below was obtained.



- (a) Describe what happened during the first 2 minutes of the experiment.
- (b) Describe what was happening from the 4- to 8-minute marks.
- (c) Give an explanation for the cause of the dip in the graph at the 8-minute mark.
- (d) What do you think might have happened at the 14-minute mark?
- (e) What do you think might have happened at the 16-minute mark?
- (f) Did the change occurring at the 16-minute mark affect the equilibrium or not? Explain.
- 26.** Ammonia may be prepared according to the equation:

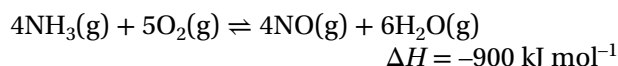


In a particular experiment using typical industrial equipment, at a particular temperature, T , equilibrium was obtained with 4.32 mol of N_2 , 2.00 mol of H_2 and 4.00 mol of NH_3 present in a 2.00 L pressure vessel.

- (a) Calculate the value of the equilibrium constant at the temperature of this experiment.
- (b) Calculate the pressure exerted by the mixture of gases at equilibrium in terms of T .
- (c) If the volume of the pressure vessel is reduced (at constant temperature), what effect would this have on the amount of NH_3 present?

Applications of equilibrium

- 27.** Nitric acid is manufactured on a large scale by the Ostwald process. Ammonia is an important input into this process. The first step in the Ostwald process involves the following reaction.



This reaction is carried out using a platinum/rhodium catalyst, at a pressure of about 10 atmospheres.

- (a) Is the formation of NO in the equation above favoured by high or low temperatures? Explain.
 - (b) Explain why a catalyst is used in the above reaction, and how its use would improve the yield of NO.
 - (c) In an industrial context, a pressure of 10 atmospheres is not considered high. The ammonia used in this process, for example, is made at a pressure of about 250 atmospheres. Explain why the reaction above is not carried out at such a high pressure.
- 28.** Making methanol on a commercial scale involves pumping a mixture of carbon monoxide and hydrogen through a reaction chamber containing a mixture of ZnO and Cr_2O_3 . This reaction is best carried out at a particular temperature and

at a particular pressure. The equation for this reaction is:



- (a) To maximise the rate of this reaction, should this reaction be carried out at higher or lower temperatures?
 - (b) To maximise the yield of this reaction, should it be carried out at high or low temperatures?
 - (c) Describe the function of the ZnO/ Cr_2O_3 mixture and how it partially solves the problem posed by your answers to (a) and (b).
 - (d) How could the methanol be easily separated from the exit gases? What should be done with the unreacted CO and H_2 ?
- 29.** Both oxygen, O_2 , and carbon monoxide, CO, can attach to the haemoglobin molecule. Under the normal biological conditions within the body, O_2 attaches itself to haemoglobin in the lungs and detaches itself when the haemoglobin is in the vicinity of respiring tissues. Carbon monoxide can also attach itself to haemoglobin while in the lungs, but is unable to detach when near respiring tissues.
- (a) Using the symbol Hb_4 as an abbreviation for the haemoglobin molecule, write an equation for the reaction between haemoglobin and oxygen.
 - (b) Write an equation for the reaction between haemoglobin and carbon monoxide.
 - (c) Write the expression for the equilibrium constant for each of the reactions.
 - (d) From the information above, comment on the relative values of the equilibrium constants for the reactions.
 - (e) From your answer to (d), explain why carbon monoxide is such a poisonous gas.

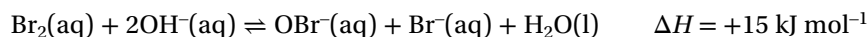


Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

1. A simple form of colorimetric analysis may be used to study the equilibrium represented by the following equation.



As molecular bromine, Br_2 , is the only coloured species in this reaction, its red-brown colour may be used to monitor various changes made to this equilibrium.

A student performed an experiment where 10 mL samples of reaction mixture were poured into identical test tubes. The four changes listed below were then made to different samples of the equilibrium mixture. The colours before and after the changes were compared.

Change 1: A small amount of solid potassium bromide was added and the mixture stirred to dissolve it.

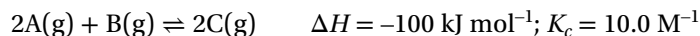
Change 2: A small amount of solid sodium chloride was added and the mixture stirred to dissolve it.

Change 3: The solution was warmed from room temperature to 50°C .

For each of these three changes:

- (a) state whether you would expect the solution to darken, lighten or stay the same **3 marks**
- (b) use Le Châtelier's principle to explain your answer in (a). **3 marks**

2. Consider an equilibrium at room temperature that is represented by the following equation.



For this reaction, it is possible to calculate the value of Q at any stage of the reaction using the following formula.

$$Q = \frac{[\text{C}]^2}{[\text{A}]^2 [\text{B}]}$$

In one particular experiment, 1.5 mol of A, 0.50 mol of B and 2.5 mol of C are mixed in a 2.0 L container at room temperature.

- (a) Calculate the value of Q at the start of this experiment. **2 marks**
- (b) Use your answer to (a) to explain how the rate of the forward reaction compares with the rate of the backward reaction at the start of this experiment. **1 mark**
- (c) Some time later, the rates of the forward and backward reactions are measured and found to be equal. What is the value of Q at this time? Explain. **2 marks**

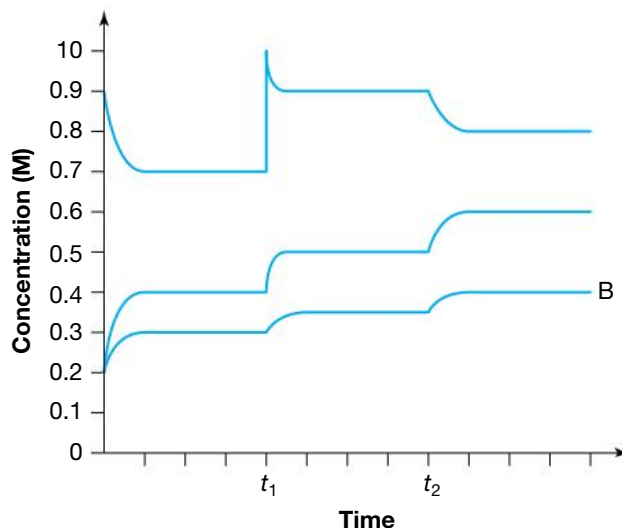
The experiment is now repeated under identical conditions, except that a catalyst is added to the initial mixture. The rates of the forward and backward reactions are again monitored over a period of time.

- (d) How would the initial rate of the forward reaction in the second experiment compare with the initial rate of the forward reaction in the first experiment? **1 mark**
- (e) How would the initial rate of the backward reaction in the second experiment compare with the initial rate of the backward reaction in the first experiment? **1 mark**
- (f) After waiting the same amount of time as for (c), what would be the value of Q in the second experiment? Explain. **2 marks**

3. The reaction represented by the equation:



is studied by monitoring the concentration of its three species over time. The graph below shows the results that were obtained. Note that one of the substances is already labelled.



(a) Label the other two lines on the graph with their correct substances.	2 marks
(b) What are the values of x and y in the equation above?	2 marks
(c) Calculate the value of the equilibrium constant immediately before time t_1 .	1 mark
(d) What change was made to this system at time t_1 ? Explain.	2 marks
(e) At time t_2 , the temperature was increased. Is this reaction exothermic or endothermic? Explain your reasoning, clearly showing any necessary calculations.	3 marks



UNIT 4

AREA OF STUDY 3

CHAPTER 7 Key practical skills and communication

AREA OF STUDY 1

CHAPTER 8 Structures and nomenclature of organic compounds

CHAPTER 9 Properties and reactions of organic compounds

CHAPTER 10 Analysis of organic compounds

AREA OF STUDY 2

CHAPTER 11 Vitamins and proteins

CHAPTER 12 Food and energy



Key practical skills and communication



Conducting properly designed experiments to investigate questions is a critical part of the scientific method. So too is communicating your findings to others in the same field so that your results can be independently replicated. In this chapter, you will build on skills learned in Units 1 and 2 to accomplish both these tasks. You will learn how to design an experiment so that its results are reliable and authentic, and to use well-established scientific conventions and practices to report to others.

YOU WILL EXAMINE:

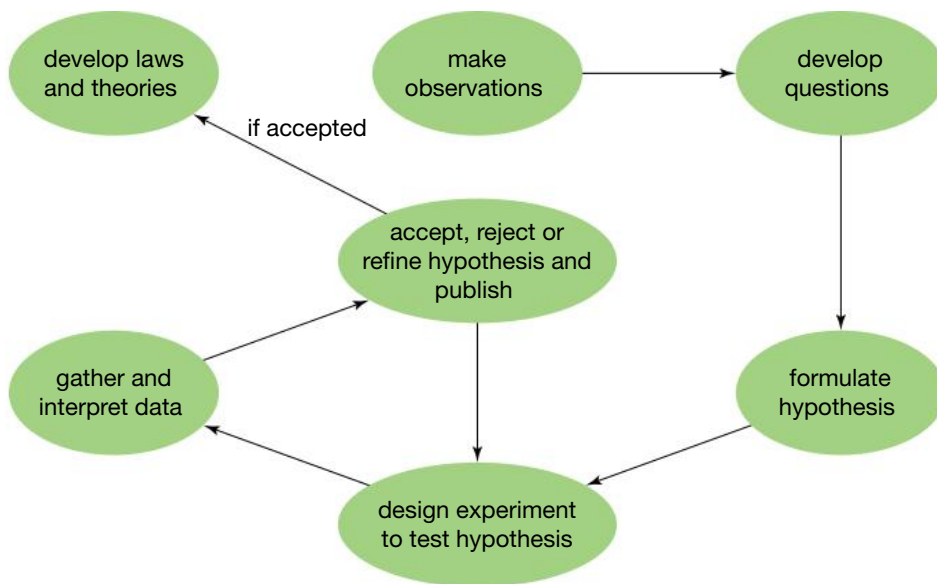
- how to decide on a suitable question, formulate an aim and write a hypothesis
- how to plan a suitable procedure that is ethical and safe and that will give results that are not compromised by unwanted variables
- how to record results of your experiment to the appropriate level of precision
- the importance of data analysis and evidence-based conclusions
- the requirements for reporting your work in the form of a scientific poster
- scientific notation, significant figures and the role of uncertainty
- the role of independent, dependent and controlled variables, as well as the importance of using a scientific control where appropriate
- how to work with tables and graphs
- how to prepare a risk analysis as part of safe working practices
- how to acknowledge sources.

Experiments must be properly designed so that they are performed safely and the results produced contain minimal errors.

Key practical skills in chemistry

Progress in chemistry (and, indeed, any branch of science) relies on formulating and answering questions followed by communication of the findings. Scientists work through a series of steps to advance their knowledge as part of this procedure. Experimental and other investigative work is central to this.

The following diagram summarises this process.

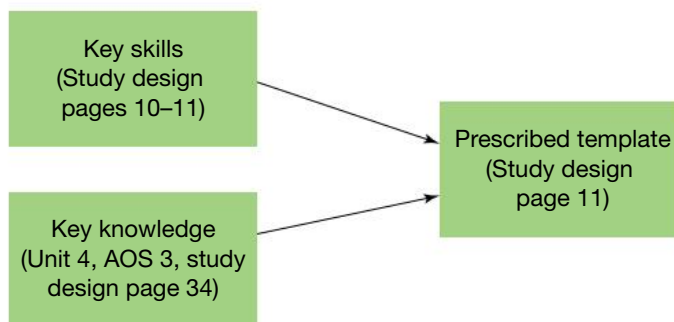


The scientific process.
Designing and carrying out
experiments is critical to this.

In Units 1 and 2, you had opportunities to begin the development of the necessary skills for designing and performing experiments. In Unit 3 and/or Unit 4, you will be required to design or adapt an experiment to answer a question that is related to either energy or food chemistry (or both).

This investigation will draw upon a number of key skills that you have been developing in Units 1 and 2, and so far in Units 3 and 4, as well as the key knowledge that is specified for Unit 4, Area of Study 3 of the study design. You will be required to produce a report in the format of a scientific poster.

To assist with this task, a prescribed template has been prepared. This is the best place to start to clarify exactly what is required. The following diagram summarises how these requirements are related.



The process that you will need to complete can be broken down into five stages:

- prepare for your experiment
- plan your experiment
- perform your experiment
- analyse your data
- produce your report.

We will now look at each of these stages in more detail.

Preparing for your experiment

You should not rush into doing your experiment. Time spent preparing will make the subsequent stages easier and your data more reliable. It may even prevent you from having to start again. There are some important things to consider at this stage.

Logbook

This may be electronic or a traditional exercise book. It should contain everything you do. Include dates, thoughts, ideas, measurements, questions, alterations, references, dates, problems, amendments and anything else that you consider to be relevant. You should not use pieces of paper or loose-leaf binders for your logbook as pieces of paper can easily be misplaced or lost from a binder.

Using and maintaining a logbook

- Your logbook is critical to the investigation. Nothing should be trusted to memory — everything should be written down, even if you do not think it is important at that stage. It is also a necessary tool for authentication by your teacher and may even be used as part of your assessment. It does not necessarily have to be neat and tidy, but you should be able to access all relevant details in it for your report.
- Record a date and heading for every entry.
- Outline your question, aim, hypothesis, list of materials and method.
- Results should be written in tables and any observations that you consider significant should be detailed. If you have a false start and need to change or modify your question, record this! If the method needs to be changed for any reason, document that as well.
- Add diagrams where appropriate, and you can even attach other relevant documents, such as videos and photographs.
- To help keep you on track, include a page for questions that arise.
- Also, use a page to record where in the experiment you have reached at the end of each lesson and what you will do at the start of the next one. This can be particularly useful if your timetable has extensive breaks between one chemistry class and the next.
- A further page to record references that you have used, and which contain a brief outline and detail of each source, will be useful when collating information later on. It is best to do this progressively as you proceed through the investigation, not at the end!
- For verification and authentication purposes, it is essential that the logbook is kept up to date at all times.
- Remember that your logbook contains everything relevant to your investigation in the one place. It is, therefore, a valuable document. Do not lose it!

Which question will you choose?

Although this sounds obvious, some questions allow you to meet the criteria better than others. You should choose a question that addresses as many of the key skills and key knowledge points as possible. Your question may lend itself to either a qualitative or a quantitative investigation. However, most people find that a quantitative investigation makes it easier to address the necessary points mentioned above. You also need to make sure that the necessary resources are available to answer your question and that the investigation can be done within a reasonable time frame. Finally, you need to consider the ethical and safety issues that might be associated with your investigation.

In light of these points, it is probably a good idea to have more than one question in mind, or at least some variations of your question. Sometimes it is easier to work around a problem by sidestepping it with a different question (or variation).

Formulating your hypothesis and aim

Your hypothesis is related to, and informed by, your question. It is an educated guess based on the theory and current knowledge related to your question. The hypothesis must be testable. In fact, it is the aim of your experiment to verify, dismiss or suggest modifications to your hypothesis, based on the data you obtain.

To write a hypothesis, a good tip is to use the *if (statement involving independent variable), then (prediction involving dependent variable)* structure. For example, consider the question: Does the number of bonds in a hydrocarbon molecule influence its use as a fuel? A reasonable hypothesis could be: *If the number of bonds in a hydrocarbon fuel is increased, then the energy output from it also increases when it is combusted in excess oxygen.*

Revision questions

1. Testing a scientific question by experiment involves a number of stages. These are shown by the statements below. Use the letters to put these stages into their correct order.
A Formulate the hypothesis. D Communicate the results.
B Decide on the question. E Plan the experiment.
C Analyse the results. F Carry out the experiment.
2. After some preliminary reading, a student has become intrigued by the possibility that fats and oils may have different energy contents. Therefore, she proposes the question: Do fats and oils have different energy contents per gram?
(a) Write a reasonable hypothesis that she could test experimentally based on this question.
(b) Which of the following is a characteristic of a good hypothesis?
A It must be proven true.
B It must be testable by observation or experiment.
C It must be based upon experiments done by other scientists.

Planning your experiment

It is important that your experiment produces reliable findings. Therefore, you need to consider the variables involved in your experiment. Which need to be controlled? Which are the dependent and independent variables? You should consider errors (both systematic and random) and how they can be minimised. Will it be practical to repeat the experiment a number of times to reduce random errors? You may need to do a trial run (pilot study) of your method and be prepared to change your method on the basis of the evidence obtained from such a trial.

On a more practical level, you need to consider the necessary skills required, as well as the time and cost of your proposed experiment. For example, are you proficient enough at titrations? You may find that you can adapt an already existing method, or you may have to design a completely new method from scratch. Will your experiment take too long to complete, given the time available? Will it require the purchase of specialist equipment or expensive chemicals?

You should also consider the most appropriate equipment to use for a particular purpose. For example, if a liquid volume of 25 mL is required, what would be the most appropriate piece of equipment to measure it? If a high-precision

measurement is required (i.e. a lower uncertainty), a 25.00 mL pipette would probably be used. If, however, this level is not required, a measuring cylinder or even a 100 mL beaker may be more appropriate.

The choice of measuring equipment in an experiment depends on the level of precision required.



Another important consideration at this point of your planning is how to address ethical and safety issues. You may be required to provide a formal assessment of how these issues will be addressed. Access to materials safety data sheets (MSDS) is critical here. Your school will have copies of these or they can easily be found online.

At the end of this stage, you should be able to produce three written documents:

- a risk analysis based on the hazards that you have identified (this is discussed in more detail later in this chapter).
- a detailed list of equipment and chemicals needed, along with approximate amounts for each chemical
- an explicit, step-by-step method that takes all of your planning into consideration, including diagrams if relevant.

Revision question

3. A student is designing an experiment that involves measuring liquid volumes at various stages. A number of glassware items are available for this purpose as shown in the following table.

	Item	Uncertainty (mL)
A	volumetric flask (250 mL)	± 0.1
B	beaker (100 mL)	± 10
C	measuring cylinder (100 mL)	± 0.1
D	burette (50 mL)	± 0.02
E	conical flask (250 mL)	± 25

Which piece(s) would be most appropriate for:

- (a) rinsing a burette with 10 mL of water
- (b) producing 250 mL of a solution of accurately known concentration
- (c) producing 250 mL of a solution of approximately known concentration
- (d) adding water to a conical flask to dissolve a previously weighed tablet, prior to titration?

Working in groups

Just as in the real world, you will probably not work alone in your investigation. However, the poster that you produce must be your own work. How do you balance these two apparent contradictions and obtain the best result for yourself?

There are a few simple points that you should bear in mind.

- As part of your planning, assign clear roles to each group member, but be prepared to rotate these from one lesson to the next. This means that every person has a function in each lesson, and each person experiences all the different roles required in the experiment.
- Every person should be prepared to jot down in their logbooks what they consider to be important observations. If large amounts of data are being collected, it may be the role of one group member to write this down. However, every other member must ensure they copy this data into their logbooks as soon as possible. Do not expect to be able to get this data at a later date.
- While it is permissible to broadly discuss the analysis and implications of your data, the final detailed analysis must be your own work. Your poster must contain your own words, drawings, calculations etc.
- Remember the importance of your logbook. It is a vital method of recording, and also critical to your teacher's authentication of your work. It should prove that you have been an active, contributing member of your group — not just someone who has sat back and obtained some results at the last minute.
- Finally, do not forget to acknowledge the help that others give you. This, of course, also applies to members of your group.



What is the reading on this scale?

Performing your experiment

Follow the method as you have written it down. Record all your measurements as accurately and consistently as possible, using appropriate units and to the appropriate precision (number of significant figures). When reading a scale, remember that you should estimate within the smallest division of the scale to get your last significant figure.

The reading on the scale at left, for example, should be recorded as 64.5. This indicates that we are certain that it lies between 64 and 65, and the '5' is the best estimate of exactly where between these values it lies. (This, therefore, gives 3 significant figures).

Also note any unplanned or 'surprise' observations. Do not just ignore these. It will be important in the next section to discuss them!

As a further means of recording your information you may even consider using photos and videos.

Revision question

4. What is the magnitude of the reading on the circular thermometer shown at right?
- A 21.8
 - B 22
 - C 23.9
 - D 24.0
 - E 24



Analysing your data

In this stage, you will look for patterns, trends and relationships that can be used to evaluate your hypothesis. These processes are often mathematical operations such as calculations (remember significant figures!), averaging, graphing, converting to and from scientific notation etc. You need to consider the limitations of your data and your method. Together with any unexpected results, these may lead to suggested modifications to your method.

Now is also the time to consider your conclusion. Remember that this must provide a response to the question. It must not draw on any new information. Rather, it should be informed by the data and the analysis that has already been performed.

Producing your poster

When writing a scientific report, it is important to write in a style that is objective. The traditional method for many years has been to write in the 'third person, past tense'. However, in recent years, this has been modified slightly. It is now sometimes permissible to use pronouns such as *I*, *we* and *you*, providing that they are not overused and that they add conciseness to your writing.

According to the study design, your poster must use the following prescribed format.

- **Title.** This is, of course, the question that you are investigating. Also, don't forget your name!
- **Introduction.** Explain why you chose the question that you did. You should discuss current theory and concepts that are relevant to this question. You should finish this section with a clear aim and state the hypothesis that you are going to test.
- **Method.** You should already have this available from carrying out your experiment. However, you may choose to rephrase sections to make it more readable to another person. The test here is that it should be clear enough for someone else (at your level) to repeat your experiment, but not contain extra details that such a person would be reasonably expected to already know.

Do not forget to highlight how the relevant ethical and safety concerns have been addressed.

You may choose to keep your method in point form (step by step), but you may also decide to run it together into a paragraph. Either way, it still must meet the test of reproducibility mentioned above.

Do not be afraid to include clearly labelled diagrams. As the saying goes — a picture is worth a thousand words!

It is also permissible to include a list of equipment and chemicals used here, although many people choose to include this under a separate heading, such as 'Materials,' immediately before this section.

- **Results.** Make sure you present your results in an organised and clear manner, following accepted conventions. For example, if tables are used, each table should have a title. Make sure you include the appropriate units and use the correct number of significant figures. Try to organise this in such a way that any patterns or relationships start to become obvious, thus making it easier to analyse in the next section.

You do *not* do any analysis in this section!

- **Discussion.** This section is particularly important. Here is where you do your analysis. Make sure you do not just repeat your results! Do the necessary calculations and identify any trends and relationships that become apparent. Comment on any unexpected results. Suggest sources of error and possible modifications to the experiment. Discuss any difficulties, and suggest improvements and future follow-up investigations.

- Check that you have used correct scientific terminology and conventions.
- **Conclusion.** This should relate to the aim and must be based entirely on the evidence obtained in the experiment. It should state whether the hypothesis is supported. This usually forms the last part of your discussion, although some people like to include it under a separate heading.
- **List of references and acknowledgements.** You should quote the sources of any content that you include that is not your own original work. Unaltered tables, diagrams and graphs are examples that fit this description, as are direct quotes. In your introduction, you may have mentioned previous work that your investigation is based on. This also needs to be acknowledged, along with any sources that inform your discussion of concepts and theory in a more general sense.

Practical investigation checklist

- ☐ Your name, the title and the aim/hypothesis are listed.
- ☐ A synopsis describes the purpose and outlines the investigation in a logical and concise manner. Key terms are defined and variables are stated clearly. Relevant theory is addressed.
- ☐ The method is outlined clearly in step form including a consideration of ethics, health and safety. A risk assessment is provided.
- ☐ Your logbook contains dates, headings and complete records.
- ☐ Results are presented in an organised way, in a table if possible. All relevant measurements are recorded with appropriate accuracy and units. Any abbreviations are explained.
- ☐ Observations are clear and concise, as are any diagrams or photos used.
- ☐ The discussion includes clear and correctly set out calculations.
- ☐ There is a concise summary and interpretation of key findings, including trends and any unexpected results. Connections to relevant chemistry are explained.
- ☐ The experimental design is evaluated and possible improvements are included.
- ☐ There are suggestions for future investigations.
- ☐ The conclusion concisely summarises how your results support or contradict your original hypothesis.
- ☐ All sources are acknowledged and references correctly cited.
- ☐ The layout of your poster is clear and logical. The use of key terms and chemical conventions, symbols and equations is appropriate.

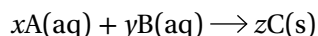
Dealing with variables

A **variable** is any factor in an experiment that can be changed, measured, observed or controlled in some way. For the results of an experiment to be reliable and authentic, it is important to consider the role of variables and how they may affect the data that you obtain.

In many experiments, there are three main types of variables: *independent variables*, *dependent variables* and *controlled variables*.

Independent variables

Independent variables are those that are changed by the experimenter. For example, in an experiment to check the stoichiometry of a reaction represented by the equation:



a student reacted variable amounts of substance A and measured the mass of substance C produced after filtering and drying. The independent variable in this experiment is therefore the amount of substance A that was used in each trial.

When graphing results, the independent variable is always placed on the horizontal axis.

Dependent variables

Dependent variables are those that are measured. In the example above, this would be the mass of substance C produced.

The dependent variable is always placed on the vertical axis of a graph.

Controlled variables

Controlled variables are any other factors that might affect your measurement of the dependent variable. In the previous case, the amount of substance B present could possibly affect the mass of substance C produced. It would, therefore, be very important to keep the amount of substance B present at a value that would reasonably be expected to be in excess.

Experiments normally have a number of controlled variables.

More about variables

In any experiment, there may also be other variables that you are unaware of or that would be reasonably expected not to affect the result.

In the previous example, the temperature of the aqueous solution might not be considered to be important. However, if substance C shows a solubility that increases dramatically with temperature, this would also affect the mass of substance C that is collected. It would then become necessary to repeat the experiment making sure that the temperature is held constant. In other words, temperature would become another controlled variable.

It is possible that a controlled variable may become an influencing variable. Once again, in the previous example, if the amount of substance A used becomes too large, substance B may no longer be in excess and would therefore affect the mass of substance C produced by becoming the limiting reagent.

Dealing with variables experimentally

There are a number of ways that an experimental method may deal with the variables involved to give fair results. One common way is to simply keep each of the identified controlled variables at a constant value. In the experiment described on the previous page, this could be achieved by keeping the amount of substance B at an amount representing a large excess, and by performing each trial at a constant temperature.

If the identification of controlled variables is complex, or many are present, it might be simpler to include a **control**. A scientific control is an experiment or observation that involves all variables except the independent variable. For example, a scientist may be trying to measure the absorbance of light by various concentrations of cobalt chloride, CoCl_2 , solutions. The independent variable in such an investigation would be the concentration of cobalt chloride, and the dependent variable would be the absorbance reading obtained. However, there are a number of other variables that may affect the result. These include the nature of the solvent, the type of glass that the containers holding the solutions are made from, the distance the light has to travel (especially through the solution) before it is measured, the temperature of the solution and so on. A convenient way to control all these variables, and maybe even some that you aren't aware of, is to use a control. Everything about the control, from the way it is prepared to how it is manipulated and measured in the experiment, is the same as for the test solutions containing cobalt chloride.

The only difference is that there is no cobalt chloride (the controlled variable) in the control. This, therefore, allows the scientist to isolate the amount of absorption in each reading that is due to the cobalt chloride alone as it is the only variable left that is responsible for any differences in absorbance readings.

Revision questions

5. A student conducted an experiment to measure the effect of changing pressure on the volume of a sample of gas. This was done in three stages using a range of pressures on various concentrations of gas at various temperatures.
Stage 1: 0.01 mol of gas at 10 °C
Stage 2: 0.02 mol of gas at 20 °C
Stage 3: 0.03 mol of gas at 30 °C
The results from each trial were then analysed to produce an overall conclusion.
- (a) State the independent and the dependent variables in this experiment.
 - (b) What were the controlled variables in this experiment?
 - (c) What was the purpose of stages 2 and 3 in this experiment?
6. The following is an excerpt from a report describing the method for an experiment on determining the optimum fertiliser level for lucerne growth.
Five seeds of *Medicago sativa* (lucerne) were planted in each of 11 identical pots using potting mix from the same packet. These pots were then placed in the same position inside a greenhouse. Each pot was watered daily with 100 mL of fertiliser solution of constant concentration. The concentrations used in the experiment ranged from 0 to 5 g L⁻¹. After 2 weeks, the shoots in each pot were cut at soil level and weighed.
- (a) What is the independent variable in this experiment?
 - (b) What is the dependent variable?
 - (c) State as many controlled variables as you can think of.
 - (d) Which pot is the control in this experiment?
 - (e) Why is the control an important part of this experiment?

Working with figures

Scientific notation

When working with the sizes of atoms, we are dealing with very, very small numbers and yet, when working with numbers of atoms, we need to use very, very large numbers. For example, depending on how it is calculated, there are 33 500 000 000 000 000 000 water molecules in a drop of water. It is really not convenient to write these figures with large numbers of zeroes before or after the decimal point. Using scientific notation, this number is written as 3.35×10^{19} water molecules.

There are two parts to scientific notation; the first part is the first digit of the number, and the second part is a decimal point followed by the remaining digits. This is multiplied by 10 raised to the power that returns the number to its original value.

Sample problem 7.1

Write 37 769 using scientific notation.

Solution: $37\,769 = 3.7769 \times 10\,000 = 3.7769 \times 10^4$

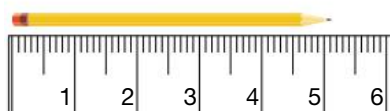
Remember that the power of 10 is positive if the number is greater than 1 and negative if the number is less than 1. On a calculator, the ^ key is used to raise 10 to a particular power. Scientific notation is also called standard form.

Revision questions

7. Express the following measurements in scientific notation.
 - (a) The wavelength of red light is 0.000 000 75 m.
 - (b) A typical page thickness is 0.0023 mm.
 - (c) The distance from the Earth to the Sun is 149 600 000 000 km.
8. Convert each of the following to scientific notation.

(a) 927 500	(d) 0.005 629
(b) 45 868	(e) 0.056 29
(c) 0.0357	(f) 0.000 000 013 457
9. Convert each of the following numbers from scientific notation to an ordinary number.

(a) 1.00×10^2	(e) 5.0×10^5
(b) 2.19×10^{-3}	(f) 5.00×10^5
(c) 3.759×10^0	(g) 5.00×10^{-5}
(d) 7.77×10^{-1}	



5.13 $\pm$ 0.01 cm

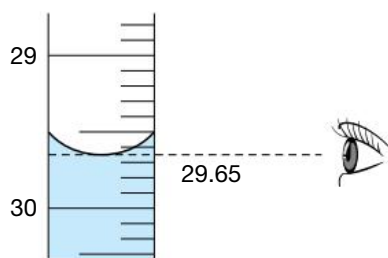
Read the scale to $\frac{1}{10}$ of the smallest division on the scale.

Significant figures

Every measurement that you make has an inherent level of uncertainty. This is due in part to the limitations of the measuring equipment itself and in part to user interpretation. Significant figures are one means of recognising these limitations. We say that significant figures indicate the level of precision in a measurement. When reading a scale, read it to $\frac{1}{10}$ of the smallest division in the scale.

Sample problem 7.2

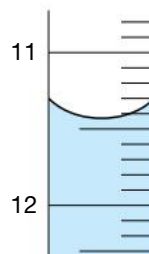
What is the reading on this burette?



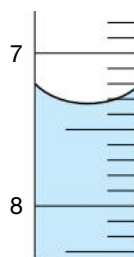
Solution: The reading at the bottom of the meniscus is 29.65 mL.

Revision questions

10. Record the reading on the burette in this diagram.



11. Explain why a student reading this burette as 8.67 mL is incorrect.



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How do we count significant figures?

When calculations are to be made from different measurements, it is important that we are able to assess the number of significant figures in each measurement. We can then quote the answer to an appropriate level of precision.

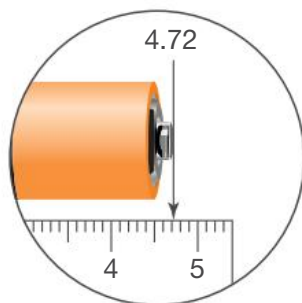
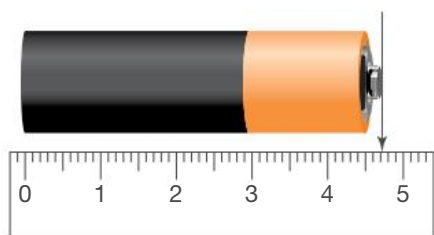
In assessing the number of significant figures in a measurement, we use two rules:

- All non-zero digits are counted.
- Zeros are counted if they come *after* a non-zero digit.

Examples

- A burette reading of 21.37 mL has 4 significant figures.
- A pipette reading of 20.00 mL has 4 significant figures.
- A measurement of 100 mL from a gas syringe has 3 significant figures.
- A mass of 1.003 g has 4 significant figures.
- A mass of 0.003 g has 1 significant figure.
- A mass of 0.300 g has 3 significant figures.

Note: Significant figures are not the same as decimal places. If a measurement is expressed in standard form, significant figures are counted from the decimal part only. For example, the Avogadro constant, when expressed as 6.02×10^{23} , contains 3 significant figures. The digits in the index are not counted.



What is the length of this battery?

How are significant figures determined experimentally?

When we use a measuring instrument, the markings on its scale allow us to be 'certain' of values up to the limits of this scale. As noted earlier, however, it is usual practice to estimate between the smallest divisions of these scales (see the previous burette examples). This means that we are 'uncertain' about the last, most precise digit. The diagram at left illustrates this point.

The length of the battery is written as 4.72 cm. The scale allows us to be certain about the '4' and the '7'. However, the final '2' is an estimate made between the smallest scale divisions.

The standard method of quoting measurements is to include all the digits you are certain of, plus the first one that you are uncertain of (because you have had to estimate it). The '4.72' in the diagram illustrates this procedure. From this, we can see that it therefore contains 3 significant figures.

If a digital measuring device is used, you may assume that the last digit is the estimated one. You may even have noticed that, on devices such as digital balances, the last digit flickers around before the balance finally provides an estimate of it.

Significant figures and calculations

The number of significant figures allowed in any calculated answer is governed by the number of significant figures in the least precise value from which that answer is calculated.

If a calculation involves defined conversion constants, these are not counted. Remember that it is only the measurements that are considered.

Working with significant figures

- When multiplying or dividing, the answer is written to the smallest number of significant digits.
- When adding or subtracting, the answer is written to the smallest number of decimal places.

Sample problem 7.3

In determining the density of a particular liquid, a student measured the volume of a sample as 8.3 mL. She then weighed the same sample and obtained a mass of 7.2136 g. Calculate the density to the correct level of precision.

Solution: $\text{density} = \frac{\text{mass}}{\text{volume}}$

$$= \frac{7.2136 \text{ (5 significant figures)}}{8.3 \text{ (2 significant figures)}}$$
$$= 0.8691 \text{ (This needs to be rounded to 2 significant figures.)}$$
$$= 0.87 \text{ g mL}^{-1}$$

Revision questions

12. How many significant figures are there in each of the following measurements?
- (a) $A_r(\text{H}) = 1.007\,94$ (c) 42.450 g
(b) $A_r(\text{H}) = 1.00$ (d) -273.14°C
13. Calculate the following to the correct number of decimal places.
- (a) $57.45 + 3.349$ (d) $35.356 - 24$
(b) $3.45 - 2.4$ (e) $34.984\,573 + 0.1$
(c) $23.9636 + 43.875$ (f) $4.275 - 6.45$
14. Solve the following problems, giving your answers with the correct unit and number of significant figures.
- (a) energy evolved (hexane) $= 5.32 \text{ mol} \times 4.158 \text{ kJ mol}^{-1}$
(b) $n(\text{Cl}) = \frac{0.23 \text{ g}}{35.5 \text{ g mol}^{-1}}$
(c) $m(\text{ethanol}) = 0.79 \text{ g mL}^{-1} \times 20.00 \text{ mL}$
(d) energy added $= 5.2^\circ\text{C} \times 1.00 \times 10^2 \times 4.18 \text{ J g}^{-1}^\circ\text{C}^{-1}$

An ambiguous case

In the third example listed on page 201, a gas syringe with a volume of 100 mL was quoted as having 3 significant figures. Because a gas syringe is quite an accurate piece of equipment for measuring gas volumes, this statement is almost certainly true. However, what if the measurement was given as 100 mL with no indication of what was used to measure it? The problem with measurements such as this (and others such as 25 000 and 3500) is that zeros are used to

mathematically allocate place value. This can cause confusion about whether they also indicate precision and uncertainty.

Let us take a closer look at this. Suppose a student has gone to a football game with a newly invented instrument called a 'crowdometer'. By simply scanning the crowd with this instrument, it can tell her how many people are present. When she does this, it returns a reading of 45 000. This could mean any (or more) of the following:

- There are between 44 999 and 50 001 people present, with 45 000 being the best estimate (5 significant figures).
- There are between 44 000 and 46 000 people present, with 45 000 being the best estimate (2 significant figures).
- There are between 40 000 and 50 000 people present, with 45 000 being the best estimate (2 significant figures).

In the first case, the last zero in 45 000 is uncertain and is presented as a 'best estimate'. In this instance, 45 000 has 5 significant figures.

In the second and third cases, however, it is the 5 in 45 000 that is uncertain and it represents a 'best estimate'. The 45 000 in these cases therefore has only 2 significant figures, with the three zeros being required to indicate that we are measuring in 'thousands'.

There are two ways to overcome this ambiguity:

- Use scientific notation. If the crowd figure is written as 4.5000×10^4 or 4.50×10^4 , the number of significant figures is immediately clear (5 and 3, respectively). A recording of 4.500×10^4 would indicate 4 significant figures with the uncertainty being the digit in the tens position.
- By indicating the level of uncertainty with the $\pm$ notation, as explained below.

Errors and uncertainties

The ideas of errors and uncertainties are related to the topic of significant figures.

Errors cause the value of a measurement to change. The errors associated with taking a measurement cause its value to be different from the true value. Errors (no matter how small) are present in every measurement we make. There are two types of errors:

- Random errors cause measurements to be sometimes higher than their true values and sometimes lower. The effect of random errors can therefore be minimised by doing a large number of measurements and averaging them.
- Systematic errors are always biased the same way. In other words, they cause values to be always too high or always too low. The effect of systematic errors cannot be minimised by multiple observations and averaging.

Uncertainty is an extension of significant figures. A plus/minus notation is used to indicate the possible range of values for the last significant figure. For example, when using an electronic balance, a student might record the result as:

$$35.964 \pm 0.002 \text{ g}$$

As discussed above, the use of 35.964 indicates that the '4' is the digit that we are least certain of. The '4' is our 'best estimate'. The uncertainty of ± 0.002 indicates how uncertain we are. In effect, we are stating that the measured mass could reasonably be expected to lie between 35.962 g and 35.966 g.

Applying this to the 'crowdometer' mentioned previously, if the results are quoted as $45\,000 \pm 10$ or as $45\,000 \pm 5000$, it is immediately obvious how precise the measurement is. It is, therefore, easy to locate the digit that represents the 'best estimate' and hence the number of significant figures.

Students often confuse errors with *mistakes*. Errors are present in every investigation and it should be the aim of the experimenter to minimise them. Mistakes, however, are just 'things done wrongly'. There is no excuse for mistakes in an experiment or a report. If something is done wrongly, you simply fix it and do it again!

Reliability and accuracy

These are two further terms that you may come across in a formal analysis of errors.

Accuracy, as the name suggests, represents how close the measured data is to the true (or accepted) value. However, it should be remembered that, in many experiments, the true value is not known. Accuracy depends on the quality of the equipment and the skill of the investigator.

Reliability refers to the consistency with which a measurement can be repeated. It is not the same as accuracy. For example, if an object is weighed on a balance by a number of students, all of the values obtained should be similar — we would say that they are reliable. If, however, the balance had not been tared correctly and was reading 3 g too much, there would be a systematic error present that would result in these weights not being accurate.

Tables and graphs

Tables are one of the best ways for organising large amounts of data. They can also organise the results of calculations made from that data. Tables can show patterns, suggest relationships between observations and indicate the precision with which measurements have been made.

All tables should:

- have a heading
- display the data in some type of logical order. For example, they should show the independent variable in the left-hand column and in increasing value.
- include units in the column headings. This removes clutter from the data entry columns.
- be designed to be easy to read. If a table becomes too complicated, it is better to break it down into a number of smaller tables. The same applies if you have a very large amount of data to display.

In most cases, tables contain the independent variable in the left-hand column, with value(s) for the dependent variable(s) in columns to the right. It is generally accepted practice to show the values for variables in columns rather than rows.

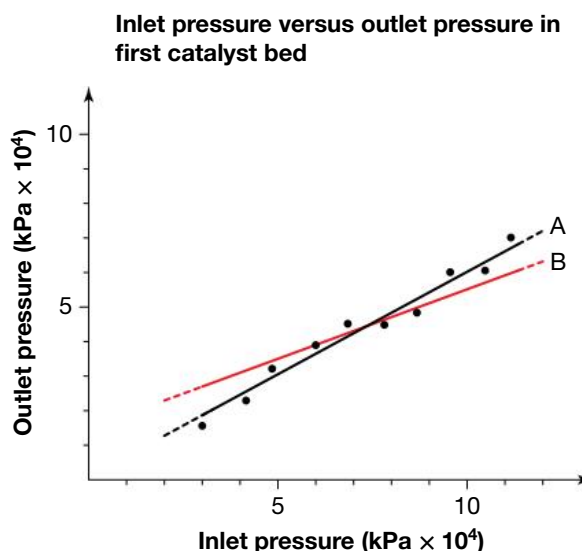
Graphs are a logical complement to tables. A graph can be a powerful tool when determining patterns and exact relationships between numeric variables. Often a relationship may be suggested by a table, and a graph can then be used to establish the precise nature of such a relationship.

Graphs have many other uses as well. Where non-numeric variables are involved, they may, in fact, be more appropriate than tables for displaying data. Pie charts, bar and column graphs often fit into this category.

When drawing graphs:

- decide on the type of graph to be used. Different types of information are better suited to different types of graphs. For example, an investigation into the number of oxidation states of the first series transition metals would be best presented as a column graph, whereas data to draw a calibration curve for an analytical instrument would require a line graph.
- no matter what type of graph you draw, it must have a title that reflects the information it contains. This often includes the variables involved in the collection of the data.
- axes should be ruled and each should be clearly labelled. Those displaying numerical variables should have a clearly marked scale and units. There should be enough values for the reader to easily understand the scale being used. Avoid marking large numbers of scale points and therefore leading to visual clutter.

- make sure your scale is suitable. The points you plot should be distributed across as much of your graph as possible, rather than clustered in a tiny section. To achieve this, it may not be appropriate to start a scale at zero. If this is the case, make certain that you clearly indicate this by following the usual conventions for this procedure.
- for continuous variables, it is often appropriate to draw a line (or curve) of best fit. This is a smooth curve or line that passes as close as possible to all the plotted points. Modern technology in the form of spreadsheets and CAS calculators can be very helpful in situations such as this and equations for these lines or curves can be easily produced.



Drawing a line of best fit. Although not passing through any points, line A is a better fit than line B.

- If you are going to use a line of best fit to make predictions that lie outside the limits of your measured data, indicate this by continuing the line or smooth curve as a dashed rather than a solid line.

Interpreting line graphs

Two procedures that scientists often use with line graphs are interpolation and extrapolation. **Interpolation** is the process of predicting values between the data points that were used to draw the graph. The accuracy of such predictions depends on the accuracy of the original data points and the care with which the line or curve of best fit has been drawn. With reasonable care, in most situations, these predictions can be quite accurate. A good example of interpolation is the use of calibration curves for some of the analytical instruments that you have studied.

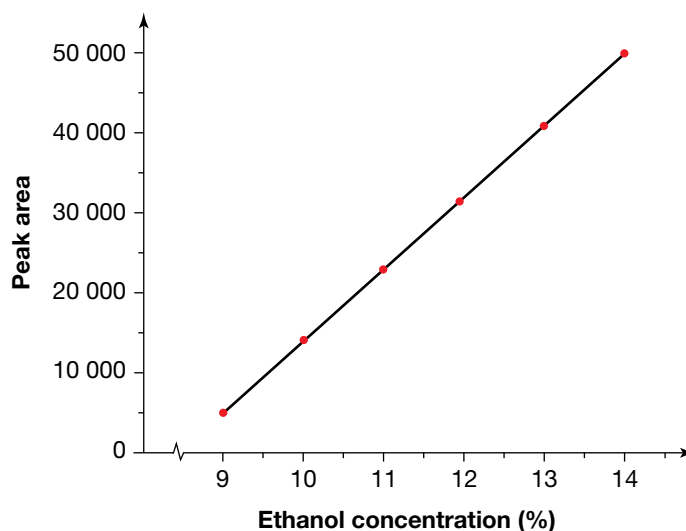
Extrapolation is the process of using a graph to predict values that lie outside the data points used to draw the graph. Great care should be taken when doing this. While a trend may be obvious (and a line of best fit produced) for the obtained results, caution needs to be exercised when predicting values beyond this range. It cannot be guaranteed that all variables involved keep behaving the same way outside the measured range). A safer option would be to repeat the experiment with an extended range to confirm your prediction. For example, to ensure that a point fits on a calibration curve, you might dilute a solution and re-test.

To further explain this, consider an experiment where a student measured the volume of a given air sample at various temperatures ranging from -40 to 150°C . After graphing his results and obtaining a straight line, he was asked to

predict the volume at -180°C . While extrapolation to values just outside the above range might be justified, -180°C is far enough outside this range that any value predicted would have to be treated with caution. In this case, -180°C is only just above the boiling temperature of oxygen (-183°C) and so other variables will almost certainly be affecting the volume.

Revision questions

15. What is the difference between systematic and random errors in an experiment? How can the effects of each be minimised?
16. The following is an extract from a student's logbook where the temperature was recorded at regular intervals during an experiment.
Initial temperature = 15.0°C
Temperature every 30 seconds after ($^{\circ}\text{C}$) = 16.5, 18.1, 19.5, 20.8, 22.4, 23.7, 24.0, 23.9, 23.5, 23.5, 23.2
Record these results in a suitably designed and labelled table.
17. An analyst used gas chromatography (GC) to measure the ethanol content of some alcoholic beverages. GC works on a similar principle to high-performance liquid chromatography (HPLC). In both instruments, it is necessary to produce a calibration curve in addition to obtaining readings for the test samples. One such calibration curve is shown below.



- (a) Sample A produced a reading of 36 000 from the GC. Estimate the level of ethanol in this sample. What is the name of the process used to obtain this answer?
- (b) Sample B produced a reading of 50 500. Estimate the level of ethanol in this sample and comment on your answer. What is the name of the process used to obtain this estimate?
- (c) Sample C produced a reading of 95 000. Is it possible to estimate the ethanol level in this sample? Explain why or why not.

Working safely

General safety rules

Some general safety precautions will help to ensure that you and others are not injured in the laboratory.

- Wear protective clothing. This might include laboratory coat, safety glasses and gloves.
- Be aware of the position of safety equipment such as fire blanket, fire extinguisher, safety shower and eye wash.
- Ask if you are unsure how to operate equipment or how to use apparatus.
- Read labels carefully to confirm contents and concentration of chemicals.
- Clean and return all equipment to the correct places.
- Read instructions carefully before commencing an experiment.
- Prepare a risk assessment for required chemicals and equipment.

Risk assessments

Risk assessment is a procedure for identifying hazardous chemicals, what the risks are and how to work safely with them. Table 7.1 lists the usual requirements for a written risk assessment.

TABLE 7.1 Requirements for a written risk assessment

summary of method	brief list of steps indicating how the chemicals and equipment will be used
chemicals used	list of chemicals used and their concentrations
chemical hazards	details of the hazards caused by the chemicals. These can be found by looking at the MSDS (materials safety data sheets), which can be accessed online.
risk control methods	precautions taken to limit risks. This will depend on the chemicals involved.
equipment	list of materials used in the experiment
equipment risk	list of hazards associated with the equipment
risk control measures	how the risks associated with the equipment will be minimised

TABLE 7.2 Sample risk assessment

Risk assessment record for chemistry experiments					
Assessor (name)	Alexis St. Martin	Date of activity	10/2/2017	Class/Year level	12
title and outline of experiment	A stomach enzyme Put a small amount of ground minced beef into each of four test tubes. Test tube 1: Add water. Test tube 2: Add dilute hydrochloric acid. Test tube 3: Add pepsin solution. Test tube 4: Add equal amounts of dilute hydrochloric acid and pepsin solution. Place the test tubes in an incubator overnight at 37 °C.				
Chemical	Amount or concentration	Hazards — risk phrases		Controls — safety phrases	
HCl, hydrochloric acid	40 mL, 1 M	corrosive to eyes harmful if swallowed harmful by inhalation skin contact may cause irritation		Do not breathe gas/fumes/vapour. Avoid contact with eyes, mouth and skin. Wear suitable protective clothing.	
pepsin solution	40 mL, 1%(m/v)	irritating to eyes, respiratory system and skin may cause sensitisation by inhalation		Avoid breathing spray/mist. Avoid contact with eyes and skin. Wear suitable protective clothing.	

(continued)

TABLE 7.2 (continued)

risk control for equipment used	Glassware may break; handle with care.		
general	Obey science safety rules. Wear lab coat, closed shoes, safety goggles and gloves. Carefully read labels on all bottles, and stopper immediately after use.		
disposal	Decant liquid from test tubes and dispose of in sink with copious amounts of water. Rinse any solids, and wrap and dispose of in garbage.		
other safety controls			
assessor (signed)	Alexis St Martin	Date of record	10/02/2017

Revision questions

18. Look around your laboratory and note its safety features and equipment. Then answer the following.
 - (a) Does it have any stored pressure fire extinguishers? How are these identified? On what types of fire can these be used and on what types of fire should they not be used?
 - (b) Does it have any dry chemical extinguishers? How are these identified? On what types of fire can these be used and on what types of fire should they not be used?
 - (c) Where is/are the fire blanket(s) located? Describe a scenario in which a fire blanket would be used and how you would use it.
 - (d) Where are the master (emergency) shut-offs for gas and electricity located?
19. The MSDS for a chemical to be used in an experiment contains the following risk phrases:
 - (a) irritating to eyes
 - (b) skin/flammable/vapours may cause dizziness.
 Suggest appropriate methods to reduce these identified risks.

Acknowledging sources

It is important that you acknowledge any work in a scientific report that your investigation is directly based on (this is particularly important for original research) and also any information from others that you use in an unaltered state. There are many ways to make such acknowledgments, and various institutions and publications often use different systems. Details of these systems can be found online and can be quite complicated. You should check with your teacher as to how this is expected to be done.

For the purpose of your poster, the following simplified method may suffice but check with your teacher first! It is based on a two-stage system whereby the piece of work is acknowledged in abbreviated form within the body of the report followed by full details in a references section at the end of the report. The following guidelines explain this further.

- Tables, diagrams, graphs etc. that are being inserted without being substantially altered can often be acknowledged by stating the details directly underneath them. Table 7.3 shows an example.

TABLE 7.3 Energy content of commonly available sleigh fuels

Fuel	Energy content (kJ L ⁻¹)
Rudolphene	45
Polar plus	29
Super sleigh	53

(Claus, 2016, p. 45)

In the list of references, this might then be quoted as follows:

Claus S. (2016). *Choosing a sleigh fuel*. Polar Press.

- Direct quotes should be followed by either an abbreviated reference (in brackets) or a 'numerical indicator' such as a superscript that refers to your list of references at the end of the report. The same applies to the authors of any work that you are using as a basis for your investigation.

For example, the introduction to a report on sleigh fuels may contain the following:

...over the past 10 years, the number of eligible children has increased (Kringle, 2008) and a need has therefore developed for sleighs to travel faster to meet the required delivery schedule. More efficient fuels are required for this purpose.

The reference list might then contain:

Kringle, K. (2008). *Journal of Polar Transport*, Vol. **34**, p. 356.

Another method of making such an acknowledgment looks like this:

...over the past 10 years, the number of eligible children has increased⁵ and a need has therefore developed for sleighs to travel faster to meet the required delivery schedule. More efficient fuels are required for this purpose.

The reference list might then contain:

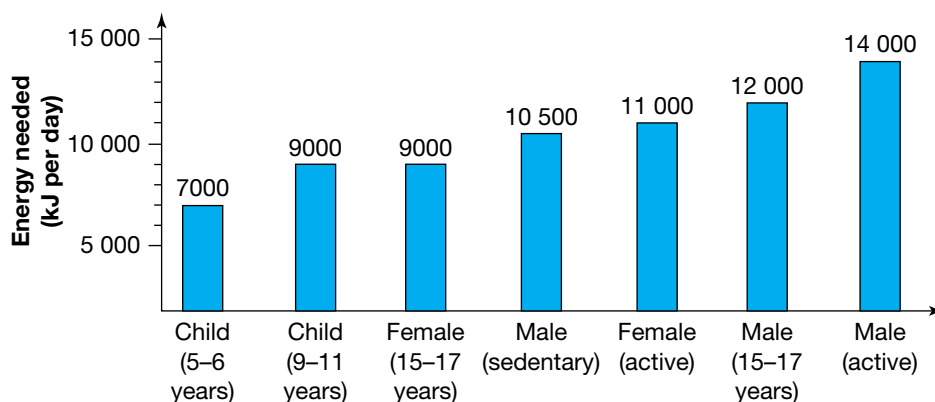
⁵ Kringle, K. (2008). *Journal of Polar Transport*, Vol. **34**, p. 356.

Bibliographies

A reference list contains full details of all sources (print, electronic and verbal) that are referred to in the report, arranged alphabetically by author. A bibliography, on the other hand, is a list of references that have been found useful in planning the investigation, but not referred to directly in your report.

Revision question

- 20.** A student found the table below in a chemistry textbook and wanted to use it in his poster. Also, some details from the imprint page of the textbook are shown on the next page.



First published 1992 by
THE JACARANDA PRESS
33 Park Road, Milton, Qld 4064
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1. Chemistry. I. Stokes, Robert. II. Title.

540

Show how this work could be acknowledged:

- (a) in the body of the poster**
 - (b) in the references section at the end of the poster.**
-

Chapter review

Multiple choice questions

- 40 mL of a solution could be most accurately measured using a:
A 50 mL beaker
B 50 mL burette
C 50 mL pipette
D 50 mL measuring cylinder.
- Any unused chemical should always be:
A returned to its original container
B placed in a new container
C disposed of in a labelled waste container
D poured down the sink.
- Using a solution that has the incorrect molarity marked on the label is an example of a:
A systematic error
B random error
C reading error
D parallax error.
- The independent variable in an experiment is:
A the variable that is observed in an experiment
B the variable that is changed in an experiment
C the variable that is kept the same in an experiment
D none of the above.
- Qualitative results are:
A results that are expected to be observed during an experiment
B results that are measured in an experiment
C results that are observed during an experiment
D none of the above.
- The safest way to treat an acid spill on the skin is to:
A wash the skin with a base such as dilute sodium hydroxide
B wash the skin under running water
C sprinkle sodium bicarbonate on the skin
D wipe the skin with paper towel immediately.
- The definition of accuracy is:
A the number of significant figures used in a measurement
B how close the measured value is to the actual value
C a measure of how often an experimental value can be reproduced
D none of the above.

Review questions

- Why is it important to conduct scientific tests more than once?
- What is the difference between the dependent and independent variable?
- You perform an experiment and record observations and data. You notice some of the data does not fit with what you expected or does not agree with the other data. What should you do?
- The alcohol 2-methylpropan-1-ol can be converted through a number of steps to produce diesel and jet fuel. If the viscosity of a fuel is not within a certain range then it can cause damage to the fuel pump and engine.

A student was asked to design an experiment to compare the viscosity of some fuels. Suggest an experiment that could be done to compare viscosities.

- Stephen decided to investigate how the rate of reaction is affected by the concentration of acid. He weighed out 3.00 g of calcium carbonate powder and put it in a balloon. He put on some safety gloves and added 50 mL of 1.0 M ethanoic acid to a flask and then stretched the balloon over the opening of the flask before mixing the two chemicals. When the bubbling stopped, he weighed the balloon and flask again. He repeated the experiment again using 3.00 g of calcium carbonate powder but used 50 mL of 2.0 M hydrochloric acid. He found that changing the concentration had little effect on the rate of reaction because there was hardly any change in mass.
(a) Comment on the safety precautions taken.
(b) Evaluate the experimental design.
(c) Rewrite the method correctly.

Structures and nomenclature of organic compounds

Organic chemistry is the study of carbon-containing compounds. Carbon is remarkable in its ability to bond in many different ways with other carbon atoms, or with atoms of other elements, to form the millions of organic compounds known to chemists. Historically, organic compounds were associated with living things, but these days chemists can manufacture organic compounds for a variety of uses. What are organic compounds and how do chemists keep track of the large number of compounds and their uses?

YOU WILL EXAMINE:

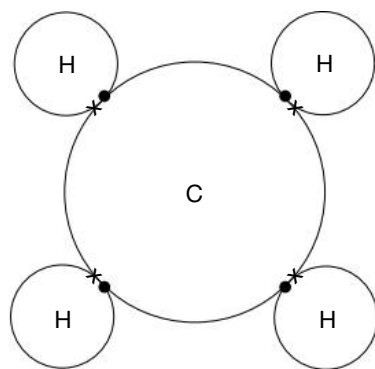
- why carbon forms so many different compounds
- structures of hydrocarbons (alkanes, alkenes, alkynes, cyclohexane and benzene)
- structures of organic compounds containing other functional groups (alcohols, aldehydes, ketones, carboxylic acids, primary amines, primary amides, haloalkanes)
- molecular, structural, skeletal and semi-structural formulas
- systematic naming of non-cyclic hydrocarbons, haloalkanes, primary amines, alcohols (primary, secondary, tertiary), carboxylic acids and non-branched esters.



Crystals of urea. Urea has a unique place in the history of chemistry. The first isolation of urea crystals from inorganic materials by Friedrich Wohler in 1828 was not well received, because until then scientists firmly believed in the theory of 'vitalism'. This theory proposed that organic chemicals could be produced only by living organisms. Like many discoveries, it was accidental. He was trying to make ammonium cyanate by mixing ammonium chloride with silver cyanate. He excitedly wrote to Berzelius: 'I must tell you that I can make urea without the use of kidneys, either man or dog.' The theory of vitalism had been discredited; gradually more and more organic chemicals were artificially produced in the laboratory and then, increasingly, on a larger scale. Now, millions of organic chemicals are involved in industrial processes each year. Urea is known to be a waste product of many living organisms, and it is the major organic component of human urine; it is the end product of a series of reactions that break down the amino acids that make up proteins.

Carbon: a unique element

It has been estimated that over four million compounds containing carbon and hydrogen (**hydrocarbons**) have formulas known to chemists. This is more than the number of compounds of all the other elements put together. Each year, chemists make thousands more new carbon compounds. Why can carbon form such an enormous number of compounds? The answer lies in its unique structural and bonding properties.



Outershell electron arrangement showing fully shared octet of electrons in methane. An outer shell of eight electrons (an octet) confers relative stability within carbon compounds.

- The electronegativity of carbon is too low for a carbon atom to attract electrons from another element to form a negative ion, and it is too high to release electrons to another element to form a positive ion. Instead, it forms **covalent bonds** with many other atoms.
- Carbon has four outershell electrons, which it can share with atoms of H, O, N, S, P and the halogens to form strong covalent bonds. In doing so, the fully shared octet of electrons is responsible for the relative stability of its compounds.
- Because of their small size, carbon atoms can get close enough to form strong double and triple bonds with itself, as well as ring structures when its ends are joined. The ability of carbon to form strong bonds to itself enables it to **catenate**, meaning that it can form chains and rings of various sizes. No element other than silicon has this ability. This is the basis for the many stable compounds of carbon.
- The ability of carbon to form four covalent bonds means that a chain of carbon atoms can have many different groups attached to it, and this leads to a wide diversity of compounds.

The bond energies in table 8.1 show that carbon forms relatively strong bonds with other carbon atoms as well as with atoms of other elements. (Bond energy is a measure of the amount of energy needed to break apart 1 mole of covalently bonded molecules in the gaseous state.)

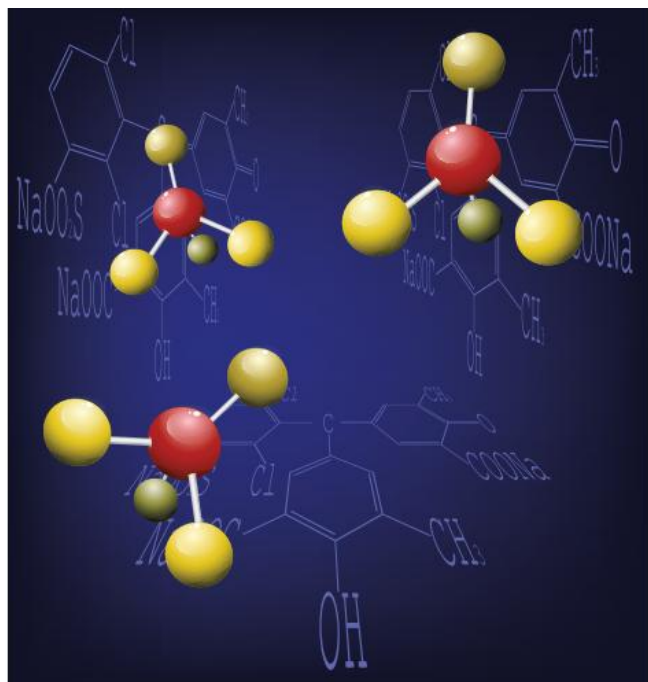
TABLE 8.1 Comparison of bond energies (kJ mol⁻¹)

Different elements								Same elements	
H—H	436	C—H	414	N—H	391	O—H	463	C—C	346
H—C	414	C—C	346	N—C	286	O—C	358	C=C	614
H—N	391	C—N	286	N—N	158	O—N	214	Cl—Cl	242
H—O	463	C—O	358	N—O	214	O—O	144	Br—Br	193
H—F	567	C—F	492	N—F	278	O—F	191	I—I	151
H—Cl	431	C—Cl	324	N—Cl	192	O—Cl	206	H—H	436

Organic chemistry

The diversity of carbon compounds is responsible for the diversity of life itself. You yourself are a unique individual made up of millions of carbon-containing molecules. For a long time, it was thought that only living things could make the more complex carbon compounds. The term 'organic' means living, and **organic chemistry** was initially the study of carbon compounds in plants and animals. As mentioned previously, we now know that many complex carbon compounds can also be artificially synthesised in the laboratory. Organic chemistry is now usually defined as the branch of chemistry concerned with the study of carbon compounds containing C—H bonds, excluding compounds such as cyanides (e.g. HCN), the oxides of carbon (e.g. CO and CO₂) and carbonates (e.g. CaCO₃), which are all inorganic compounds. (In contrast, the study of chemistry in living things is called biochemistry.)

Organic chemistry is the study of carbon-containing compounds and their properties.



Organic chemistry provides the basis for many useful chemicals.

The knowledge that carbon forms the basis of the molecules of life means that the study of organic chemistry is of central importance to the understanding of the chemistry and biology of living systems. Knowledge of organic chemistry enables chemists to develop and manufacture drugs, agricultural chemicals, anaesthetics and other chemicals essential to human life processes. Other non-biological organic compounds that are important to our modern society are polymers, such as plastics and nylon, soaps, detergents and dyes.

Organic chemists can organise this vast number of compounds into a relatively small number of categories based on their chemical properties and behaviours in chemical reactions. To identify each unique organic compound from the millions of compounds, chemists use a formal set of nomenclatural rules agreed upon by an international committee. Many of the organic substances that we come across in our everyday lives are known to us by their common names, such as aspirin instead of 2-acetoxybenzoic acid. When we are sick, doctors may prescribe penicillin rather than 6[(5-amino-5-carboxyl-1-oxopentyl)amino]-3,3-dimethyl-7-oxopentyl-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid! In this chapter, we will look at the structures and nomenclature of the organic family groups of alkanes, alkenes and alkynes, and how functional groups can be

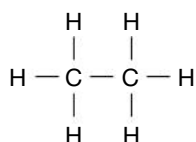
added to them to alter the physical and chemical properties of these groups of compounds.

TABLE 8.2 Some examples of natural and synthetic organic compounds

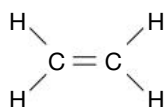
Natural compounds	
Type of compound	Occurrence and use
carbohydrates (sugars and starches)	source of energy found in food
protein	source of compounds for the growth and repair of tissues, e.g. hair and muscles
fats and oils	source of energy found in food and stored (as fats) in the body; used in cooking and for making soaps
hydrocarbons	many found in crude oil and natural gas; used as fuels, e.g. octane compounds form a large part of petrol, and methane is a gas used for cooking
enzymes	complex protein molecules found in plants and animals; catalysis of biochemical reactions
vitamins	complex molecules found in many foods and required in the diet for good health, e.g. ascorbic acid (vitamin C) is present in citrus fruits such as oranges
alkaloids	found in a variety of compounds including medicines such as quinine; betel nut contains about nine alkaloids
Synthetic compounds	
Type of compound	Examples
soaps and detergents	sodium palmitate, $C_{15}H_{31}COONa$, a soap made from palm oil
antibiotics	penicillin
polymers	plastics, which are polymers of different monomers, e.g. polyethene, polystyrene, nylon

Hydrocarbons

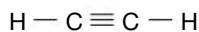
Hydrocarbons are the simplest organic compounds and are composed solely of carbon and hydrogen. They are obtained mainly from crude oil and are used as fuels or solvents or in the production of plastics, dyes, pharmaceuticals, explosives and other industrial chemicals. The organic families studied in this chapter contain various percentages of carbon and hydrogen atoms; they include the alkanes, alkenes and alkynes, which are classified as **aliphatic** compounds, and benzene, which is an **aromatic** compound.



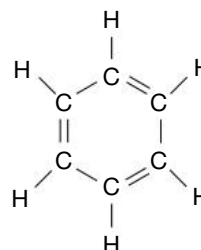
ethane



ethene



ethyne



benzene



The benzene ring is usually drawn as a circle inside a hexagon.

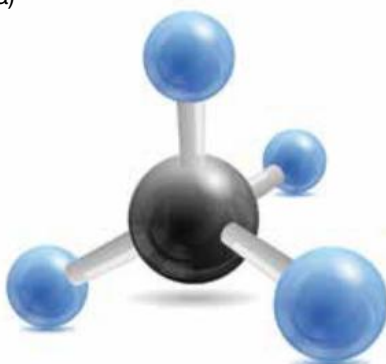
Carbon compounds — the structural arrangement of ethane, ethene, ethyne and the benzene ring. Carbon can form a ring structure as well as single or multiple bonds with itself.

Alkanes

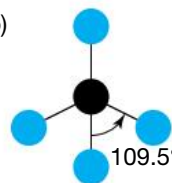
The simplest family of hydrocarbons is the **alkanes**. Alkane compounds have single carbon-carbon bonds. They are said to be saturated organic compounds since each carbon atom is bound to the maximum number of four other atoms. Being **saturated hydrocarbons**, they cannot take up any more hydrogen atoms, whereas **unsaturated hydrocarbons** can take up more hydrogen or other single atoms (such as Cl) or groups of atoms (such as the —OH group).

A methane molecule. (a) and (b) are ball-and-stick models of methane showing its tetrahedral arrangement. The bond angles are 109.5° each. (c) and (d) show two ways of representing the structural arrangement of methane: a simple representation and a tetrahedral structural arrangement of the molecule. Hydrocarbon chains with two or more carbon atoms are not really straight but zigzag because of the bond angles of 109.5° .

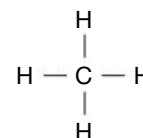
(a)



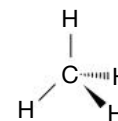
(b)



(c)



(d)



The simplest alkane is methane, CH_4 , which is a colourless gas. The four hydrogen atoms in methane are covalently bonded to the carbon atom, and methane takes the shape of a regular tetrahedron. The addition of a $-\text{CH}_2$ unit to methane forms the next alkane member, ethane, CH_3CH_3 or C_2H_6 . Addition

Alkanes are saturated hydrocarbons containing only single carbon bonds, C—C. They have the general formula C_nH_{2n+2} .

of two $-CH_2$ units gives propane, $CH_3CH_2CH_3$ or C_3H_8 . Alkanes with carbon atoms in long chains are known as straight-chain hydrocarbons. Alkanes have the structural formula C_nH_{2n+2} , where n is an integer.

A family of carbon compounds that are structurally related and where members of the family can be represented by a general formula is called a **homologous series**. Successive members of a homologous series have formulas that differ by CH_2 . Each is named for the number of carbon atoms in the longest chain. The first four alkanes are gases at room temperature.

Propane is used to heat the air in hot air balloons. Propane is a member of the alkane homologous series.



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Naming alkanes
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TABLE 8.3 The first four members of the alkane homologous series

Alkane	Semi-structural (condensed) formula	Source	Uses
methane	CH_4	natural gas or biogas	• fuel • synthesis of other chemicals
ethane	CH_3CH_3	natural gas	• manufacture of ethene • refrigerant in cryogenic systems
propane	$CH_3CH_2CH_3$	natural gas processing or petroleum refining	• fuel, e.g. in gas cylinders for heating • propellant for aerosols
butane	$CH_3CH_2CH_2CH_3$	natural gas processing or petroleum refining	• fuel, e.g. cigarette lighters and portable stoves • synthesis of other chemicals • propellant for aerosols

The next four members of the alkane homologous series are:

- pentane, C_5H_{12}
- hexane, C_6H_{14}
- heptane, C_7H_{16}
- octane, C_8H_{18} .

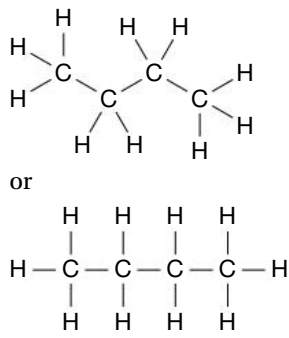
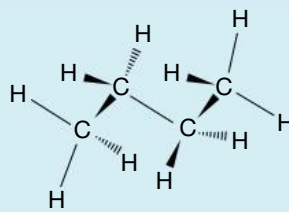
Revision questions

1. What is organic chemistry? Give three examples of organic compounds and three examples of inorganic compounds.
2. If the bond energy of H—F is 565 kJ mol^{-1} , what is the overall bond energy of 2 moles of HF?
3. What is the molecular formula of the alkane containing 18 hydrogen atoms?

Formulas

There are many ways that formulas of compounds can be written. Using butane as an example, some are listed in table 8.4.

TABLE 8.4 Different ways of representing butane molecules

Formula	Example	Notes
molecular	C_4H_{10}	This shows the number and kinds of atoms in a molecule.
empirical	C_2H_5	This shows the simplest whole number ratio of atoms in a molecule.
structural		This shows the actual arrangement of atoms in a molecule. As molecules become longer, the second example of a structural formula tends to be used.
semi-structural or condensed	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	These can be written on a single line, with each carbon atom being followed by the atoms that are joined to it. Repeated CH_2 groups can be collected together in brackets with a subscript as shown.
skeletal		There is a carbon atom at each join and at the ends of the line. There are enough hydrogen atoms to complete the octet of electrons around each carbon atom. This representation is usually used for more complex molecules.
3D structural		This shows the 3D arrangement of atoms, with the bonds represented as follows: • The continuous line is in the plane of the paper. • The dashed line extends to the back of the paper. • The solid wedge comes out of the plane of the paper.

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Isomers

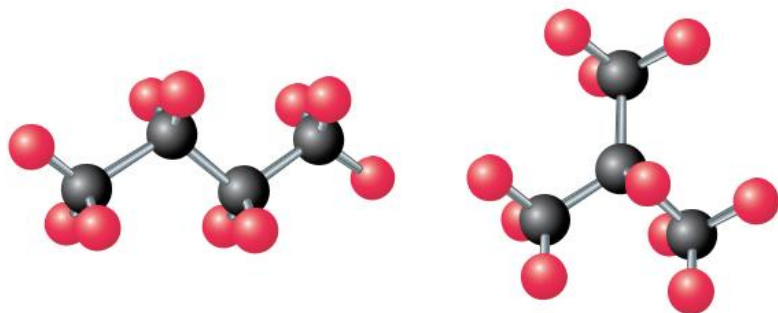
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Branched hydrocarbon chains and isomers

For the first three alkanes — methane, ethane and propane — there is only one way of arranging the atoms and that is the *straight-chain* arrangement. There are two ways of arranging the carbon and hydrogen atoms in butane; hence there are two structures. One is the straight-chain structure and the other is the *branched-chain* structure.

Each of the two structures of butane satisfies the valence of carbon and hydrogen atoms, and each is a neutral and stable molecule. Their chemical

Structural isomers have the same molecular formula but different arrangements of atoms and, therefore, different unique names.



Models of butane and 2-methylpropane

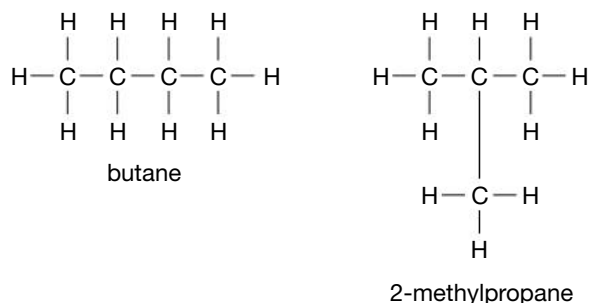
and physical properties are similar but not identical. For instance, straight-chain butane has a boiling point of $-1\text{ }^{\circ}\text{C}$, while the branched chain molecule, 2-methylpropane, has a boiling point of $-12\text{ }^{\circ}\text{C}$. Butane and 2-methylpropane are called **structural isomers** because they have the same molecular formula but different arrangements of atoms.

The number of possible ways of combining the atoms to form isomers increases with the number of carbon atoms in the molecule. Pentane, C_5H_{12} , has three isomers, heptane, C_7H_{16} , has nine, while decane, $\text{C}_{10}\text{H}_{22}$, has 75 isomers. For $\text{C}_{15}\text{H}_{32}$, there are 4347 possible isomers and for $\text{C}_{40}\text{H}_{82}$, there are more than 6×10^{13} possible isomers. Isomerism is responsible for the enormous number of organic compounds that are known. Isomers are discussed in more detail in chapter 9.

Sample problem 8.1

Write the structural isomers for molecules with the formula C_4H_{10} .

Solution:



Revision questions

4. Show the molecular, empirical, semi-structural and skeletal structures of propane.
5. (a) Draw the structural formulas for the three isomers of C_5H_{12} .
(b) Draw skeletal formulas for the three isomers of C_5H_{12} .
6. How many isomers are there for hexane? Draw their structural formulas.
7. Why can carbon form such an enormous number of different compounds?

Nomenclature: the system for naming organic compounds

Having many different structures for compounds with the same molecular formula can cause problems when discussing organic compounds. A system for naming each is essential for scientists to be able to identify each isomer. Chemists follow the International Union of Pure and Applied Chemistry (IUPAC) method of systematically naming the vast number of organic compounds.

A branched chain alkane is named using the following rules.

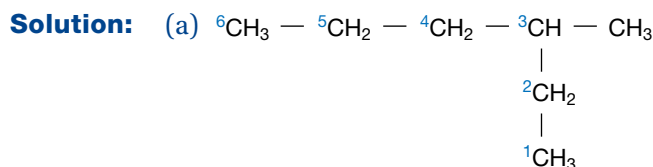
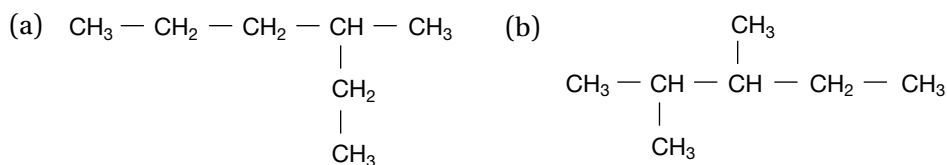
1. Identify and name the longest unbranched carbon chain. (It is helpful to highlight this chain.)

The International Union of Pure and Applied Chemistry is an international organisation that represents chemists in different countries.

2. Number the carbon atoms in the longest unbranched chain, starting with the carbon atom at the end nearest the branch.
3. Identify the branching group(s) of atoms, and state the number of the carbon atom to which it is attached. Branches are named using *-yl*. For example, a branched group of —CH_3 would be named methyl, $\text{CH}_3\text{CH}_2\text{—}$ would be ethyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$ would be propyl, and so on.
4. For molecules with two or more branches of the same type, the branch type is named and a prefix (*di-*, *tri-*, *tetra-* etc.) is used to indicate the number of branches.
5. Branches are listed in alphabetical order, ignoring the prefix in rule 4, e.g. ethyl is written before methyl or dimethyl.

Sample problem 8.2

Use the rules for naming organic compounds to systematically name the following compounds.

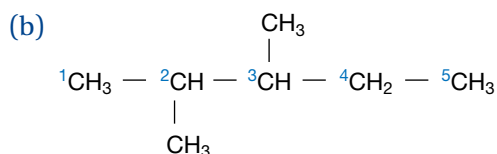


Rule 1: The longest unbranched carbon chain contains 6 carbon atoms, so it is a hexane.

Rule 2: The carbon atoms of the longest unbranched chain are numbered from right to left, because the —CH_3 branch is closest to the right and so it is attached to the lowest numbered carbon atom.

Rule 3: The branching chain is —CH_3 , so it is methyl and is attached to carbon atom 3.

Therefore, the name of the molecule is 3-methylhexane. Note that the name is written without spaces.



Rule 1: The longest unbranched carbon chain contains 5 carbon atoms, so it is a pentane.

Rule 2: The carbon atoms of the longest unbranched chain are numbered from left to right, because the branches are closest to the left.

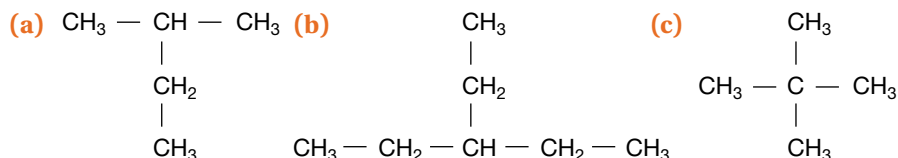
Rule 3: The branching chains are —CH_3 , so they are methyls and attached to carbon atoms 2 and 3.

Rule 4: The two branches are both —CH_3 , so they are named dimethyl.

Therefore, the name of the molecule is 2,3-dimethylpentane.

Revision questions

8. Name the following compounds.



9. Write the semi-structural formulas for the compounds in question 8.

10. (a) What is wrong with the name 3-methylbutane?

(b) What is wrong with the name 3-ethylpropane?

study on

Unit 4

AOS 1

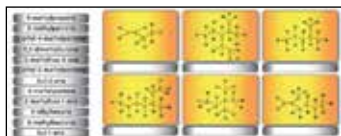
Topic 2

Concept 2



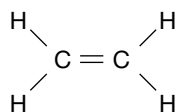
Do more

Systematic naming
of alkanes and
alkenes

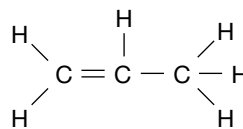


Alkenes

Double bonds between carbon atoms are formed when two hydrogen atoms are removed from alkanes. These hydrocarbons are said to be unsaturated. Hydrocarbons with one or more carbon-carbon double bonds per molecule are members of the homologous series called **alkenes**. The general formula for alkenes is C_nH_{2n} . The first two members of the alkene series are ethene, C_2H_4 , and propene, C_3H_6 . Their structural formulas are shown below.



ethene



propene

Ethene is also commonly known as ethylene. It is produced naturally by some plants, and it aids in ripening fruit. It can also be produced artificially by heating petroleum in the absence of air in a process called cracking. Ethene is an important raw product for making many chemicals and plastics.

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Experiment 8.1 Constructing models
of hydrocarbons

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Homologous series of alkenes

eles-2477

TABLE 8.5 Members of the alkene homologous series up to C_8

Systematic name	Formula	Structural formula
ethene	C_2H_4	$\text{H}_2\text{C}=\text{CH}_2$
prop-1-ene	C_3H_6	$\text{H}_2\text{C}=\text{CHCH}_3$
but-1-ene	C_4H_8	$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3$
pent-1-ene	C_5H_{10}	$\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}_3$
hex-1-ene	C_6H_{12}	$\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CH}_3$
hept-1-ene	C_7H_{14}	$\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{CH}_3$
oct-1-ene	C_8H_{16}	$\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CH}_3$

Nomenclature of alkenes

Table 8.5 shows the first seven members of the alkene series. Alkenes are named using the same general rules described for alkanes except that the suffix *-ene* is added instead of *-ane*, and the number of the carbon atom after which the double bond is positioned is indicated. The longest unbranched chain must contain the double bond, so the molecule $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$ is named pent-2-ene.

- The '2' indicates the position of double bond between carbon atoms 2 and 3 (the lower number is used in the formula, and numbering starts from the carbon atom closest to the double bond)
- 'pentene' indicates that five carbon atoms are present in the unbranched chain. Some people prefer to name it 2-pentene. Either way, the number of carbon atoms in the chain and the position of the carbon bond are indicated. For consistency, we will use the first naming method.

These tomatoes are the same age but the red one has been ripened using ethene gas.

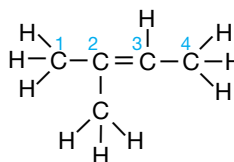


Alkenes are unsaturated hydrocarbons containing one or more carbon double bonds, $C=C$. Alkenes with one double bond have the general formula C_nH_{2n} .

For example, the molecule $CH_3C(CH_3)=CHCH_3$ would be butene:



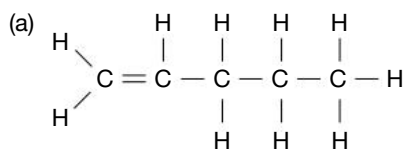
- There are four carbon atoms in the longest unbranched chain containing the double bond.
- Carbon atom 2 is the position of the double bond.
- The branching chain is -methyl, CH_3 , and is branched from carbon atom 2. Hence, the full name of this alkene is 2-methylbut-2-ene.



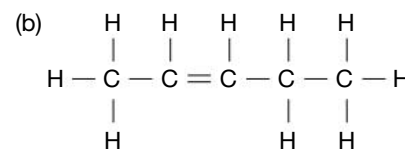
2-methylbut-2-ene

The alkenes also display structural isomerism. While ethene and propene do not display isomerism, there are three isomers for butene. Shown below are the structural isomers for pentene. Note that, if there are two double bonds in the chain, the compound is called a diene, e.g. buta-1,2-diene or hexa-1,4-diene. Note the extra 'a' inserted after the prefixes *but-* and *hex-*.

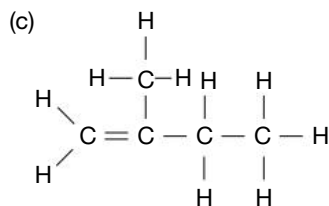
Structural isomers of C_5H_{10}



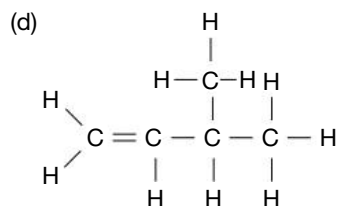
pent-1-ene



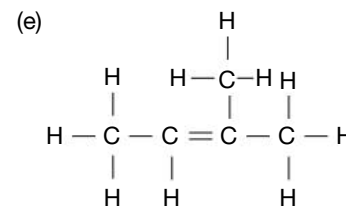
pent-2-ene



2-methylbut-1-ene



3-methylbut-1-ene



2-methylbut-2-ene

Alkynes are unsaturated hydrocarbons containing one or more triple carbon bonds, $\text{C}\equiv\text{C}$. Alkynes with one triple bond have the general formula $\text{C}_n\text{H}_{2n-2}$.

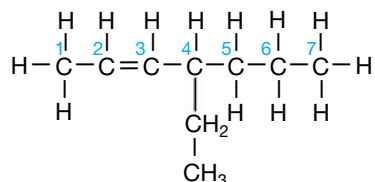
Alkynes

Alkynes are named using the same general rules as for alkanes, but the *-ane* is dropped and replaced with *-yne*. Alkynes contain a carbon-carbon triple bond and have the general formula $\text{C}_n\text{H}_{2n-2}$. Examples include ethyne, HCCH , and propyne, HCCCH_3 . Ethyne is used to produce ethane and also in oxyacetylene torches for welding to join metals. It can heat objects up to 3000°C .

Sample problem 8.3

Write the structural formula for 4-ethylhept-2-ene.

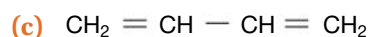
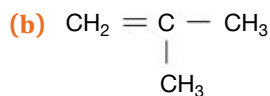
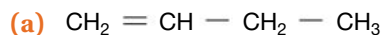
Solution:



Cutting metal with an ethyne (acetylene) torch

Revision questions

11. Name these alkenes.



12. Write the structural formulas for these alkenes.



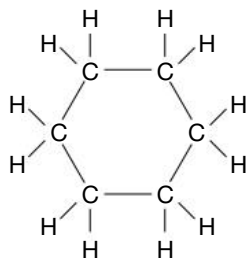
13. What is the general formula for the alkenes? Why are there no alkenes with $n = 1$?

14. Write the structural isomers for the three alkenes for which $n = 4$.

Cyclohexane is an aliphatic ring compound, and benzene is an aromatic ring compound.

Carbon rings

Nylon, the synthetic fibre used to make a variety of clothing and ropes, is manufactured from chemicals formed from cyclohexane, one of carbon's many ring arrangements. **Cyclohexane**, C_6H_{12} , is a colourless, flammable liquid. The cyclohexane molecule has six carbon atoms joined by single bonds. Each carbon atom has two hydrogen atoms attached, but the atoms do not lie in a flat plane. Cycloalkanes are classified as aliphatic compounds together with the unsaturated and saturated compounds discussed so far in this chapter.



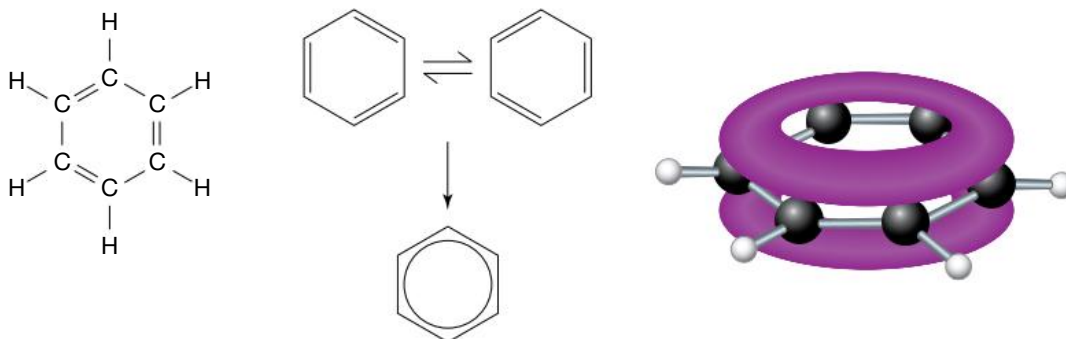
Cyclohexane, C_6H_{12}



Nylon rope

Compounds containing a **benzene** ring are classified as aromatic compounds. They are described as aromatic because they often have an odour or fragrance. The benzene, C_6H_6 , molecule consists of six carbon atoms arranged in a ring with one hydrogen atom bonded to each carbon. Originally, it was thought that there were alternating single and double carbon-carbon bonds in the ring. However, the lack of reactivity, high stability and same bond lengths between the carbon atoms did not support this theory. The current description of the molecule has the six electrons from the three double bonds shared by all of the carbon atoms in the ring. The attraction of the electrons to all of the carbon atoms gives the molecule stability. Benzene is a very important compound in organic chemistry. Even though benzene itself is carcinogenic, many of the chemicals produced from it are not. In fact, many foods and pharmaceuticals, such as paracetamol, contain benzene rings.

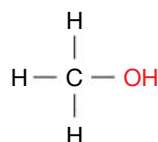
There are various ways of representing the benzene ring, as shown below.



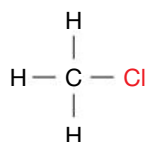
Functional groups

An atom or a group of atoms in a molecule that determines the physical and chemical properties of that molecule is called a functional group.

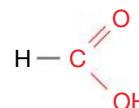
Different functional groups ($-\text{OH}$, $-\text{Cl}$ and $-\text{COOH}$) attached to the basic carbon skeleton of methane



CH_3OH
methanol



CH_3Cl
chloromethane



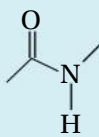
HCOOH
methanoic acid

As with the alkanes and alkenes, compounds containing the same functional group form a homologous series (a family with similar properties). The fact that the millions of carbon compounds known to chemists can be grouped in series helps to make sense of their chemistry. This is because the same group of atoms in the same series usually behaves a similar way in all compounds and helps determine the characteristics of compounds in that particular series. The $-\text{OH}$ functional group is known as the **hydroxyl group** and is present in the homologous series of **alcohols**. The $-\text{COOH}$ group is known as the **carboxyl group** and belongs to the series known as **carboxylic acids**. Functional groups are so called because they determine the chemical and functional nature of an organic compound. The hydrocarbon backbone of these compounds remains relatively unreactive. Table 8.6 shows the common functional groups of organic compounds.

TABLE 8.6 Common functional groups

Group		Homologous series	Method of naming	Examples
Formula	Name			
$-\text{O}-\text{H}$	hydroxyl	alcohol	suffix <i>-ol</i>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, propan-1-ol (1-propanol)
$\begin{array}{c} \text{O} \\ // \\ -\text{C} \\ \backslash \\ \text{H} \end{array}$	aldehyde	aldehyde	suffix <i>-al</i>	CH_3CHO , ethanal (acetaldehyde)
$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$	carbonyl	ketone	suffix <i>-one</i>	$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$, pentan-3-one (3-pentanone)
$\begin{array}{c} \text{O}-\text{H} \\ / \\ -\text{C} \\ \backslash \\ \text{O} \end{array}$	carboxyl	carboxylic acid	suffix <i>-oic acid</i>	CH_3COOH , ethanoic acid (acetic acid)
$\begin{array}{c} \text{O}- \\ / \\ -\text{C} \\ \backslash \\ \text{O} \end{array}$	ester	ester	as alkyl alkanoate	$\text{CH}_3\text{CH}_2\text{COOCH}_3$, methyl propanoate

TABLE 8.6 (continued)

Group		Homologous series	Method of naming	Examples
Formula	Name			
	ether	ether	as alkoxyalkane, or name the two groups attached to the ether linkage	CH ₃ OCH ₃ , methoxymethane or dimethyl ether
	amine	amine	suffix <i>-amine</i>	CH ₃ NH ₂ , methanamine CH ₃ CH ₂ NH ₂ , ethanamine
	amide	amide	suffix <i>-amide</i>	CH ₃ CONH ₂ , ethanamide, and CH ₃ CH ₂ CONH ₂ , propanamide
—Cl —Br —I	chloro bromo iodo	haloalkanes	prefix <i>chloro-</i> prefix <i>bromo-</i> prefix <i>iodo-</i>	CH ₃ Cl, chloromethane CH ₃ CH ₂ Br, bromoethane ICH ₂ CH ₂ I, 1,2-diiodoethane

Alcohols are characterised by the hydroxyl group, —OH.

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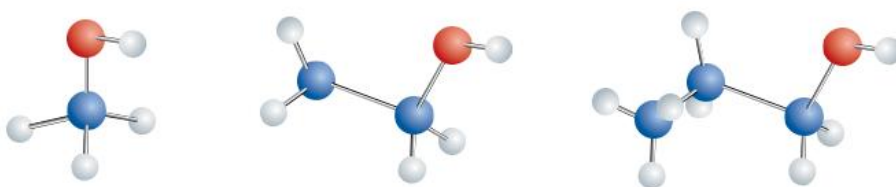
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Molecular representations of butan-1-ol
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Alcohols

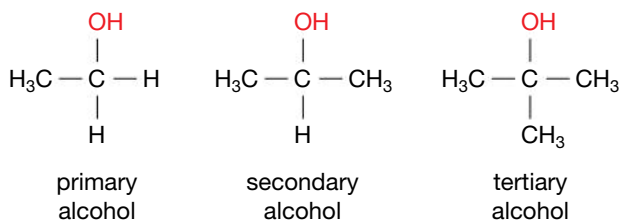
Organic hydroxyl compounds containing the —OH group belong to the homologous series called alcohols. A study of the properties of the —OH group is important to chemists because of the industrial importance of compounds containing this functional group, and because of its wide occurrence in biological molecules. Ethanol is the most common alcohol and it has many uses. It is present in beer, wine and spirits. It is used in the preparation of ethanoic acid (acetic acid) and for sterilising wounds. Methylated spirits (containing 95% ethanol) is a very useful solvent and is used in the manufacture of varnishes, polishes, inks, glues and paints. Other alcohols that are volatile at low temperatures are also good solvents are used in deodorants, colognes and after-shave lotions. Glycerol, C₃H₅(OH)₃, is used for making fats and soaps.

Structural models for the first three alcohols: methanol, ethanol and propan-1-ol



Alcohols are classified as primary, secondary and tertiary, based upon the number of carbon atoms connected to the carbon atom that is attached to the hydroxyl functional group.

- Primary (1°): The C—OH is attached to one other carbon atom.
- Secondary (2°): The C—OH is attached to two other carbon atoms.
- Tertiary (3°): The C—OH is attached to three other carbon atoms.



Types of alcohols

Nomenclature of alcohols

Alcohols are named by replacing the last *-e* in the name of the corresponding alkane with *-ol*. Their general formula is $R\text{—OH}$, where R is an alkyl group. The first eight alcohols of the homologous series are listed in table 8.7.

TABLE 8.7 The first eight alkanols. The —OH group is attached to the first carbon atom in each case.

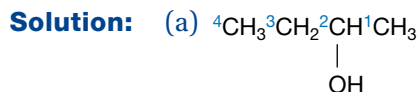
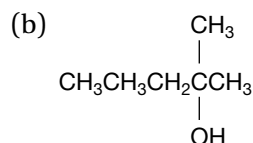
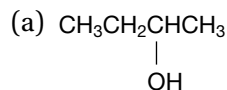
Systematic name	Formula
methanol	CH_3OH
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$
propan-1-ol	$\text{CH}_3(\text{CH}_2)_2\text{OH}$
butan-1-ol	$\text{CH}_3(\text{CH}_2)_3\text{OH}$
pentan-1-ol	$\text{CH}_3(\text{CH}_2)_4\text{OH}$
hexan-1-ol	$\text{CH}_3(\text{CH}_2)_5\text{OH}$
heptan-1-ol	$\text{CH}_3(\text{CH}_2)_6\text{OH}$
octan-1-ol	$\text{CH}_3(\text{CH}_2)_7\text{OH}$

The systematic naming of alcohols follows similar rules to those described previously for the alkanes.

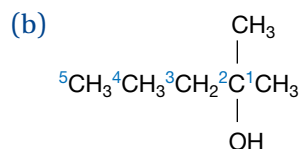
1. Find the longest chain that has the hydroxyl group attached, and replace the last *-e* in the name of the corresponding alkane with *-ol*.
2. Number the carbon atoms in the main chain. Begin at the end nearest the hydroxyl group.
3. Indicate which carbon atom is bonded to the hydroxyl group by placing the number either at the beginning of the name or before the *-ol*, e.g. 2-pentanol or pentan-2-ol. For consistency, we will use the second option.

Sample problem 8.4

Name the following alcohols.



This is butan-2-ol, since the —OH group is located on the second carbon atom of the longest 4-carbon chain (*butan-*).



The longest carbon chain has five carbon atoms, making it *pentan-*. The —OH group makes it *-ol*, hence pentanol. Both the methyl, —CH_3 , and hydroxyl, —OH , groups are at position 2 of the chain. This is 2-methylpentan-2-ol.

Revision questions

15. (a) What is the general formula for the family of alcohols?
(b) Write the structural formulas for:
(i) butan-1-ol (ii) pentan-3-ol (iii) $\text{C}_2\text{H}_5\text{OH}$ (iv) 2-methylpropan-1-ol
(v) 2,2-dimethylhexan-3-ol (vi) $\text{C}_7\text{H}_{15}\text{OH}$.
16. Draw the structures of the following alcohols, and explain whether they are primary, secondary or tertiary alcohols.
(a) propan-2-ol
(b) 2-methylpropan-1-ol

Aldehydes contain the $\text{—C}\begin{array}{l} \text{O} \\ \parallel \\ \text{H} \end{array}$ functional group and are named by adding the suffix *-al*.

Aldehydes

Aldehydes have characteristic odours. The familiar smells of vanilla and cinnamon are caused by aldehydes. Low-molecular-weight aldehydes, such as methanal (formaldehyde) and ethanal, have unpleasant odours; formaldehyde was previously used as a preservative but is now suspected to be carcinogenic. High-molecular-weight compounds have sweet, pleasant smells and are used

in perfumes. Other uses of aldehydes include solvents and the manufacture of plastics, dyes and pharmaceuticals.

Aldehydes contain the —CHO group and are named by replacing the last *-e* on the name of the corresponding alkane with *-al*. Propane, for example, becomes propanal.

Aldehydes have the C=O bond at the end of the carbon chain, at C1 . As aldehydes are always named from C1 , they do not need a number in the name to reference where the functional group is.



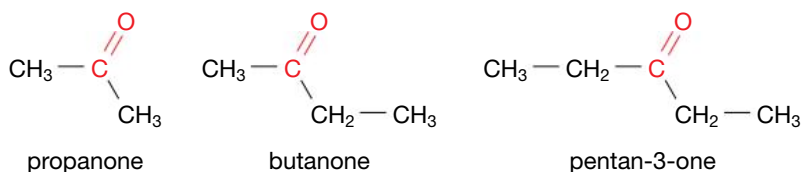
Aldehydes and ketones are used to manufacture perfumes.

Ketones contain the >C=O functional group and are named by adding the suffix *-one*.

Ketones

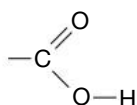
Ketones are characterised by the presence of a carbonyl group in which the carbon atom is bonded to an oxygen atom by a double covalent bond. They are named by replacing the last *-e* in the name of the corresponding alkane with *-one*. Butane, for example, becomes butanone. The position of the >C=O group differentiates a ketone from an aldehyde. If the C=O bond in a compound contains the terminal carbon atom, it is an aldehyde $\text{—C}\begin{array}{l} \text{O} \\ \parallel \\ \text{H} \end{array}$. If the C=O bond is connected to adjacent carbon atoms, it is a ketone.

Ketones are used extensively to produce pharmaceuticals, perfumes, solvents and polymers. They have important physiological properties and are found in medicinal compounds and steroid hormones, including cortisone. The most familiar ketone is propanone (acetone), which has unlimited solubility in water and is a solvent for many organic compounds. It evaporates readily because of its low boiling point, which contributes to its usefulness.



Examples of ketones

Carboxylic acids are characterised by the carboxyl functional group.



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Unit 4

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Topic 2

Concept 7

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Carboxylic acids

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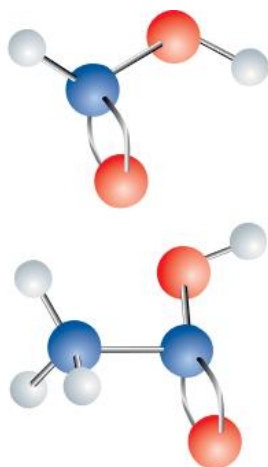
Carboxylic acids

How are an ant and a pickled onion related? Both contain *carboxylic acids*. An ant bite stings because it injects methanoic acid (formic acid) into your skin. An onion is pickled with ethanoic acid (acetic acid), which is present in vinegar. Carboxylic acids are generally weak acids and occur widely in nature. Some common examples include citric acid found in citrus fruits such as oranges and lemons, malic acid found in apples, and ascorbic acid (vitamin C) found in a number of foods. Other carboxylic acids such as stearic acid and oleic and palmitic acids are used in the formation of animal and vegetable fats. Carboxylic acids are also used in making soaps and polyesters.

The C_4 to C_8 carboxylic acids have a strong, unpleasant smell and are found in cheese, perspiration and rancid butter.

TABLE 8.8 Some carboxylic acids and their uses

Systematic name	Formula	Non-systematic name	Occurrence and uses
methanoic acid	HCOOH	formic acid	used by ants as a defence mechanism; also used in textile processing and as a grain preservative
ethanoic acid	CH_3COOH	acetic acid	found in vinegar; used in making artificial textiles
propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$	propionic acid	calcium propanoate used as an additive in bread manufacture
butanoic acid	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	butyric acid	present in human sweat; responsible for the smell of rancid butter
benzoic acid	 -COOH	benzoic acid	used as a preservative



Structural models of methanoic and ethanoic acids



Dogs can be trained to find fruit by sniffing out distinctive carboxylic acids, such as malic acid, which is found in apples. Sniffer dogs play an important part in quarantine procedures to prevent the illegal import and export of fruit.

Nomenclature of carboxylic acids

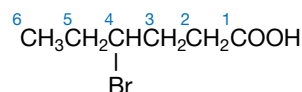
The functional group in carboxylic acids is the *carboxyl* group, —COOH . Carboxylic acids are generally written as RCOOH , where R is a hydrogen atom or an alkyl group. Their names are based on the names of the corresponding alkanes with the same number of carbon atoms. The last *-e* in the name of the alkane is replaced by *-oic acid* in the corresponding carboxylic acid. Hence, the carboxylic acid derivative of methane is methanoic acid and that of heptane is heptanoic acid. Carboxylic acids are sometimes called alcanoic acids.

TABLE 8.9 The first eight compounds of the carboxylic acid homologous series

Systematic name	Structural formula
methanoic acid	HCOOH
ethanoic acid	CH_3COOH
propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$
butanoic acid	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$
pentanoic acid	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$
hexanoic acid	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$
heptanoic acid	$\text{CH}_3(\text{CH}_2)_5\text{COOH}$
octanoic acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$

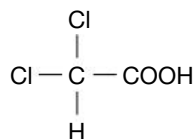
Methanoic acid and ethanoic acid are the first two members of the carboxylic acid series and are still often called by their old names, formic acid and acetic acid, respectively.

Carboxylic acids are named systematically using the same rules as those for the alkanes. Counting must commence with the carbon atom in the carboxyl group but it is not necessary to include the '1' in the name of the acid.



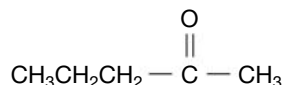
For example, the compound above is 4-bromohexanoic acid. The carboxyl group is associated with a six-carbon chain, making it hexanoic acid. The Br atom is located on the fourth carbon atom of the chain, making it 4-bromohexanoic acid.

The structural formula for dichloroethanoic acid is:



Revision questions

17. Draw the structure of propanone (acetone), $(\text{CH}_3)_2\text{CO}$.
18. Which homologous series does this molecule belong to?



19. Draw the structural formulas for butanoic and octanoic acids.
20. Draw the structural formula for:
 - (a) chloroethanoic acid
 - (b) dichloroethanoic acid
 - (c) trichloroethanoic acid.

Is it possible to have tetrachloroethanoic acid? Explain your answer.
21. Name and draw the structures of the ketones containing five carbon atoms.
22. Draw the structural formulas for:
 - (a) propanoic acid
 - (b) 2-methylpropanoic acid.

Esters

When you eat a banana or a pear or remove nail polish with a solvent, the strong sweet fruity odour that you smell is that of an **ester**. In a typical ripe pineapple, you will find about 120 mg per kg of the ester ethyl ethanoate, 60 mg of ethanol and small amounts of other esters. Ethyl ethanoate (also called ethyl acetate) is a volatile liquid with a fruity odour. It is found in a number of tropical fruits. Esters are good solvents and are used in paints and lacquers. Ethyl ethanoate is used in nail polish remover. A less volatile ester such as butyl ethanoate is used in nail polish because its boiling point is higher than that of water, enabling it to remain until the water vapour has evaporated (so as not to spoil the gloss). Esters are also used in perfumes, cosmetics and artificial flavourings. Another use of esters is in the formation of polyester, an artificial fibre.

Animal fats and vegetable oils (such as peanut, coconut and olive oils) are esters of carboxylic acids with glycerol. Stearic, oleic and palmitic acids are typical carboxylic acids found in natural fatty esters.

Esters are widely used as solvents and flavourings and to make fibres.

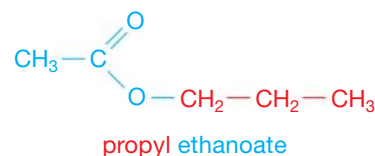
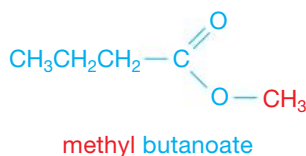
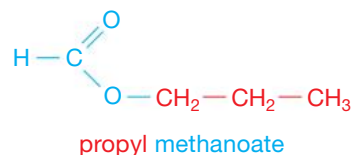
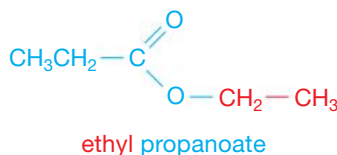
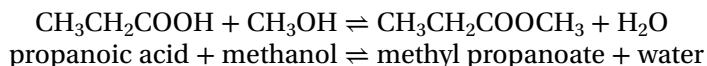
Esters are characterised by the ester link $\begin{array}{c} \text{O} - \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array}$.



Pineapples contain the ester ethyl ethanoate.

Nomenclature of esters

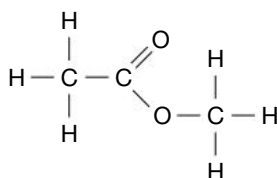
Esters all contain the ester functional group —OCO— and are formed from the reaction of a carboxylic acid and an alcohol. The name of an ester is derived from the alkyl group of the alcohol, with the suffix *-yl*, followed by the stem from the carboxylic acid with the suffix *-oate*. Hence, the ester derived from methanol and propanoic acid is called methyl propanoate.



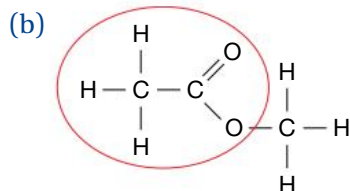
Examples of esters

Sample problem 8.5

- (a) Name the ester formed as a result of the reaction between ethanol and propanoic acid.
 (b) Name the ester that has this structure.



Solution: (a) The first part of the name is derived from the alcohol, with *-anol* replaced by *-yl*. The second part comes from the carboxylic acid, in which *-oic acid* becomes *-oate*. The name is ethyl propanoate.

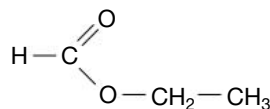


Circle the section of the molecule that contains the ester group —OCO— . This has two carbon atoms and comes from the carboxylic acid and is therefore *ethanoate*. The remaining part of the molecule has one carbon atom and comes from the alcohol and so is *methyl*. Therefore, the name of the ester is methyl ethanoate.

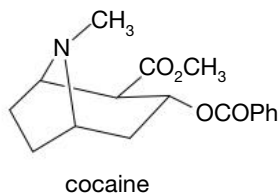
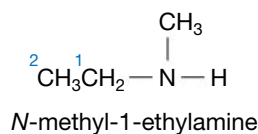
Revision questions

23. Name the ester formed from the reaction between methanol and ethanoic acid.
 24. Write the semi-structural formula of the ester butyl methanoate.

25. Name the following ester.



Primary amines have the structure $R-\text{NH}_2$ and are named by adding the suffix *-amine*: for example, methylamine, CH_3NH_2 .



Amines are organic derivatives of ammonia, NH_3 . Plants have many of these amines as nitrogenous compounds. Natural alkaloids extracted from plants using organic solvents are amines. Cocaine, nicotine and natural alkaloids are nitrogen heterocycles and are well known for their potent pharmacological activities. A study of alkaloids is crucial to understanding the biological action of these pharmaceutical products and their manufacture in the pharmaceutical industry.

Amines

Fishy smells and smells associated with decaying animal tissues are due to amines such as putrescine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, and cadaverine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. The $-\text{NH}_2$ group belongs to the homologous series called amines. Amines are essential to life and play a part in the formation of amino acids, which are the building blocks of proteins and many vitamins.

Table 8.10 shows the first eight compounds of the amine homologous series.

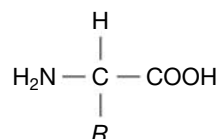
Primary amines have the structure $R-\text{NH}_2$ where R is an alkyl group. Primary amines are named by replacing the last *-e* in the name of the corresponding alkane with *-amine*. For example, CH_3NH_2 is known as methanamine, and $\text{CH}_3\text{CH}_2\text{NH}_2$ is ethanamine. Using the same rules as those for naming organic compounds, the systematic name for $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{CH}_3$ is pentan-2-amine.

TABLE 8.10 The first eight compounds of the amine homologous series

Systematic name	Structural formula
methanamine	CH_3NH_2
ethanamine	$\text{CH}_3\text{CH}_2\text{NH}_2$
propan-1-amine	$\text{CH}_3(\text{CH}_2)_2\text{NH}_2$
butan-1-amine	$\text{CH}_3(\text{CH}_2)_3\text{NH}_2$
pentan-1-amine	$\text{CH}_3(\text{CH}_2)_4\text{NH}_2$
hexan-1-amine	$\text{CH}_3(\text{CH}_2)_5\text{NH}_2$
heptan-1-amine	$\text{CH}_3(\text{CH}_2)_6\text{NH}_2$
octan-1-amine	$\text{CH}_3(\text{CH}_2)_7\text{NH}_2$

An amine has the prefix *amino-* only when a higher functional group exists on the molecule. See page 234 for the hierarchy.

Amino acids, the building units for proteins, are organic acids with an amine group attached to a hydrocarbon chain containing an acid group ($-\text{COOH}$). The general structure for amino acids is:



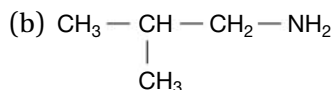
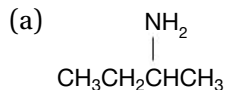
where R is a polar or non-polar group. You will learn more about the significance of the amine group in amino acids in chapter 9.

Many permanent hair dyes are derivatives of an aromatic amine called paraphenylenediamine (PPD), which is used particularly when brown shades are required. The dyeing process involves a redox reaction, and the colourant may absorb into or adsorb to the hair shaft to mask the natural colour.

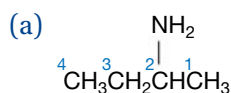


Sample problem 8.6

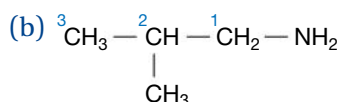
Name the following amines.



Solution:



The longest alkyl stem is 4 carbon atoms (butane); the amine group is attached to the second carbon atom, so the name is butan-2-amine.



The longest alkyl stem is 3 carbon atoms (propane); the methyl group is attached to the second carbon atom, so the name is 2-methylpropan-1-amine.

Amides are used to colour crayons.



Amides

Amides contain the —CONH_2 group. The simplest amides are methanamide and ethanamide. Ethanamide is a liquid at room temperature, but other amides are solid. The high melting points for these small amides is due to the formation of H bonds with other amide molecules. Amides are used as solvents in a variety of pharmaceuticals, including penicillin and pain killers, and in the manufacture of nylon and other polymers. They are used to colour crayons, pencils and inks. Amide linkages are critical in the body as they connect amino acids in proteins. They are called peptide bonds when they occur in the main chain of a protein. The end product of the metabolism of protein is urea, $\text{CO(NH}_2)_2$, an amide.



Do more

Systematic naming
of organic molecules

Haloalkanes

Alkanes can undergo substitution reactions by replacing one of their hydrogen atoms with a halogen atom to form a haloalkane. As shown in table 8.11, the prefix *chloro-* is used to systematically name the members of the chloroalkane homologous series. The first member of the chloroalkane series is chloromethane. It is also known as methyl chloride and is used as a refrigerant and as a local anaesthetic.

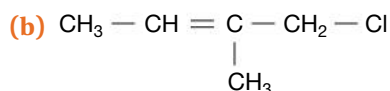
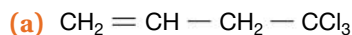
In a similar fashion, the prefixes *fluoro-*, *bromo-* and *iodo-* are used for fluorine, bromine and iodine respectively.

TABLE 8.11 The first eight compounds of the chloroalkane homologous series

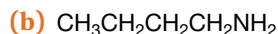
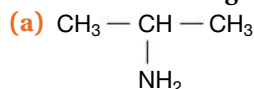
Systematic name	Structural formula
chloromethane	CH_3Cl
1-chloroethane	$\text{CH}_3\text{CH}_2\text{Cl}$
1-chloropropane	$\text{CH}_3(\text{CH}_2)_2\text{Cl}$
1-chlorobutane	$\text{CH}_3(\text{CH}_2)_3\text{Cl}$
1-chloropentane	$\text{CH}_3(\text{CH}_2)_4\text{Cl}$
1-chlorohexane	$\text{CH}_3(\text{CH}_2)_5\text{Cl}$
1-chloroheptane	$\text{CH}_3(\text{CH}_2)_6\text{Cl}$
1-chlorooctane	$\text{CH}_3(\text{CH}_2)_7\text{Cl}$

Revision questions

26. Name these structures.



27. Name the following amines.



28. Draw the structural formulas for:

(a) pentan-3-amine

(b) 2-methylpropan-2-amine

(c) 2,2-dimethylhexan-3-amine.

29. Draw the structural formulas for chloromethane, dichloromethane, trichloromethane and tetrachloromethane.

Compounds containing more than one functional group

Compounds of this type are classified by the principal group (the main functional group) that is highest on the following priority scale:

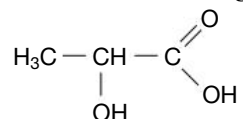
carboxylic acid > ester > aldehyde > ketone > alcohol > amine >
alkyne = alkene > alkane

The parent name is derived from the principal group.

- The numbering system used is that for the principal group.
- An alcohol is regarded as a hydroxyl side group, an amine as an amino side group and a ketone as a carbonyl side group.
- A compound containing both alcohol and aldehyde functional groups is named as an aldehyde with a hydroxyl side group.
- A compound containing an alcohol, a ketone and an acid is named as an acid with hydroxyl and carbonyl side groups.

Sample problem 8.7

(a) Name the following molecule.



(b) Name the following compound.



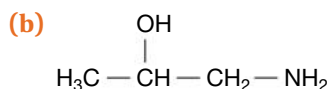
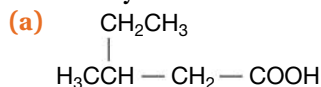
Solution:

- (a) This molecule has a hydroxyl group and a carboxyl group. The carboxyl group has priority, and the longest carbon chain that contains this functional group has three carbon atoms. It is, therefore, a substituted propanoic acid. The hydroxyl group is attached to the second carbon atom counting from the carboxyl group (principal group), and so the name is 2-hydroxypropanoic acid.
- (b) The alcohol group has priority, and there are three carbon atoms, so it is propanol. The amino group is attached to the furthest carbon atom from the —OH. Therefore, the name is 3-aminopropan-1-ol.

Revision questions

30. Write the semi-structural formula for 4-aminopentan-1-ol.

31. Give the systematic names of the following compounds.



Chapter review

Summary

- Organic chemistry is the study of the compounds of carbon. This does not include the inorganic compounds of cyanides, carbonates and oxides of carbon.
- Carbon can form many different compounds due to its ability to create four covalent bonds with itself or other elements.
- In the methane molecule, a carbon atom can form covalent bonds with four other atoms. The resulting shape is tetrahedral, resulting in bond angles of 109.5° .
- Hydrocarbons are organic compounds consisting of carbon and hydrogen atoms only.
- A functional group is an atom or a group of atoms that confers a distinct set of chemical and physical characteristics on an organic compound.
- A homologous series is a group of organic chemical compounds that have a similar structure and whose structures differ only by the number of CH_2 units in the main carbon chain. They are compounds containing the same functional group and have similar properties.
- The alkanes, alkenes and alkynes are hydrocarbons and form homologous series with general formulas of $\text{C}_n\text{H}_{2n+2}$, C_nH_{2n} and $\text{C}_n\text{H}_{2n-2}$, respectively.
- Saturated hydrocarbons have only single C—C covalent bonds.
- Alkanes are saturated hydrocarbons. Alkenes and alkynes are unsaturated hydrocarbons with double and triple carbon bonds, respectively.
- Carbon compounds with the same molecular formulas but different structural arrangements are called structural isomers.
- Rules for naming organic compounds:
 - Identify and name the longest unbranched carbon chain containing the principal functional group. (It is helpful to highlight this chain.)
 - If more than one functional group is present, the order of decreasing priority in determining the suffix is carboxylic acid > ester > aldehyde > ketone > alcohol > amine > alkyne = alkene > alkane.
 - Number the carbon atoms in the longest unbranched chain, starting with the carbon atom nearest the functional group or branch (if an alkane).
 - Identify the branching group(s) of atoms, and state the number of the carbon atom to which it is attached. Branches are named using *-yl*.

For example, a branched group of $-\text{CH}_3$ would be named methyl, CH_3CH_2- would be ethyl, $\text{CH}_3\text{CH}_2\text{CH}_2-$ would be propyl and so on. These go before the name of the longest chain.

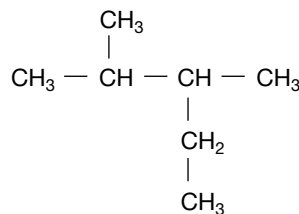
- For molecules with two or more branches of the same type, the branch type is named and a prefix (*di-*, *tri-*, *tetra-* etc.) is used to indicate the number of branches.
- Branches are listed in alphabetical order, ignoring the prefix in the previous rule. Ethyl is written before methyl or dimethyl.

Note: Adjacent numbers in a name are separated by a comma. Numbers are separated from words by a hyphen.

- Carbon compounds in the form of rings, such as benzene, belong to a group called aromatic compounds.
- Alcohols have the functional group $-\text{OH}$ (hydroxyl group) and are named using the suffix *-ol*.
- Aldehydes have the functional group $-\text{CHO}$ (aldehyde group) and are named using the suffix *-al*.
- Ketones have the functional group $-\text{CO}-$ (carbonyl group) and are named using the suffix *-one*.
- Carboxylic acids have the functional group $-\text{COOH}$ (carboxyl group) and are named using the suffix *-oic* followed by *acid*.
- Primary amines have the functional group $-\text{NH}_2$ (amino group) and are named using the suffix *-amine*.
- Amides have the functional group $-\text{CONH}_2$ (amide group)
- Haloalkanes have the functional group $-\text{X}$ (where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I) and are named using the prefix *-fluoro*, *-chloro*, *-bromo* or *-iodo*.

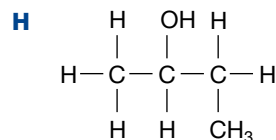
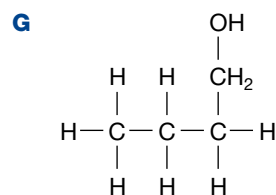
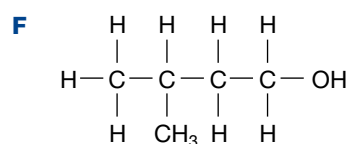
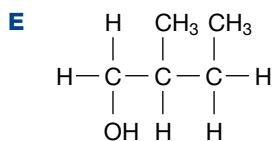
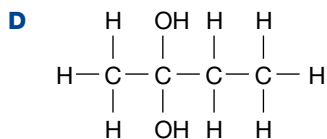
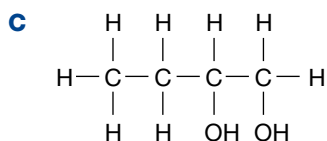
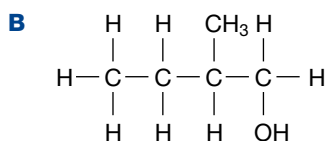
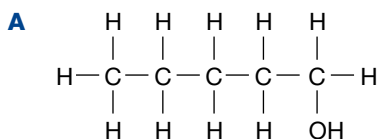
Multiple choice questions

1. The name of the organic compound shown is:



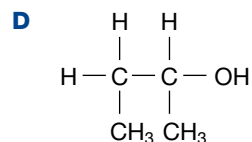
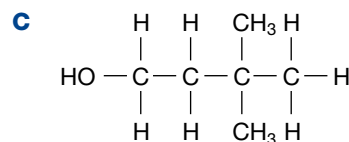
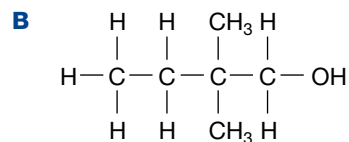
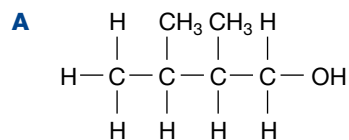
- A 2-methyl-3-ethylbutane
- B 1,2-dimethylpentane
- C 2,3-dimethylheptane
- D 2,3-dimethylpentane.

2. Which of the following does *not* apply to alkanes?
- They have the general formula C_nH_{2n} .
 - They contain C and H.
 - Each has at least one C—C bond.
 - They are saturated hydrocarbons.
3. Which of the following compounds is not regarded as an organic compound?
- C_5H_{10}
 - H_2CO_3
 - C_2H_5OH
 - $ClCH_3$
4. Which of the following compounds is correctly classified as a tertiary alcohol?
- 3-methylbutan-1-ol
 - 2-methylbutan-1-ol
 - 3-methylbutan-2-ol
 - 2-methylbutan-2-ol
5. Which of the following apply to alkenes?
- They are saturated hydrocarbons.
 - They have the formula C_nH_{2n} .
 - Each has a saturated covalent bond.
 - They contain C, H and O.
6. The functional groups and suffixes for naming alcohols and carboxylic acids are respectively:
- OH, COOH, -oate, -ol
 - COOH, OH, -ol, -oic
 - OH, COOH, -ol, -oic
 - OH, COOH, -ol, -oate.
7. Two structural isomers with the same molecular formula as butanol are:



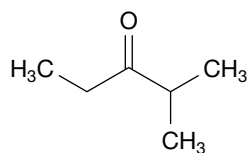
8. The systematic name of the compound $CH_3(CH_2)_5COOH$ is:
- hexanoic acid
 - heptanoic acid
 - hexanol
 - heptanol.

9. The structural arrangement of 2,2-dimethylbutan-1-ol is:



10. Cycloalkanes have the same molecular formula as:
- alkanes
 - alkenes
 - alkynes
 - benzene.
11. Which group of compounds does benzene belong to?
- Alkanes
 - Alkenes
 - Alkynes
 - Aromatics
12. In the IUPAC nomenclature system, the name of which of the following would end in -al?
- An alcohol
 - An aldehyde
 - An alkane
 - A ketone

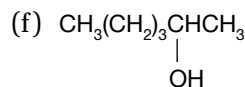
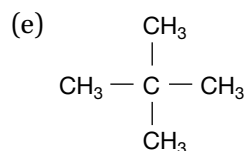
13. The correct name for HCHO is:
A methanal **C** ethanal
B methaldehyde **D** methanone.
14. The ester with the formula $\text{CH}_3\text{COOC}_2\text{H}_5$ is made from:
A ethanol and methanoate
B ethanol and methanoic acid
C ethanol and ethanoate
D ethanol and ethanoic acid.
15. This compound is:



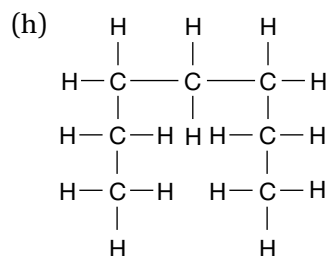
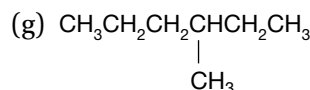
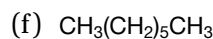
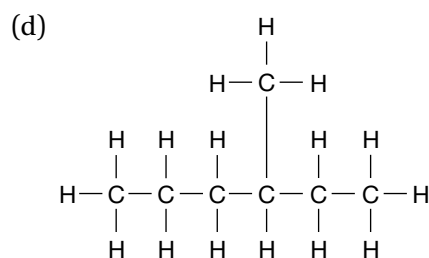
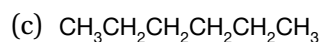
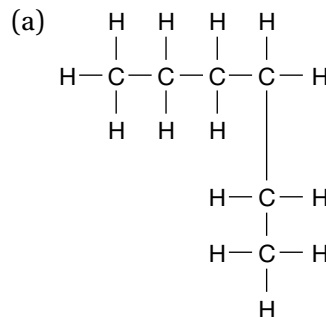
- A** an ester **C** a ketone
B an aldehyde **D** a carboxylic acid.
16. Which type of compound does not contain a carbonyl group?
A Ester **C** Alcohol
B Aldehyde **D** Ketone
17. The common name for the compound $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ is:
A propanamine **C** aminobutane
B propylamide **D** propanamide.
18. The IUPAC name for the compound $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{CH}_3$ is:
A 2-methylpentanamine
B 4-methylpentan-2-amine
C 2-methyl-4-pentanamine
D 4-methyl-2-pentanamine.
19. Which two functional groups are never found at the end of a carbon chain?
A Alcohol and aldehyde
B Ester and aldehyde
C Ketone and acid
D Ester and ketone

Review questions

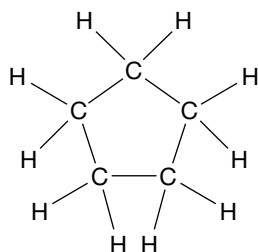
- Define the following terms.
 - Hydrocarbon
 - Homologous series
 - Saturated hydrocarbon
 - Unsaturated hydrocarbon
 - Structural isomer
- Define the terms 'alkane' and 'alkene', and describe their similarities and differences.
- Name the following organic compounds.
 - $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$
 - $\text{CH}_2=\text{CHCl}$
 - CF_2Cl_2
 - $\text{CH}_3\text{CH}_2\text{OH}$



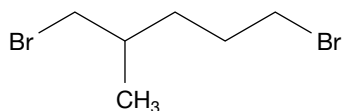
4. Write structural formulas for all alkenes with the molecular formula C_5H_{10} , and name the compounds. How many are there?
5. In what way do functional groups help the study of the vast number of organic compounds?
6. The following structural formulas represent only three different substances. Some of the formulas are equivalent to others. Which formulas are equivalent to which?



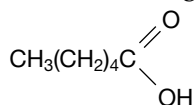
7. What are the molecular formula and name of this compound?



8. Draw the skeletal formula for the compound $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$.
9. Name this compound.



10. Draw the structures of cyclohexane and benzene. What are their similarities and differences?
11. Write the structural formulas for the following compounds.
(a) 2-methylpentan-3-ol
(b) butan-2-ol
(c) 2,2-dimethylbutan-1-ol
(d) 2,3-dimethylpentan-2-ol
(e) pentanoic acid
(f) 2-methylpropanoic acid
(g) butanoic acid
(h) pentanal
(i) 2-chloropropan-1-amine
(j) butyl methanoate
(k) butanone
(l) 2-pentyne
12. Draw and name the four isomers for the compound with molecular formula $\text{C}_4\text{H}_9\text{OH}$.
13. Name the following compounds.



- (b)
-
- (c)
-
- (d)
-
- (e)
-
- (f)
-
- (g)
-
- (h)
-
- (i)
-
- (j)
-
- (k)
-
- (l)
-



Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Multiple choice questions

1. The number of isomers with the formula $C_4H_8O_2$ that are carboxylic acids is:

A 1
B 2
C 3
D 4.

1 mark

2. Which of the following is the systematic name for the molecule below?



A 3-chlorohexane
B 4-chlorohexane
C 3-chloroheptane
D 4-chloroheptane

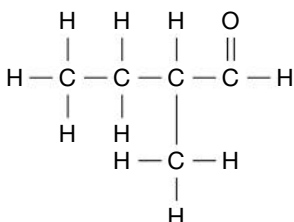
1 mark

3. The structural formula for pentyl ethanoate (banana flavouring) is:

A $CH_3(CH_2)_4COOCH_3$
B $HCOOCH_2CH_2CH_2CH_2CH_3$
C $CH_3COO(CH_2)_4CH_3$
D $CH_3CH_2CH_2CH_2CH_2COOCH_2CH_3$.

1 mark

4. Which is the correct name for:



A pentan-3-al
B pentan-3-one
C 2-methyl-1-butanal
D 2-methylbutanal

1 mark

Extended response questions

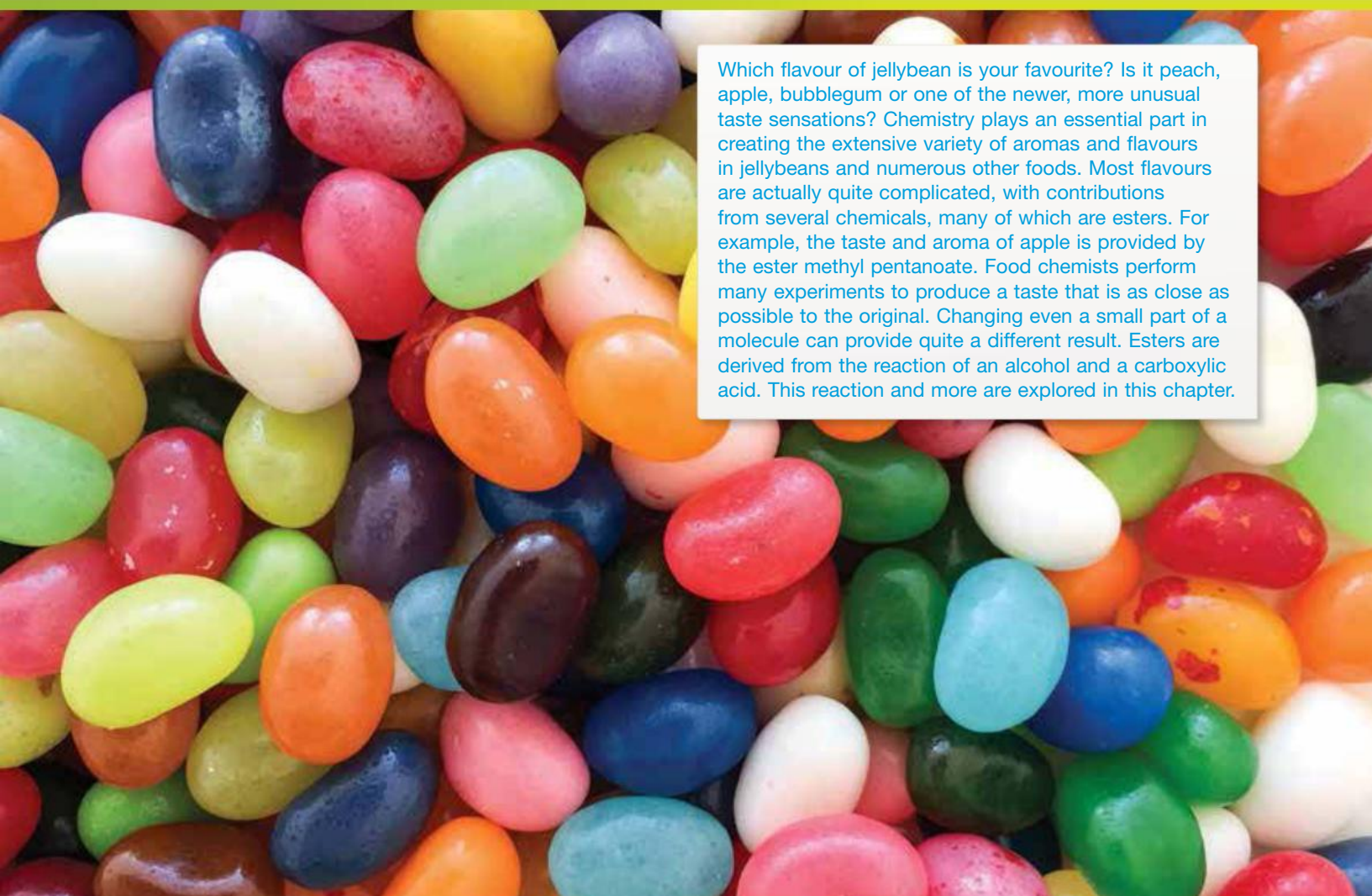
1. Draw and name the isomers of $C_2H_3Cl_3$. 4 marks
2. Sketch the structural formulas and then write the semi-structural formulas for:
- (a) 2-methylbutanoic acid 2 marks
 - (b) 2-ethylpentan-2-ol 2 marks
 - (c) 3-heptyne 2 marks
 - (d) 2-methylbutanamine 2 marks
 - (e) 1,2-dichloropentane. 2 marks

9 Properties and reactions of organic compounds

Organic reactions are chemical reactions that take place between organic compounds, and these reactions depend on the properties of the compounds. The number of all the possible organic reactions that can occur is essentially infinite because of the myriad combinations of compounds. However, there are certain general patterns that can be observed to describe many common and useful reactions. It is not unusual to find that different pathways can be taken to produce the same organic substance.

YOU WILL EXAMINE:

- bonding in organic compounds
- structural isomers and stereoisomers
- the effect of different structures on properties
- physical properties of hydrocarbons
- physical properties of alcohols, aldehydes, ketones, carboxylic acids and esters
- reactions of hydrocarbons
- reactions of haloalkanes, alcohols, carboxylic acids, esters and amines
- organic pathways
- yield and atom economy.



Which flavour of jellybean is your favourite? Is it peach, apple, bubblegum or one of the newer, more unusual taste sensations? Chemistry plays an essential part in creating the extensive variety of aromas and flavours in jellybeans and numerous other foods. Most flavours are actually quite complicated, with contributions from several chemicals, many of which are esters. For example, the taste and aroma of apple is provided by the ester methyl pentanoate. Food chemists perform many experiments to produce a taste that is as close as possible to the original. Changing even a small part of a molecule can provide quite a different result. Esters are derived from the reaction of an alcohol and a carboxylic acid. This reaction and more are explored in this chapter.

Physical and chemical properties of organic compounds

The physical and chemical properties of organic compounds provide information that helps us understand and evaluate the interactions between organic chemicals. Depending on the types of atoms present in compounds, these interactions determine how organic molecules react to produce important chemicals for fuels, pharmaceuticals, manufacturing, industry and biological processes. The number of all the possible organic reactions that can occur is essentially infinite because there are so many combinations of organic compounds. However, certain general patterns involving addition, decomposition, combination, substitution or rearrangement of atoms or groups of atoms can be used to describe many common and useful reactions. It is not unusual to find that different pathways can produce the same organic substance.

Properties and bonding

The trends in physical properties of organic compounds, such as melting point, boiling point, viscosity, flashpoint and solubility, can be deduced from their structure, including size, shape and any functional groups. These factors depend on the strength of the intermolecular forces present. In molecules (where atoms are connected by *intramolecular* covalent bonds), *intermolecular* forces may be of three types: dispersion forces, dipole–dipole attractions and hydrogen bonding.

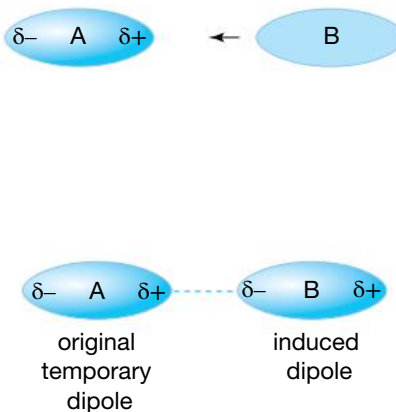
Bonding in and between organic molecules

The millions of organic compounds known to chemists are mainly covalent molecules. These molecules could be simple molecules, such as methane and ethanol, or macromolecules, such as polyethene and proteins. The physical properties and behaviours of organic molecules are influenced by their size, shape, structure and degree of polarisation of their covalent bonds. In general, simple organic compounds are gases, volatile liquids, or solids with low melting and boiling temperatures. This is because the intermolecular forces between these organic molecules are weak. These intermolecular forces include:

- *dispersion forces* (also called van der Waals forces): In non-polar molecules such as methane, CH_4 , wax and oils, electrons may momentarily be distributed unevenly within the molecules, inducing a temporary dipole. Neighbouring molecules with similar temporary dipoles are attracted weakly to each other. This results in weak dispersion forces between the molecules. The strength of the dispersion forces is affected by the size and shape of molecules.

Dispersion forces are due to temporary dipoles between molecules.

Temporary dipoles giving rise to intermolecular attractions (dispersion forces). Molecule A has a temporary polarity due to uneven distribution of electrons. As the non-polar molecule B approaches A, its electrons are redistributed, as there is a tendency for them to be attracted to the δ^+ end of A. This sets up an induced dipole in B. These intermolecular attractions are called dispersion forces. Dispersion forces are weak and temporary, as electrons tend to redistribute themselves at different instances.



Candle wax consists of long hydrocarbon molecules held together by dispersion forces. The strength of dispersion forces increases with molecular size.



Dipole-dipole interactions are the result of permanent dipoles.

Hydrogen bonding occurs between a molecule that contains an H atom and a molecule that contains an F, O or N atom.

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Hydrogen bonding
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- **dipole-dipole attractions:** Molecules such as HCl, HBr and CH_3Cl are polar and have permanent dipoles. The partial positive charge on one molecule is electrostatically attracted to the partial negative charge on a neighbouring molecule. Dipole-dipole attractions are stronger intermolecular forces than dispersion forces.
- **hydrogen bonding:** This takes place between a molecule containing hydrogen atoms bonded to one of the three highly electronegative elements F, O and N, and another molecule that must also contain an electronegative atom, such as oxygen and nitrogen. Hydrogen bonds are stronger intermolecular forces than both dispersion forces and dipole-dipole attractions. Hydrogen bonding occurs between water molecules and also between organic compounds such as alcohols (e.g. methanol, CH_3OH), carboxylic acids (e.g. ethanoic acid, CH_3COOH) and organic amines (e.g. methylamine, CH_3NH_2).

Hydrogen bonding is stronger than dipole-dipole attractions due to the larger dipole moment that exists within these molecules as well as to the small size of the hydrogen atom involved. This allows the molecules to get closer to each other than in dipole-dipole attractions, thus increasing the force of attraction.

Revision questions

1. State whether the intermolecular forces acting between molecules of the following compounds are dispersion forces, dipole-dipole attraction or hydrogen bonding.
(a) CH_3OH (c) $\text{CH}_3\text{CH}_2\text{Cl}$
(b) CH_3CH_3 (d) CH_3NH_2
2. Which one of each of the following pairs would have the stronger intermolecular forces?
(a) CH_4 and CH_3CH_3
(b) CH_3OH and CH_3Cl
(c) $\text{CH}_3\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{CH}_3$

Isomers — same but different

Another reason for the enormous number of organic compounds is the existence of isomers, as was briefly discussed in chapter 8. Two or more compounds with the same molecular formula but different arrangements of atoms are known as isomers. The effect on the properties of the substances depends on the type of isomerism present. If the atoms are arranged in different orders, then they are **structural isomers**. If the atoms are connected in the same order but are oriented differently in space, they are **stereoisomers**. In many cases, three-dimensional structural formulas (using wedges and dashes) are used to

Boiling point depends on the strength of intermolecular forces.

The atoms in structural isomers are connected in different orders; they can also contain different functional groups.

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Experiment 9.1 Constructing models of structural isomers
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represent three-dimensional molecular structures. They were described in chapter 8.

Boiling points provide a good indication of the strength of the intermolecular forces that hold the molecules of a substance together, so it is useful to compare the boiling points of related compounds to see how structural differences account for the differences in intermolecular attractions.

Structural isomerism

Structural isomers can have different physical and chemical properties if they contain different functional groups. Three types of structural isomers are chain, positional and functional isomers. The physical properties of **chain isomers** show a difference in boiling point, with more branched isomers having lower boiling points. For example, the boiling point of butane is -0.5°C , and the boiling point of methylpropane is -11.7°C . The second molecule is more spherical and has less surface area for the dispersion forces to act.

In **positional isomers**, the position of the functional group may affect not only the compactness of the molecule but also its polarity.

If isomers have **functional isomerism**, then they have different functional groups, and this affects their intermolecular forces, resulting in significantly distinct properties.

Examples of structural isomers can be found in table 9.1.

TABLE 9.1 Types of isomers

Isomer	Example
Structural isomers	
Chain isomers different branching in carbon chain	$\begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & & & \\ & \text{H} & & \text{H} & & \text{H} & & \text{H} \end{array}$ butane $\begin{array}{ccccccc} & & & \text{H} & & \text{CH}_3 & & \text{H} \\ & & & & & & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & & & \\ & & & \text{H} & & \text{H} & & \text{H} \end{array}$ methylpropane
Positional isomers different positions of the functional group, which is usually indicated by a number in the name	$\begin{array}{ccccccc} & \text{OH} & & \text{H} & & \text{H} \\ & & & & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & \\ & \text{H} & & \text{H} & & \text{H} \end{array}$ propan-1-ol $\begin{array}{ccccccc} & \text{H} & & \text{OH} & & \text{H} \\ & & & & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & \\ & \text{H} & & \text{H} & & \text{H} \end{array}$ propan-2-ol
Functional isomers same atoms but different functional groups	$\begin{array}{ccccccc} & \text{H} & & \text{H} & & & & \text{O} \\ & & & & & & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & \\ & & & & & & & \backslash \\ & \text{H} & & \text{H} & & & & \text{H} \end{array}$ propanal $\begin{array}{ccccccc} & \text{H} & & & & \text{H} \\ & & & & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & & & \\ & \text{H} & & & & \text{O} & & \text{H} \end{array}$ propanone (acetone)
Stereoisomers	
cis and trans isomers different arrangements of atoms around a double bond or in a ring, which restricts rotation. If the groups on each carbon atom are on the same side of the molecule, that molecule is the <i>cis</i> isomer. If they are on opposite sites, it is the <i>trans</i> isomer.	$\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$ <i>cis</i>-but-2-ene $\begin{array}{ccc} \text{H} & & \text{CH}_3 \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{CH}_3 & & \text{H} \end{array}$ <i>trans</i>-but-2-ene
Enantiomers or optical isomers non-superimposable mirror images containing an asymmetric carbon atom. These molecules are referred to as chiral.	$\begin{array}{c} \text{H} \\ \\ \text{C} \\ / \quad \backslash \\ \text{Br} \quad \text{F} \\ \quad \quad \\ \quad \quad \text{Cl} \end{array}$ $\begin{array}{c} \text{H} \\ \\ \text{C} \\ / \quad \backslash \\ \text{F} \quad \text{Cl} \\ \quad \quad \\ \quad \quad \text{Br} \end{array}$

Stereoisomers have the same molecular formula and sequence of bonded atoms, but their arrangements in space are different.

Stereoisomerism

Stereoisomers include *cis* and *trans* isomers and enantiomers. ***cis-trans* isomers** have different physical and chemical properties. These isomers are formed when there are two different groups on each of the carbon atoms in a carbon-carbon double bond. A *cis* isomer has both of the groups on the same side of the double bond, and a *trans* isomer has the groups on different sides of the double bond. Boiling points are affected by the polarity of the molecules, but the arrangements of the molecules in the solids affects their melting points. For example, in *cis*-1,2-dichloroethene, each C—Cl bond is polar, so the overall molecule is polar. However, in *trans*-1,2-dichloroethene, the individual dipoles in the bonds cancel out, and so the molecule is non-polar. The result is that the boiling point of the *cis* isomer (60.2 °C) is higher than that of the *trans* isomer (48.5 °C).

trans and *cis* isomers of dichloroethene

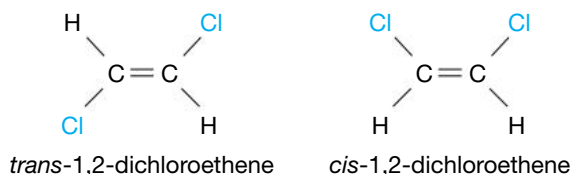


TABLE 9.2 Melting and boiling points of the *cis* and *trans* isomers of 1,2-dichloroethene

Isomer	Melting point (°C)	Boiling point (°C)
<i>cis</i>	−81.5	60.2
<i>trans</i>	−49.4	48.5

It is interesting to note that the melting points do not follow the same pattern as the boiling points. In the solid state, the *trans* isomers can pack more closely than the *cis* isomers, making the intermolecular forces more effective. *cis* and *trans* isomers can also occur in ring structures. *cis-trans* isomers belong to a larger group of stereoisomers called **diastereomers**, which includes other stereoisomers that are not mirror images of each other.

Some molecules can be described as **chiral**. They have what is known as an asymmetric carbon atom or **chiral centre**; this means that they cannot be superimposed on their mirror images. We are familiar with many chiral objects. For example, seashells, scissors, gloves, hands and feet cannot be matched directly with their mirror images, whereas mittens and socks can fit on either hand or foot. Chiral molecules that are non-superimposable mirror images of one another are called **enantiomers**. These molecules are not symmetrical and can be recognised because the chiral carbon atom is bonded to four different atoms or groups. The physical properties of enantiomers are identical (except for optical activity), and their chemical properties are generally the same, but they react differently with other molecules that have optical properties. The significant implications of this in biological systems will be discussed in chapter 11.

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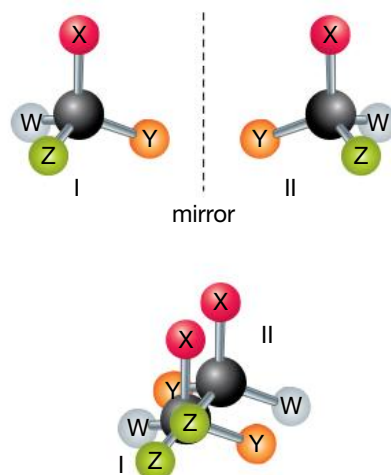
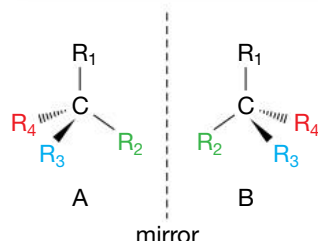
Experiment 9.2 Investigating optical isomers

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Chiral objects are non-superimposable mirror images of each other.

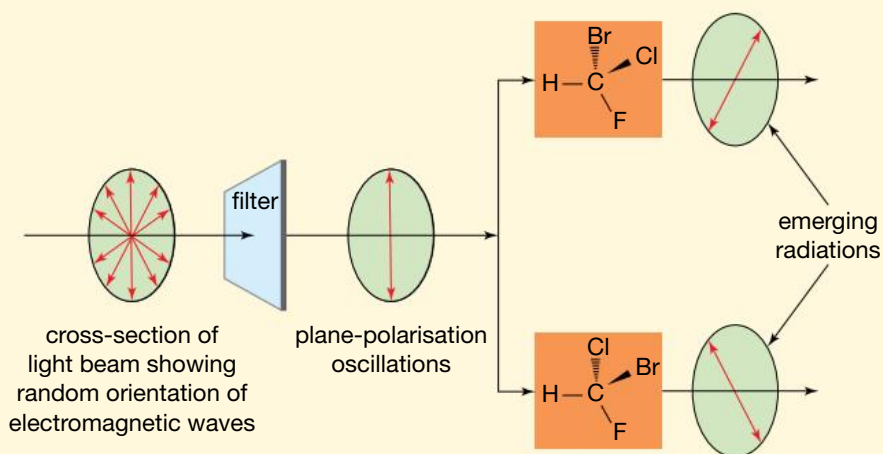


Chiral molecules are not superimposable on their mirror images. In the example on the right, no matter how the molecules are rotated, the W and Y atoms do not line up. The example below depicts a similar scenario using 3-dimensional structural formulas to represent the 3-D structures of A and B. In this image, the R₄ and R₂ atoms cannot be superimposed, no matter the rotation of the molecule.



Enantiomers can be distinguished by their ability to rotate plane-polarised light in equal but opposite directions. This optical activity is the reason why they are also called optical isomers. When optically active substances are synthesised in the laboratory, they are often a 50/50 mixture of the two enantiomers. This is known as a racemic mixture or racemate. A racemic mixture does not affect plane-polarised light. Stereoisomers formed in biological systems consist of the one enantiomer.

Normally, a light wave is made up of a mixture of waves vibrating in every direction perpendicular to its direction of movement. Unpolarised light can be converted into a single polarised beam by passing it through a polarising filter. Sunglasses use a polarising filter to limit glare. Optically active molecules can rotate the plane of polarisation of plane-polarised light. An instrument called a polarimeter can be used to analyse this rotation. If it is rotated clockwise it is the (+) enantiomer; if it is rotated anticlockwise, it is the (–) enantiomer.



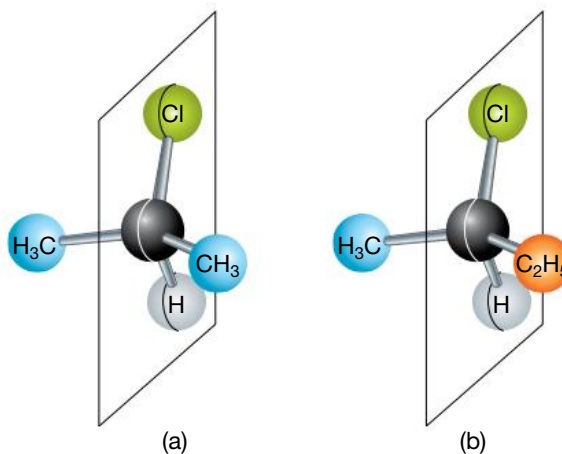
A polarimeter is used to distinguish between optical isomers.

Identifying chiral molecules

Building models of molecules and trying to superimpose them is a good way of determining whether a molecule is chiral or achiral. Chiral molecules are not

Chiral molecules have four different groups attached to a carbon atom.

superimposable. If two or more groups attached to the tetrahedral atoms in a molecule are the same, then the molecule is achiral (not chiral). If the molecule has a plane of symmetry, as shown in the diagram below, it is achiral. And, as mentioned previously, if four different groups are attached to a carbon atom, then it is a chiral molecule. The carbon atom in CH_2 or CH_3 groups is not a chiral centre.

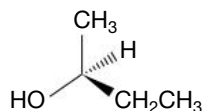


(a) The chloropropane molecule is achiral as it has a plane of symmetry. (b) The chlorobutane molecule does not have a plane of symmetry and so is chiral.

Sample problem 9.1

Explain why the molecule $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ is described as a chiral molecule.

Solution: Draw the structure.

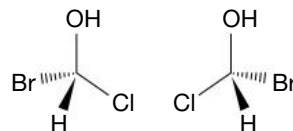


The second carbon atom has four different groups attached — a hydroxyl group, a hydrogen, a methyl group and an ethyl group — so is a chiral molecule. This means that it cannot be superimposed on its mirror image, and so it is an enantiomer.

Revision questions

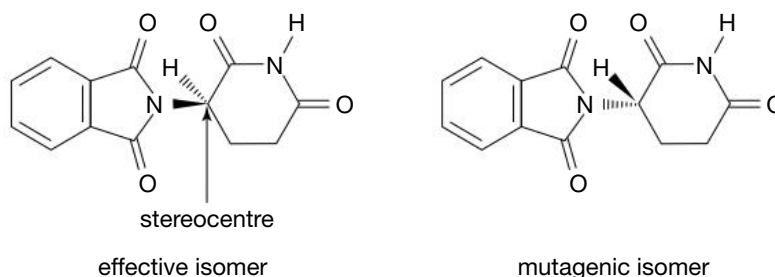
3. Classify each of the following objects as chiral or achiral.
 - (a) Nail
 - (b) Baseball bat
 - (c) Golf club
 - (d) Tennis racquet
 - (e) Ear
 - (f) Mug
 - (g) Car
 - (h) Scissors
 - (i) Socks
4. How many chain isomers of the molecular formula C_5H_{12} are there?
5. Draw the structure of the molecule $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, and name a positional isomer of it.

6. Draw the structure of a functional group isomer of ethanol, $\text{C}_2\text{H}_5\text{OH}$.
7. Draw and label the *cis* and *trans* isomer forms of pent-2-ene.
8. Describe the type of isomerism that exists in these two molecules.



Examples of chiral molecules

From 1957, the drug thalidomide was used to treat morning sickness in pregnant women. Over 10 000 children were born with horrific birth defects as a result of this drug. Eventually, investigations found that thalidomide was a racemic mix of two enantiomers due to the presence of one chiral carbon atom. While one enantiomer did indeed cure morning sickness, the other enantiomer caused deformities in organs and limbs. The chiral carbon atom is unstable, and enzymes in the liver can convert (racemise) the therapeutic form into the harmful form, so it is very difficult to isolate the beneficial enantiomer. Thalidomide is currently used, under strict regulations, to treat some cancers and other conditions including leprosy.



Enantiomers of thalidomide

Ibuprofen, which is used for pain relief and reducing fever and inflammation, is another familiar example of an enantiomer. Again, one enantiomer is effective, whereas the other is inactive. As a large proportion of the inactive molecule is converted into the active molecule in the body, it is sold as a racemic mixture; there is not enough advantage to warrant the expense of manufacturing the active isomer alone.

The pharmaceutical industry is now much more aware of the possibility of the effects of different enantiomers when developing new medications. Most pharmaceuticals under development are chiral. Therefore, either pure samples of the active isomer are produced or the two isomers in a racemic mixture are separated. Separation can be achieved using chromatography with a single-enantiomer stationary phase.

Physical properties of hydrocarbons

The physical properties of compounds depend on their structures.

Alkanes

Alkanes are colourless compounds that are less dense than water and have weaker intermolecular attractive forces. Alkanes consist of non-polar molecules. The first four in the series are gases. As the size of the molecule increases, so does the influence of the dispersion forces; therefore, the melting and boiling points increase, as can be seen in table 9.3. Another factor that

The intermolecular forces in hydrocarbons are dispersion forces, which increase as the size of the molecule increases.

The properties of hydrocarbons are affected by the strength of the dispersion forces.

affects the boiling point is the degree of branching; as the amount of branching increases, the boiling point decreases. This is due to the inability of molecules to get closer to each other; as the dispersion forces operate over a small distance only, the attraction is diminished. Alkanes are insoluble in water because of their non-polar structures, but they are soluble in organic solvents because dispersion forces between the alkane molecules and the solvent replace the dispersion forces between the alkane molecules.

TABLE 9.3 Melting and boiling points of alkanes

Alkane	Formula	Semi-structural formula	Melting point (°C)	Boiling point (°C)	State
methane	CH ₄	CH ₄	−183	−164	gas
ethane	C ₂ H ₆	CH ₃ CH ₃	−182	−87	gas
propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃	−190	−42	gas
butane	C ₄ H ₁₀	CH ₃ (CH ₂) ₂ CH ₃	−135	−1	gas
pentane	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	−130	36	liquid
hexane	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	−94	68	liquid
heptane	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	−90	98	liquid
octane	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	−57	126	liquid



Honey is a viscose liquid because of strong intermolecular forces.

The **viscosity** of liquid alkanes also increases with the number of carbon atoms. Viscosity is the resistance to flow of a liquid, and it is affected by intermolecular forces and the shapes of the molecules; honey has high viscosity and water has low viscosity. The increased number of intermolecular forces in larger molecules, together with the possibility of branched molecules becoming tangled, results in higher viscosity. Viscosity decreases as the temperature increases because the molecules attain enough energy to overcome the forces holding the molecules together.

Flashpoint

Organic chemicals can be classified as flammable or combustible according to their flashpoints. The **flashpoint** of a volatile liquid is the lowest temperature at which the liquid gives off enough vapour to start burning at its surface on application of an ignition source. Below the flashpoint, there is not enough vapour available to support combustion. A flammable liquid is any liquid with a flashpoint below 37.8 °C. Liquids classified as combustible are harder to ignite and have a flashpoint of 37.8 °C and above.

Flammable liquids ignite and burn easily at lower temperatures. Combustible liquids can burn at temperatures that are usually above room temperature. It is not actually the liquid that burns; it is the mixture of its vapours that burns in the oxygen in the air. Smaller hydrocarbons have weaker intermolecular forces and are more easily vaporised; therefore, they have lower flashpoints and are more flammable. The vaporisation rate increases as the temperature increases. Therefore, flammable and combustible liquids are more hazardous at temperatures higher than room temperature. If a fuel has a flashpoint below room temperature, such as petrol and alcohol, it is a safety hazard, as a spark could cause immediate ignition.

TABLE 9.4 Flashpoints of some organic compounds

Substance	Flashpoint (°C)
pentane	−40
hexane	−22
propanone	−19
methyl acetate	−10
ethyl ethanoate	−4
heptane	−4
1,1,1-trichloroethane	−1
methanol	11
ethanol	12
propan-2-ol	12
octane	13
propyl ethanoate	13
propan-1-ol	25
2-methylpropan-1-ol	28
butanol	29
trichloroethene	32

Alkenes and alkynes

Alkenes generally have similar physical properties to alkanes, except that the double bond limits rotation, resulting in some compounds forming *cis-trans* isomers, as discussed earlier in the chapter. Alkenes are more reactive than alkanes due to the high electron density available within their bonds and because the electrons in the carbon-carbon double bond are more accessible. Alkynes are compounds with low polarity, and they have physical properties that are essentially the same as those of the alkanes and alkenes. Many are highly flammable.

Revision questions

- Describe the intramolecular and intermolecular bonding that exists in hydrocarbons.
- Methane, CH_4 , and candle wax, $\text{C}_{25}\text{H}_{52}$, are alkanes, but methane is a gas and candle wax is a solid. Explain why this occurs.
- (a) Explain why the flashpoint of propan-1-ol is higher than the flashpoint of propan-2-ol.
(b) Predict which of the compounds in (a) has the higher boiling point.

How do functional groups affect physical properties?

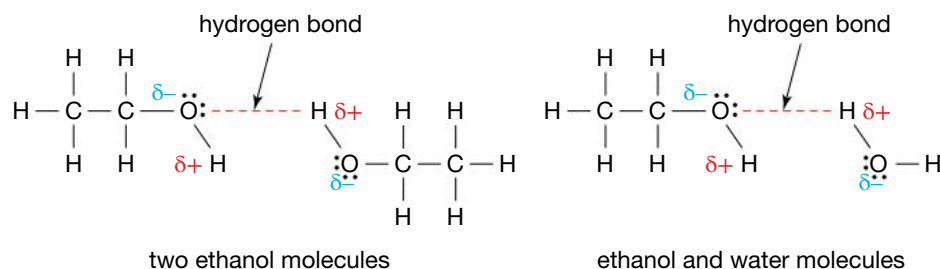
Functional groups affect the properties of organic compounds.

The presence of functional groups containing atoms other than hydrogen affects the properties of organic compounds. For example, the existence of a halogen in an organic molecule may result in a polar molecule. This would increase the strength of the intermolecular forces because dipole-dipole attractions would be present in addition to dispersion forces. When oxygen or nitrogen is involved, hydrogen bonding will be present.

Alcohols

The hydroxyl group in alcohols has a significant effect on properties. It can form hydrogen bonds with other alcohol or water molecules. Consequently, alcohols have a higher boiling point than corresponding alkanes, and smaller alcohols (three or fewer carbon atoms) are soluble in water. The boiling point of primary alcohols increases with increasing chain length due to the increasing number of dispersion forces, whereas the solubility decreases with increasing chain length due to the increasing length of the non-polar (hydrophobic) section of the molecules. The effect of the increased number of dispersion forces explains why volatility (tendency to vaporise) decreases with molecular size whereas viscosity increases.

Alcohols can form hydrogen bonds with other alcohol molecules or water.



This bar is made almost entirely of ice. The alcoholic drinks do not freeze even though they are served in ice vessels. Alcohol has a lower freezing point than water.



Burning ethanol on a Christmas pudding

Many alcohols are highly flammable (with flashpoints below 37.8 °C), especially methanol (11 °C) and ethanol (17 °C). The flammability of alcohols decreases as the molecules increase in size and mass due to the increased strength of attraction between the molecules. Volatility also decreases as the size of the molecule increases.

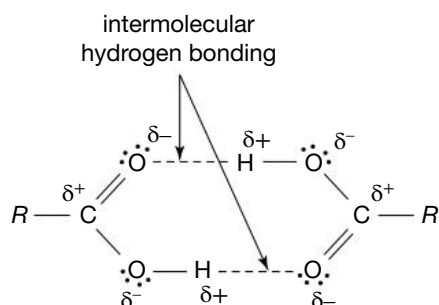
You may have experienced the low flashpoint of ethanol at Christmas dinner when a flaming pudding has been ceremoniously delivered from the kitchen. The alcohol needs to be warmed because, if the temperature is too far below its flashpoint, it does not ignite as there are not enough vapours. It is interesting that the pudding is not burned in this process because the alcohol used

is about half water, and the evaporating water keeps the temperature low. Another aspect of Christmas chemistry is that the oxygen in the alcohol causes it to completely combust with a blue flame, as distinct from the yellow flame observed when burning hydrocarbons in candle wax, which produces a cooler, sooty and yellow flame.

Carboxylic acids

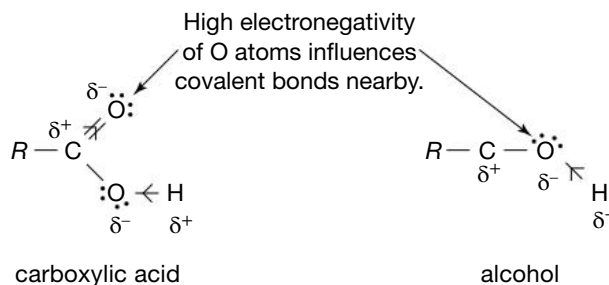
Alcohols and carboxylic acids with a small number of carbon atoms are soluble in water. As the number of carbon atoms increases, they tend to be more insoluble.

Like the alcohols, the first few members of the carboxylic acid homologous series are very soluble in water due to their capacity for strong hydrogen bonding with water molecules. Carboxylic acids have much higher boiling points than the previously discussed homologous series because carboxylic acid molecules can form two hydrogen bonds with each other.

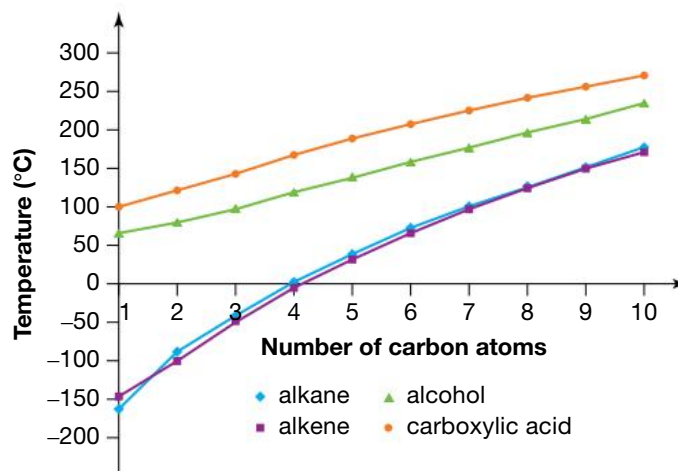


A dimer (a pair of molecules) is formed by carboxylic acid molecules.

Carboxylic acids are weak acids that only partially ionise in water. They are still stronger acids than their corresponding alcohols because the —OH group is more polarised in the —COOH group by the presence of the highly electronegative O atom of C=O. This double-bonded O atom attracts the electrons away from the —OH group. Therefore, the H (from the hydroxyl group) is more weakly bonded to O and is more easily donated.



Polarisation of the —OH group in an alcohol and a carboxylic acid



A graph showing the relative boiling points of the homologous series of alkanes, alkenes, alcohols and carboxylic acids

Aldehydes, ketones and esters

Aldehydes and ketones are volatile compounds and are commonly found in perfumes and flavourings. Smaller molecules of these compounds are soluble

Aldehydes, ketones and esters are volatile compounds with distinctive odours.

Smaller amides are soluble, but they are less soluble than comparable amines and carboxylic acids.



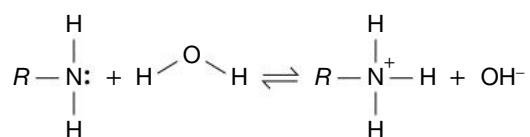
Amines are said to have an unpleasant odour similar to that of rotting fish.

because they can form hydrogen bonds with water, but solubility decreases with increasing length of the non-polar chain. These molecules cannot hydrogen bond with each other, but the polarity of the molecule means that the boiling point is higher than for similar-sized alkanes but lower than for alcohols and carboxylic acids, which have hydrogen bonding between hydroxyl groups.

Esters are very commonly found in plants and are responsible for many distinctive odours and flavours. Esters have lower boiling points than carboxylic acids. This is because esters cannot form hydrogen bonds with each other since they do not have an O—H bond. Esters with very short carbon chains are soluble in water, whereas those with longer chains are less soluble.

Amines and amides

Amines are very stable compounds that generally have strong or unpleasant odours, similar to rotting fish. They are weak bases because they can accept a proton. For example:



Hydrogen bonding is possible in amines (due to the presence of N—H bonds) but their boiling points are lower than the corresponding alcohols. The first two members of the homologous series are gases at room temperature, whereas the larger members are liquids. As with the other polar compounds containing hydrogen bonding, the solubility decreases with chain length.

Amides have higher melting and boiling temperatures than similar-sized organic compounds due to their capacity to form multiple hydrogen bonds between molecules. Methanamide is a liquid at room temperature, but larger amides are solids because of the increased number of dispersion forces. Smaller amides are soluble but less soluble than comparable amines and carboxylic acids; their solubility is similar to that of esters.

Revision questions

12. Arrange the following compounds in order of increasing boiling point, and give reasons for your answer.
pentane, propane, propan-1-ol, pentan-1-ol
13. Explain why methane and ethane are insoluble in water whereas methanol and ethanol are soluble.
14. Use examples to explain whether replacing one or more hydrogens in methane with chlorine would always result in a polar molecule.
15. Explain which has the higher boiling point: butanamide, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$, or ethyl ethanoate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$.

Reactions of organic compounds

We are surrounded by organic reactions occurring both outside and inside our bodies. They include combustion of fuels for heating, transport and providing energy for our bodies to function. Most of the materials that we see around us have been produced as a result of reactions involving organic compounds. Can you name some of these products?

Ethane and ethene are used to produce many other important organic chemicals.

Reactions of alkanes and alkenes

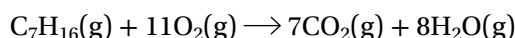
Ethane and ethene can be used as starting materials in chemical reactions that lead to the production of many other organic substances, such as alcohols and carboxylic acids. The remainder of this chapter will look at some of the more common chemical reactions of organic compounds.

Combustion of alkanes and alkenes

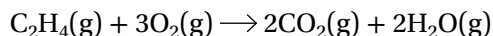
Alkanes are saturated compounds with strong covalent C—C and C—H bonds, making them stable and fairly unreactive with many of the common laboratory reagents. They do not dissolve in water and do not react with acids, bases or strong oxidising agents in standard laboratory conditions. Their inert chemical behaviours make larger alkanes useful as non-polar solvents and lubricating oils. They do, however, undergo combustion with oxygen and react with the halogens.

Alkanes and alkenes react with excess oxygen in combustion reactions to produce carbon dioxide and water.

Another important use of alkanes is as fuels. Although alkanes are kinetically stable in the presence of oxygen, combustion occurs when they are supplied with the necessary activation energy such as during ignition. The oxidation of alkanes is an exothermic reaction and the combustion products are carbon dioxide and water if a plentiful supply of oxygen is available and complete combustion occurs. For example:



Like the alkanes, alkenes burn in air to form carbon dioxide and water. For example, ethene combusts with oxygen according to the equation:



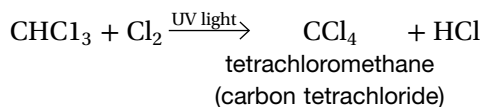
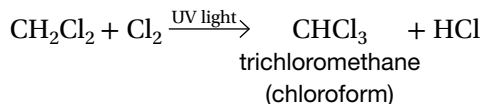
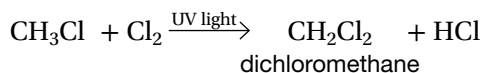
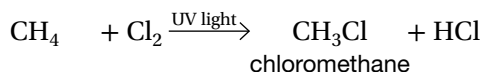
If the supply of oxygen is limited, carbon monoxide is formed instead of carbon dioxide.

The combustion of hydrocarbons and the alkanes in particular is of immense importance as this process is used in power stations, furnaces, domestic heaters, candles, internal combustion engines and many other devices that are essential for living in a technological society. An understanding of the nature of the combustion process is critical to the design of such devices. An important and familiar example is the petrol engine in cars.

Substitution reactions of alkanes

Alkanes can undergo substitution reactions in which an atom or group of atoms replaces a hydrogen atom.

The alkanes undergo **substitution reactions** with the halogens in which the halogen atoms replace hydrogen. For example, the successive chlorination of methane to form chloromethanes occurs as follows:



In the reactions at the bottom of the previous page, ultraviolet light is the source of energy to break the Cl—Cl bond to produce chlorine free radicals:

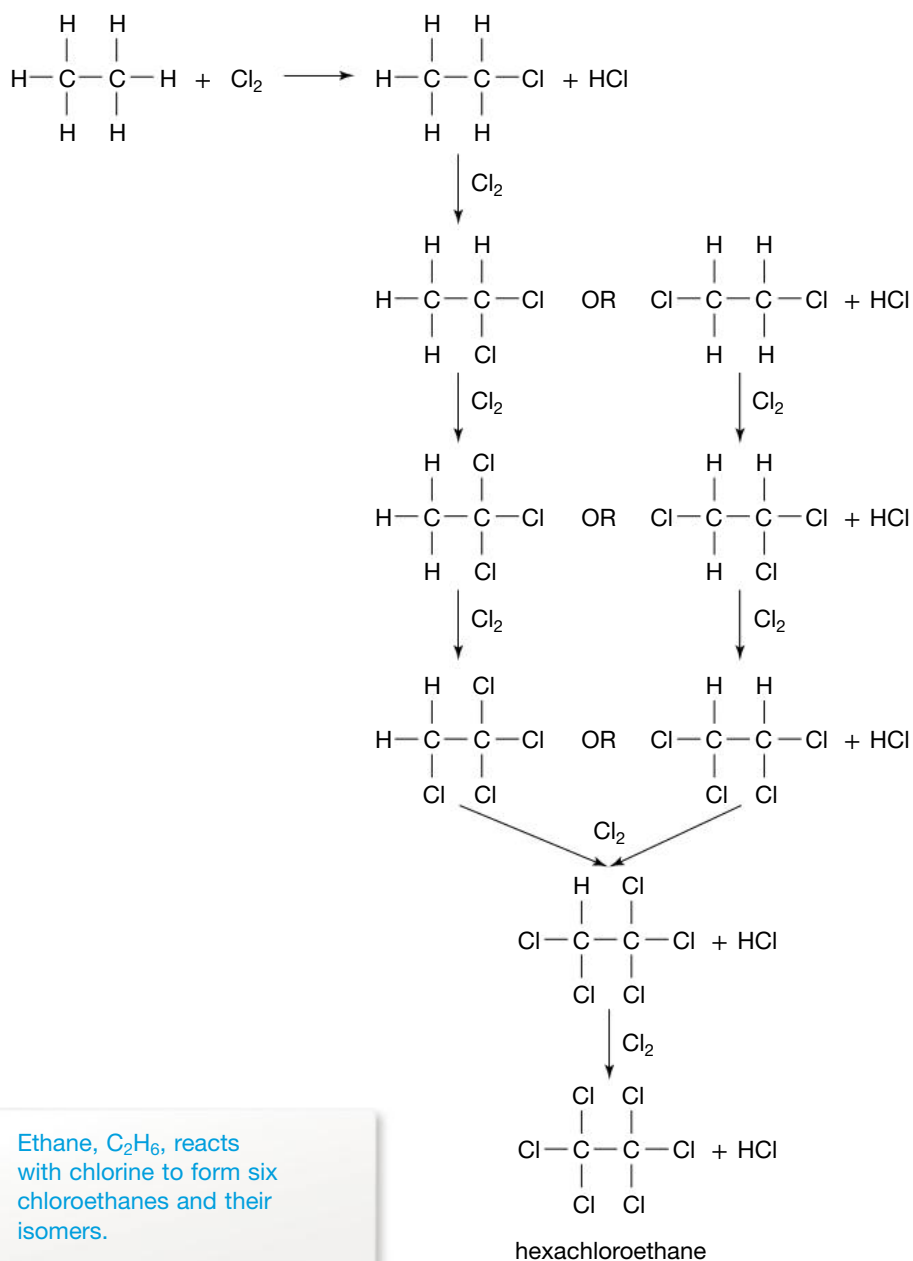


The small dot indicates an unpaired electron in the chlorine free radical, which makes it very reactive and able to attack the C—H bond.

Chloromethane (also known as methyl chloride) is used as a refrigerant and as a local anaesthetic (it acts by freezing the skin). Dichloromethane (also known as methylene dichloride) and tetrachloromethane (also known as carbon tetrachloride) are used as solvents.

Other alkanes react similarly with chlorine except that a larger number of chloroalkanes are formed. For example, ethane, C_2H_6 , reacts with chlorine to form six chloroethanes and their isomers, as shown in the figure below.

Alkanes react with other halogens in a similar manner.



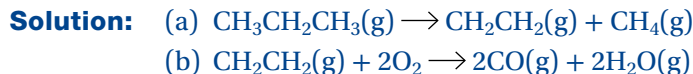
Cracking

Cracking is a process that uses heat and pressure, and sometimes a catalyst, to break larger hydrocarbon molecules into smaller molecules, including an alkene and hydrogen, or an alkane.

Sample problem 9.2

Write a semi-structural equation for each of the following.

- Ethene is produced from the cracking of propane.
- Carbon monoxide is produced by incomplete combustion of ethene in limited air.



Revision questions

- Write an equation for the complete combustion of octane, C_8H_{18} .
- The alkenes burn in a similar way to alkanes. Write an equation for the complete combustion of propene.
- How many possible products are there when ethane reacts with bromine? Write the name of each of these products.

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Unit 4

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Concept 2



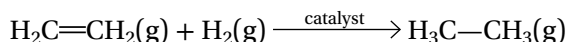
Do more

Comparison of substitution and addition reactions

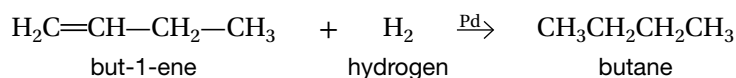
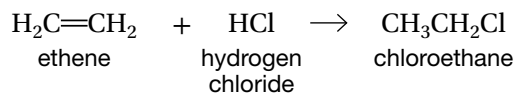
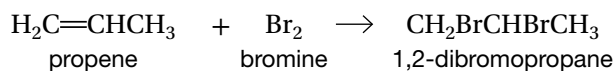
Alkenes undergo addition reactions where the $\text{C}=\text{C}$ bonds are broken and new single bonds are formed.

Addition reactions of alkenes

Alkenes are more reactive than alkanes. They are unsaturated hydrocarbons and undergo **addition reactions** in which the $\text{C}=\text{C}$ bond is broken and new single bonds are formed. This is because the energy required to break the double bond is less than the energy released in the formation of two single bonds. For example, hydrogenation of ethene produces ethane and releases energy.



Substances that undergo addition reactions with alkenes include H_2 , Cl_2 , Br_2 , HCl , HBr and HI . Addition of H_2 requires the presence of a catalyst, such as finely divided Pt, Pd or Ni. The others react without the need for catalysis. The equations below are examples of addition reactions with alkenes. Note that the reactants Br_2 , HCl and H_2 in these reactions add *across* the double bond. Therefore, 1,2-dibromopropane is the only product.



The reaction of an alkene with bromine is used as a test for unsaturation. When red-brown bromine water is shaken with an unsaturated hydrocarbon, the reaction mixture becomes colourless due to the formation of the dibromo derivative.

Ethene is used as a raw material in a fast method to produce the large amounts of ethanol needed for industrial use. Ethene is mixed with steam and passed over a phosphoric acid catalyst at 330°C . The reaction of the direct

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Catalysis: hydrogenation of ethylene

eles-1673

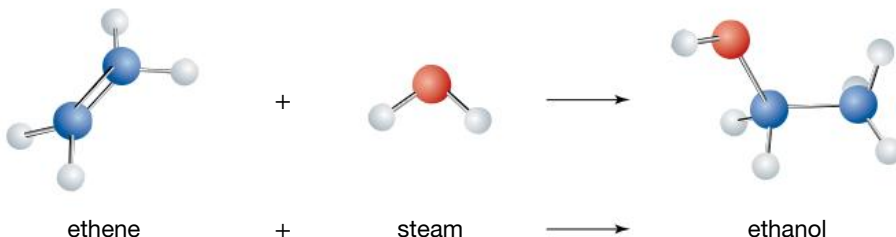
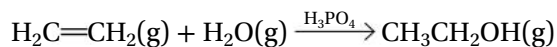
Bromination of ethylene

eles-1674

Ethanol can be produced by hydration of ethene or a substitution reaction of a haloalkane.

Model equation for the direct hydration of ethene to form ethanol

catalytic hydration of ethene in the vapour phase is an addition reaction and is shown below.



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Indirect hydration of ethylene
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In addition polymerisation, many small molecules (monomers) combine to form very large molecules (polymers).

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See more

Addition reactions
of alkenes

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Addition polymerisation of ethylene
eles-1675

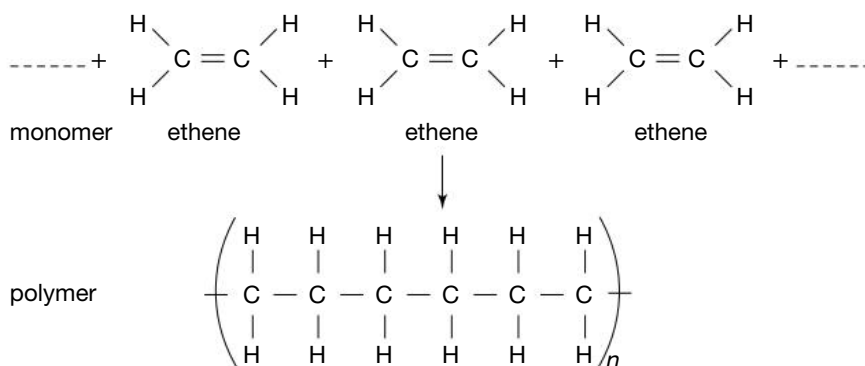
Interactivity

Making polymers
int-3849

Addition polymerisation

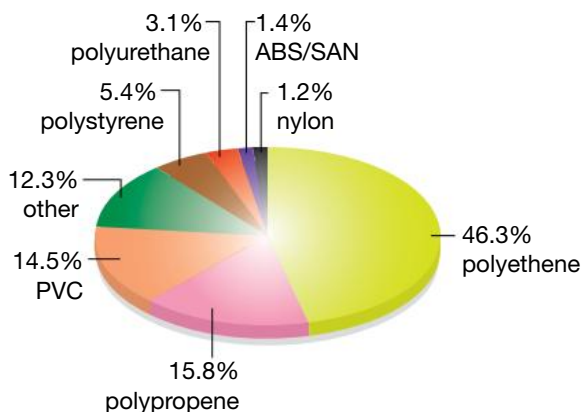
Another important reaction of some unsaturated hydrocarbons is **polymerisation**, a process in which many small molecules (monomers) are joined together to form a large molecule (polymer).

The **monomer** ethene, containing a double bond, undergoes **addition polymerisation** readily to form polyethene (also known as polyethylene or polythene). This product is one of the most commonly used synthetic **polymers**. Low-density (melting at lower temperature) polyethene is used for making film, garbage bags and plastic wrappers and for making moulded articles such as squeeze bottles. High-density (containing linear rather than branched chains and melting at a higher temperature) polyethene is more rigid and is used for moulding items such as bread and drink crates.



Addition polymerisation of ethene to form polyethene

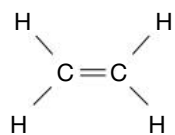
This pie chart shows Australia's consumption of different types of polymers.



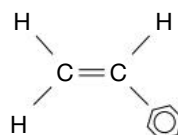


Most of the materials in this surfboard are organic polymers designed for a specific purpose. The tough polyurethane outer coating protects the light polystyrene core. Even the wax on the deck is an organic product.

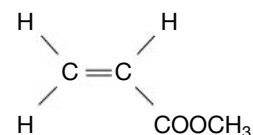
A number of other useful plastics can be produced by making minor alterations to the ethene molecule.



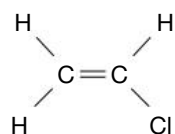
(a) ethene



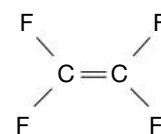
(c) styrene



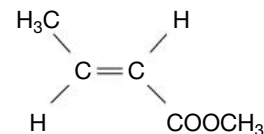
(e) vinyl acetate



(b) vinyl chloride



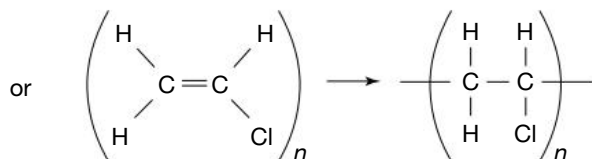
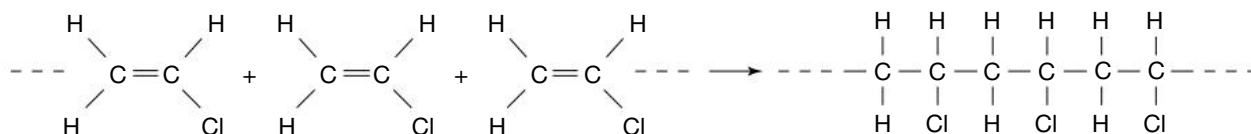
(d) tetrafluoroethene



(f) methyl methacrylate

The structural formulas for (a) ethene, (b) vinyl chloride, (c) styrene, (d) tetrafluoroethene, (e) vinyl acetate and (f) methyl methacrylate. These monomers make, respectively, polyethene, PVC, polystyrene, Teflon, PVA and perspex. Note their obvious similarity to the structure of ethene.

This leads to a larger range of other useful plastics and polymers. Polyvinylchloride (PVC or 'vinyl') is a good example. The following represents the polymerisation of vinyl chloride to polyvinylchloride.



Sample problem 9.3

How many products are produced from the reaction between hydrogen chloride and but-2-ene? Write semi-structural equations to show the reaction.

Solution: $\text{H}_3\text{CHC}=\text{CHCH}_3 + \text{HCl} \longrightarrow \text{CH}_3\text{CH}_2\text{CHClCH}_3 \text{ or } \text{CH}_3\text{CHClCH}_2\text{CH}_3$

However, the formulas for these potential products represent the same structure, so there is only one product.

Revision questions

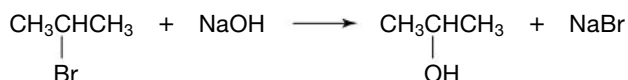
- Write the structural equations for the reactions of chlorine, hydrogen and hydrogen chloride with propene. Name the compounds formed.
- Red bromine, Br_2 , liquid is decolourised in an addition reaction with an alkene. Explain, with reference to ethane and ethene, how this reaction could demonstrate which substance is unsaturated.
- Write the addition reaction for five monomers of tetrafluoroethene. The tetrafluoroethane monomer has the structural formula $\text{F}_2\text{C}=\text{CF}_2$.

Haloalkanes undergo substitution reactions.

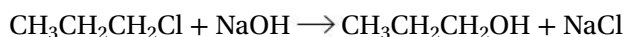
Reactions of haloalkanes

As discussed earlier, haloalkanes can be prepared from alkanes using substitution reactions, or from alkenes using addition reactions. Haloalkanes are widely used but most do not occur naturally and must be produced synthetically. One of the first used was chloroform in the American Civil War (1861) where it was used as an anaesthetic for amputations and treatment of soldiers. Haloalkanes are now widely used in medicine, agriculture and production of polymers.

Although haloalkanes have a number of uses in their own right, they are particularly useful as precursors to the preparation of further substances. Alcohols can be prepared from haloalkanes in substitution reactions by reacting them with dilute solutions of either sodium or potassium hydroxide. For example, propan-2-ol can be made by reacting either 2-chloropropane or 2-bromopropane with dilute sodium hydroxide.



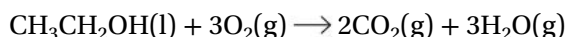
Either 1-chloropropane or 1-bromopropane could be used to make propan-1-ol.



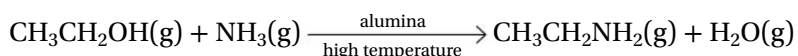
Reactions of alcohols

Alcohols undergo oxidation (as in combustion with oxygen from the air), substitution and more general types of oxidation reactions.

All alcohols are flammable and burn in air to produce carbon dioxide and water. For this reason, ethanol is added to petrol to produce various ethanol blends.

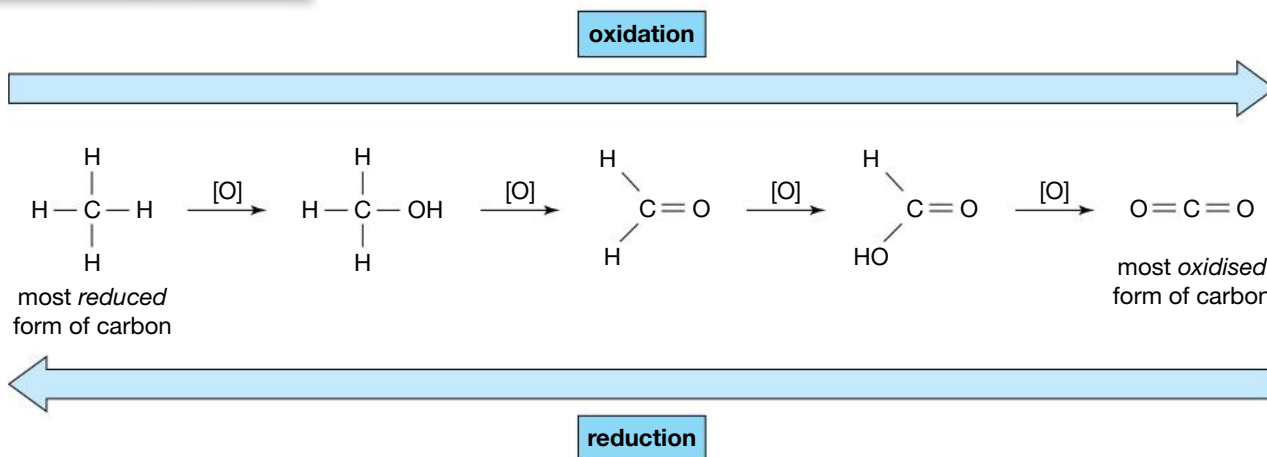


It is also possible to remove the —OH functional group and substitute it with a different group. For example, the amine group, —NH₂, can be added by passing the appropriate alcohol and ammonia over an alumina, Al₂O₃, catalyst at high temperatures. The production of ethanamine from ethanol is an example of such a reaction.

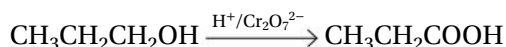


Stages of oxidation of carbon compounds. Notice the increase in oxidation number of carbon from left to right.

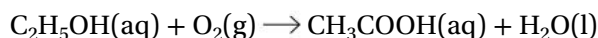
Primary alcohols are easily oxidised in the laboratory, first to aldehydes and then to carboxylic acids, using either acidified permanganate, H⁺/MnO₄[−](aq), or acidified dichromate, H⁺/Cr₂O₇^{2−}(aq), solution (or another oxidising agent). [O] is the symbol for oxidising agent.



In these oxidation reactions, there is an increase in the oxygen to hydrogen ratio; that is, there is more oxygen and less hydrogen. The product of these reactions is a carboxylic acid. For example, propan-1-ol can be converted into propanoic acid as shown below.



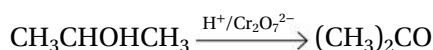
The oxidation of ethanol in wine takes place when it is left exposed to air for some time. Such wine has a sour taste of ethanoic acid, commonly known as acetic acid. The oxidation reaction that takes place is:



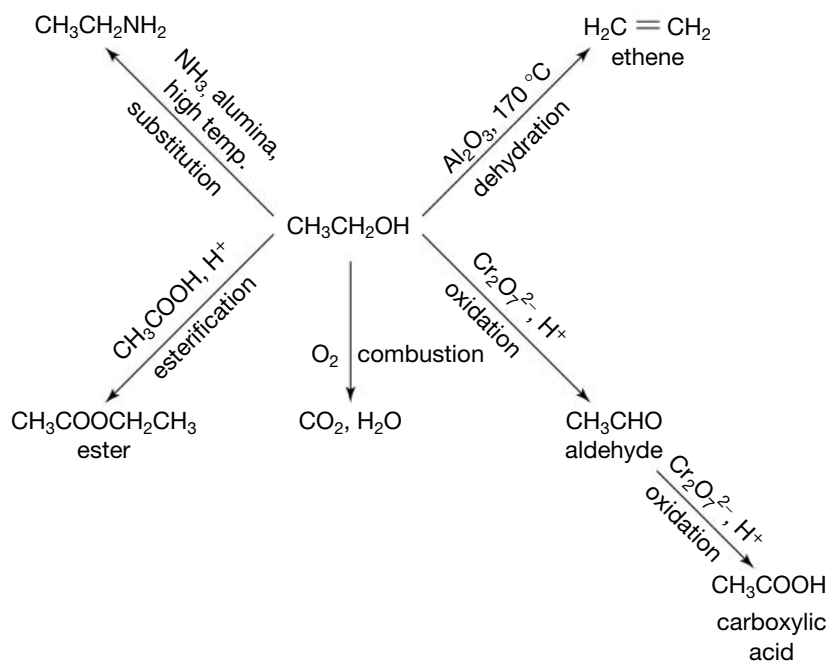
Ethanol is oxidised to produce ethanoic acid when exposed to oxygen in the air.

The reaction is catalysed by the presence of the micro-organism *Acetobacter aceti* in the exposed wine.

Secondary alcohols are oxidised to ketones, which do not undergo further oxidation. For example, propan-2-ol is oxidised to propanone.



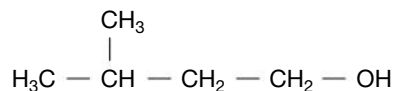
Reactions of alcohols – summary



Some important reactions of alcohols (using ethanol as an example)

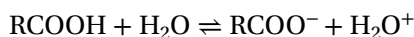
Revision questions

22. What type of reaction is involved in the conversion of a haloalkane to an alcohol?
23. Alcohols make good fuels. For example, ethanol is used as an additive in petrol. Write an equation for the combustion of ethanol (in a plentiful supply of oxygen).
24. (a) Name the alcohol on the right.
 (b) Give the name and structure of the product formed by the complete oxidation of this alcohol by acidified potassium dichromate.



Reactions of carboxylic acids

Carboxylic acids contain the carboxyl (—COOH) functional group. They are weak acids because they hydrolyse to a small extent in water according to the following general equation.



(where R represents either a single H atom or an alkyl group such as —CH_3 or $\text{—CH}_2\text{CH}_3$).



Apple cider vinegar, white vinegar and grape vinegar. The acid present in vinegar is ethanoic acid, CH_3COOH . Ethanoic acid is commonly known as acetic acid.

As expected, carboxylic acids show typical reactions of acids. For example, they react readily with bases, magnesium metal and metal carbonates. Due to the reaction shown above, solutions of carboxylic acids all have a pH less than 7.

An important subgroup of carboxylic acids are the fatty acids. A typical fatty acid may contain from 16 to 22 carbon atoms and is therefore insoluble. Fatty acids are also called long-chain carboxylic acids.

Another important reaction of carboxylic acids is their reaction with alcohols to form esters.

Formation of esters

Esters are products of **condensation reactions** between alcohols and carboxylic acids. A typical *esterification* (process of ester formation) reaction is the formation of ethyl ethanoate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$, by heating ethanol, $\text{C}_2\text{H}_5\text{OH}$, and ethanoic acid,

CH_3COOH , in the presence of an acid such as concentrated sulfuric acid. During the condensation reaction, a water molecule is produced. The ester formed is partially insoluble in water and can be purified by mixing it with cold water. The ester forms a sweet-smelling insoluble layer on top of the water, while sulfuric acid and unreacted ethanol and ethanoic acid dissolve in the water.

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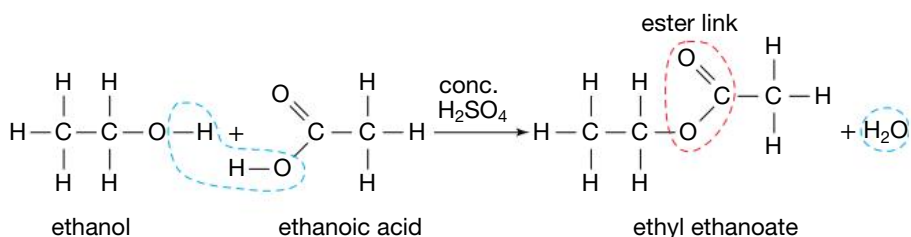
Unit 4

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See more
Ester formation



A typical esterification reaction

Esters are products of condensation reactions between alcohols and carboxylic acids.

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Experiment 9.3 Esterification

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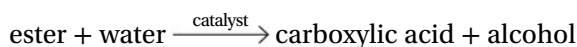
Esterification

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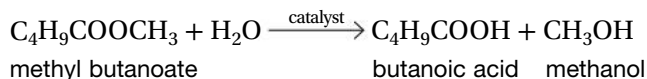
This process is called a condensation reaction because a small molecule (water) is split off as the two molecules join together. In general:



Esters can be converted back into their respective carboxylic acid and alcohol. This reaction is called *hydrolysis*, because water is used to split the ester molecule. Dilute acid or alkali is used as a catalyst and the mixture is heated.



For example:



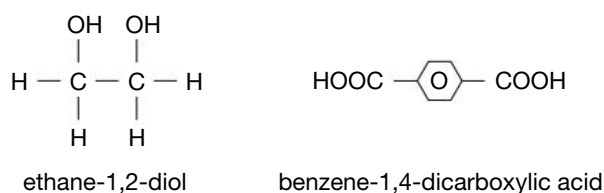
Sample problem 9.4

Name the carboxylic acid and alcohol that have been reacted together to produce the ester $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$.

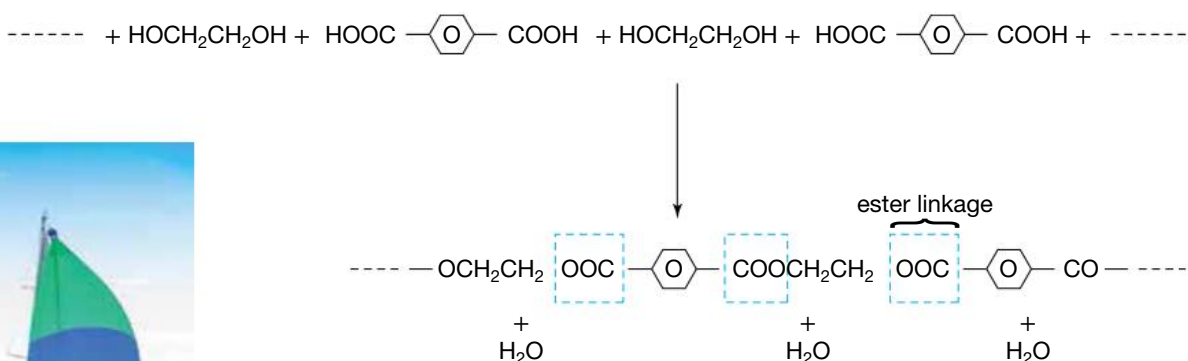
Solution: Since the ester link $-\text{COO}$ is formed from the carboxylic acid reactant, the carboxylic acid must be propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$. The other reactant, the alcohol, must have $-\text{OH}$ attached; therefore, the alcohol must be ethanol, $\text{CH}_3\text{CH}_2\text{OH}$. The ester is called ethyl propanoate.

Polyesters

Polyesters are synthetic fibres used as a substitute for cotton and wool and are formed as a result of ester linkages between monomers to form the polymer. A common polyester is terylene, which is poly(ethane-1,2-diylbenzene-1,4-dicarboxylate). This polyester is made by the esterification of ethane-1,2-diol (also known as ethylene glycol) and benzene-1,4-dicarboxylic acid (also known as terephthalic acid). The structures of these molecules are shown in the figure below. These monomer units are joined together to form polyester.



The structures of ethylene glycol (left) and terephthalic acid (right)



Esterification to form terylene



Most sails today are made of polyester.

Polyesters have great tensile strength and are used as the bonding resin in glass fibre plastics. They have a wide variety of uses in the textile industry. Many yachts have sails made of polyester as it is stronger than natural fibres and does not rot. Polyesters are mixed with cotton to make fabric for clothing. They are crease resistant and do not shrink or stretch. The oven bags that you use for roasting are also made of polyester as it can withstand high temperatures.

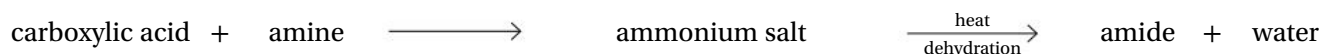
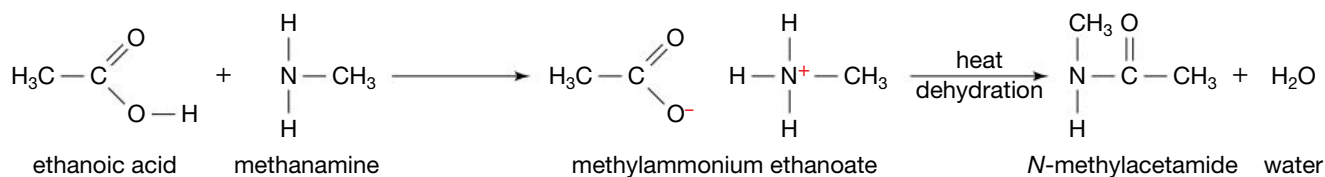
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Acid-base reaction of an amine
with a carboxylic acid

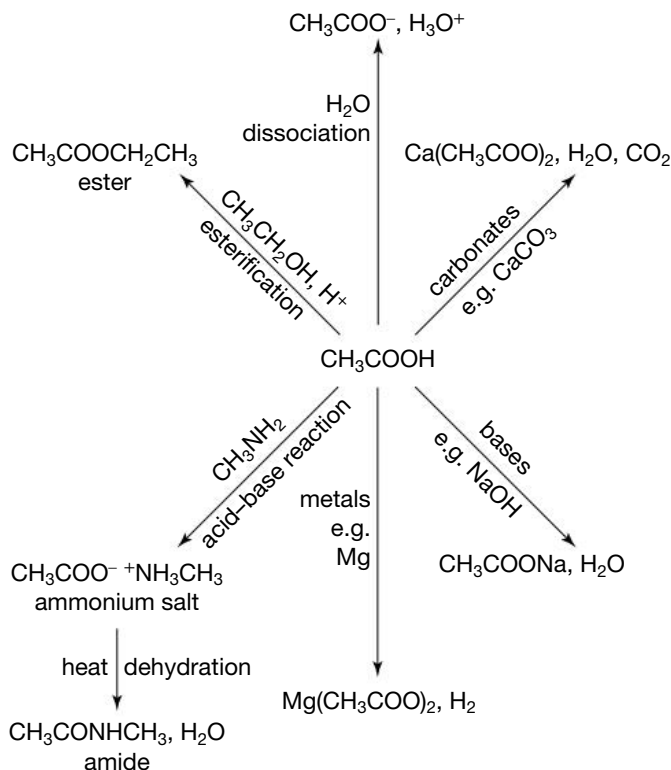
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Reaction of carboxylic acids with amines

Small amines react in a similar manner to ammonia, which is a weak base. Therefore, carboxylic acids can donate a proton to a primary amine. An example is the acid-base reaction of ethanoic acid with methanamine to produce the salt methylammonium ethanoate. This salt is heated to over 100 °C, water is removed, and an amide is formed.



Reactions of carboxylic acids – summary



Some important reactions
of carboxylic acids (using
ethanoic acid as an example)

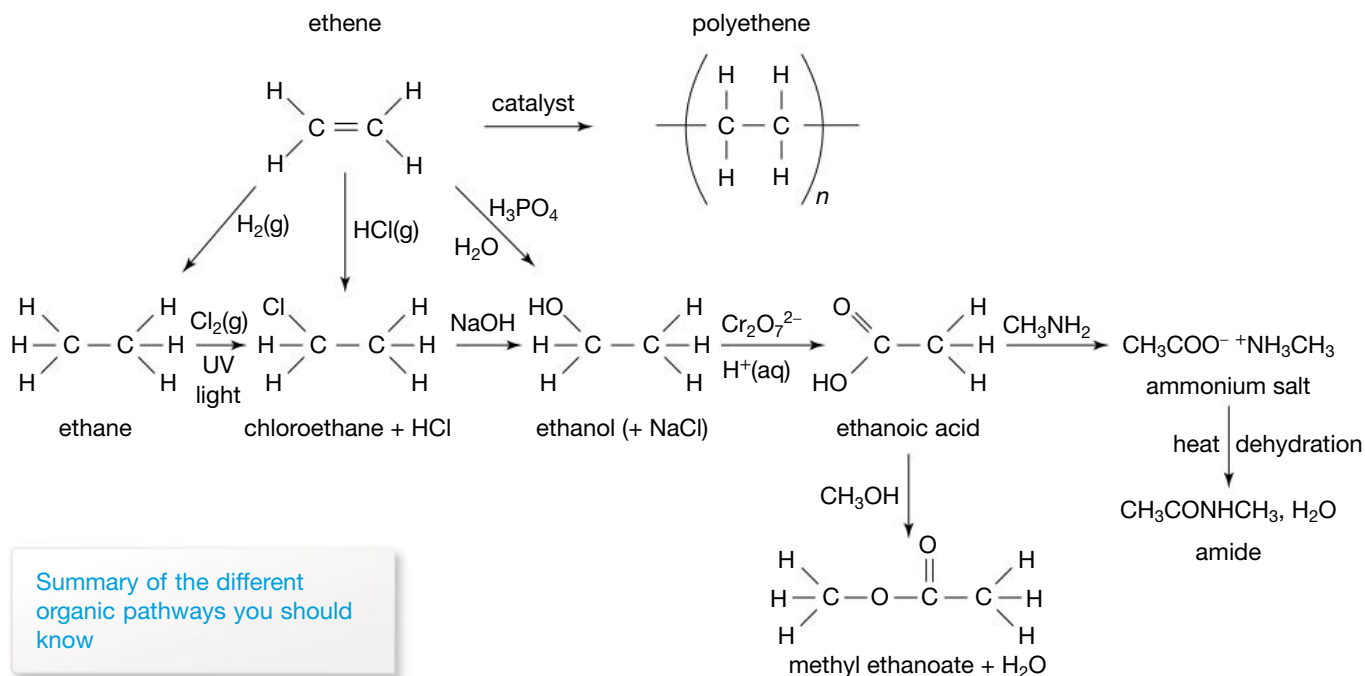
Revision questions

25. Write the equation representing the reaction between aqueous solutions of ethanoic acid and potassium hydroxide.
26. Name and draw the structures of two esters that are structural isomers of ethyl ethanoate.
27. Write an equation showing the reaction between methanol and propanoic acid.
28. Write an equation for the hydrolysis of butyl methanoate.

Organic pathways

Different pathways, involving the formation of different products along the line, can be used to arrive at the same organic product.

There are often different pathways that organic reactions can follow to arrive at the same product. For instance, ethanol can be produced industrially in three ways: from ethene, from chloroethane and from ethane.



Summary of the different organic pathways you should know

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Unit 4

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Do more

Reaction pathways

Revision questions

29. Ethanol is used in alcoholic drinks and as a fuel and a solvent. Write the structural equations for the chemical reactions involved in the three ways that ethanol can be produced.
30. Describe the steps involved in producing the flavouring ethyl ethanoate, commencing with ethane.

Measuring the efficiency of reactions

There are a number of ways of evaluating the efficiency of a chemical process. Factors that could be considered include energy consumption, cost of chemicals and equipment, and environmental impact. Traditionally, the efficiency of a reaction has been determined by calculating the percentage yield.

Percentage yield

Sometimes when chemical reactions are performed, not all of the reactants are converted into the desired products. This could be due to many factors including:

1. the reaction being an equilibrium reaction and not going to completion
2. losses when transferring liquids between containers
3. losses when filtering
4. losses when heating
5. presence of unreactive impurities
6. decomposition of product

7. some liquid lost due to evaporation
8. other side reactions.

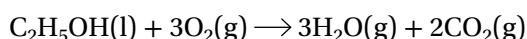
Chemical processes have been designed to manufacture the maximum amount of product from a given amount of raw materials. This is called the yield of a reaction and can be calculated using the following formula.

$$\% \text{ yield} = \frac{\text{mass of product actually made}}{\text{theoretical mass of product that could be made}} \times 100$$

The theoretical mass of the product is calculated using the given amount of the limiting reactant in the reaction.

Sample problem 9.5

2.18 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is reacted with excess oxygen to produce 3.63 g of carbon dioxide according to the equation:



What is the percentage yield of this reaction?

Solution:

$$n(\text{C}_2\text{H}_5\text{OH}) = \frac{2.18 \text{ g}}{46.0 \text{ g mol}^{-1}} = 0.0474 \text{ mol}$$

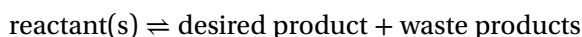
$$\text{theoretical } n(\text{CO}_2) = 2 \times 0.0474 = 0.0948 \text{ mol}$$

$$m(\text{CO}_2) = 0.0948 \text{ mol} \times 44.0 \text{ g mol}^{-1} = 4.17 \text{ g}$$

$$\begin{aligned} \% \text{ yield } (\text{CO}_2) &= \frac{3.63 \text{ g}}{4.17 \text{ g}} \times 100 \\ &= 87.0\% \end{aligned}$$

Atom economy

Calculating the yield, however, does not give an indication of how effectively the reactants have been used to generate the product with minimal waste. Atom economy is another method for measuring the efficiency of a reaction that takes into account the amount of waste produced.



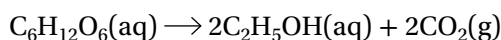
The atom economy of a reaction considers the amount of useful product produced from a particular amount of reactants. Measuring atom economy enables sustainable development by using less natural resources and minimising waste. The optimal situation is where the yield of a reaction is maximised, and as many atoms as possible of the reactants are incorporated into the final product. It is preferable to decrease the amount of waste produced rather than have to deal with it at the end of the process.

Atom economy of a reaction can be calculated as:

$$\% \text{ atom economy} = \frac{\text{mass of atoms in desired product}}{\text{mass of atoms in reactants}} \times 100$$

Sample problem 9.6

Ethanol can be produced through the process of the fermentation of glucose in the absence of air.



What is the atom economy of this reaction?

Solution: The desired product is ethanol. From the equation, 1 mole of glucose produces 2 moles of ethanol.

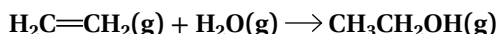
$$M(\text{CH}_3\text{CH}_2\text{OH}) = 2 \times (2 \times 12.0 + 6 \times 1.0 + 1 \times 16.0) = 92.0 \text{ g mol}^{-1}$$

$$M(\text{C}_6\text{H}_{12}\text{O}_6) = (6 \times 12.0 + 12 \times 1.0 + 6 \times 16.0) = 180 \text{ g mol}^{-1}$$

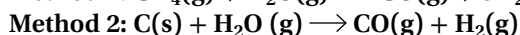
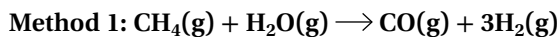
$$\% \text{ atom economy} = \frac{92.0}{180} \times 100 = 51.1\%$$

Revision questions

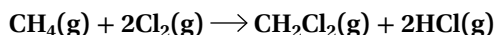
31. 30.3 g of ethanoic acid, CH_3COOH , is obtained from the oxidation of 26.8 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$. What is the percentage yield?
32. The complete combustion of 82.2 grams of propane produces a 73.2% yield. How many grams of CO_2 would be produced?
33. Ethanol is manufactured industrially by reacting ethene with steam.



- (a) What is the % atom economy for this reaction?
- (b) How does your answer to (a) compare with the calculated value in sample problem 9.6?
- (c) Which is the more efficient process?
- (d) What other factors need to be considered when choosing which process to use?
34. Two methods of producing hydrogen are shown below. Which has the higher % atom economy?



35. Methane and chlorine react to produce the solvent dichloromethane according to the following equation.



Calculate the % atom economy for the formation of CH_2Cl_2 in this reaction.

Chapter review

Summary

- The boiling points and other physical properties of organic compounds are influenced by the size, shape, structure and degree of polarisation of their covalent bonds. The intermolecular forces involved are dispersion forces, dipole-dipole attractions and hydrogen bonding.
- Isomers are compounds with the same molecular formula but different arrangements of atoms.
- In structural isomers, the atoms are arranged in different ways. Therefore, the chemical bonding is different. Structural isomers have different physical properties and, if different functional groups, chemical reactivities.
 - Chain isomers have different branching in the carbon chain.
 - Positional isomers show different positions of the particular functional group, which is usually indicated by a number in the name.
 - Functional isomers have the same atoms but different functional groups.
- Stereoisomers have the same sequence of bonded atoms, but the spatial arrangement of atoms differs.
 - *cis-trans* isomers are non-mirror-image molecules that have the same chemical bonding but different spatial arrangements of atoms. *cis-trans* isomers involve atoms or groups that can be either next to each other (*cis* isomer) or on opposite sides of the molecule (*trans* isomer) in restricted bonded compounds.
 - Enantiomers, or optical isomers, are mirror-image molecules that cannot be superimposed on each other. These molecules are described as chiral. Enantiomers have identical physical properties. Their chemical properties are also generally the same (except interactions with other molecules with optical properties). A chiral molecule rotates the plane of polarised light passing through the solution. Optical isomers can have radically different biological effects.
- Alkanes, alkenes and alkynes consist of non-polar molecules. Smaller molecular mass hydrocarbons are gases, and their boiling points increase with size due to the increased effect of dispersion forces. They are also insoluble in water but soluble in organic solvents. They are colourless and have low density.
- Alcohols are flammable and form hydrogen bonds with adjacent molecules. As a result, the smaller alcohols are liquids at room temperature and soluble in water. Solubility decreases with increasing chain length, whereas boiling point increases.
- Carboxylic acids form stronger hydrogen bonds than alcohols because their —OH group is more polarised due to the presence of the electron-withdrawing group C=O. The —COOH group is more acidic than the —OH group of alcohols, but carboxylic acids are much weaker acids than inorganic acids such as sulfuric acid.
- Smaller aldehydes have an unpleasant smell, but those with higher molar mass have a pleasant smell. Aldehydes and ketones have lower boiling points than alcohols because, although the C=O (carbonyl group) is polar, they do not have a hydroxyl group and so do not form hydrogen bonds between molecules.
- Esters are volatile liquids at room temperature. Smaller molecules are polar and soluble in water, but their solubility decreases with increased size.
- All alkanes and alkenes undergo complete combustion with excess oxygen (air) to produce carbon dioxide and water. The exothermic nature of these reactions is the reason for the use of these hydrocarbons as fuels.
- Alkanes undergo substitution reactions with halogens to produce a range of haloalkanes.
- Alkenes are more reactive than alkanes (because of the C=C double bond) and undergo addition reactions with a wide range of substances.
- A number of monomers of alkenes can undergo addition polymerisation reactions to form large molecules called polymers.
- Alcohols burn in air to form carbon dioxide and water. They undergo substitution reactions, for example, with ammonia to form amines. Primary alcohols are oxidised to aldehydes and then to carboxylic acids using acidified dichromate or permanganate ions. Secondary alcohols are oxidised to ketones but do not undergo further oxidation. Tertiary alcohols cannot be oxidised.
- Carboxylic acids are weak acids that undergo reactions with metals, bases and metal carbonates. Carboxylic acids react with amines in acid-base reactions, followed by dehydration to form amides.
- Esters are formed by condensation reactions between alcohols and carboxylic acids in the presence of heat and an acid catalyst. A water molecule is eliminated in the process.
- Polyesters are synthetic fibres manufactured from a diol and a dicarboxylic acid monomer.
- In some chemical reactions, not all of the reactants are converted into the desired products. The percentage

yield is the amount of product produced from a given amount of raw materials. It is calculated as:

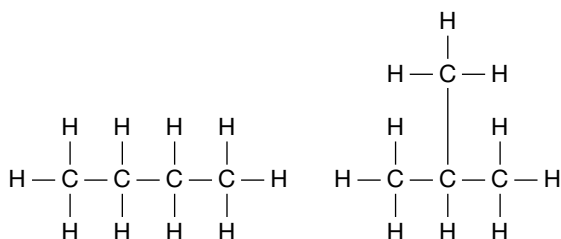
$$\% \text{ yield} = \frac{\text{mass of product actually made}}{\text{theoretical mass of product that could be made}} \times 100$$

- Atom economy is another method of measuring the efficiency of a reaction that takes into account the amount of waste produced. It is a measure of the amount of reactants that become useful products. It is calculated as:

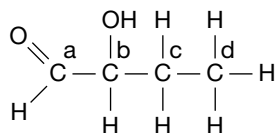
$$\% \text{ atom economy} = \frac{\text{mass of atoms in desired product}}{\text{mass of atoms in reactants}} \times 100$$

Multiple choice questions

- Which of the following compounds are isomers?
 - propanoic acid and ethanoic acid
 - propanol and propanal
 - propan-1-ol and propan-2-ol
 - propane and propan-1-ol
- The two molecules shown below are best described as:



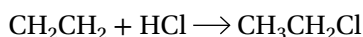
- optical isomers
 - structural isomers
 - cis-trans* isomers
 - stereoisomers.
- Identify the chiral carbon atom in this molecule.



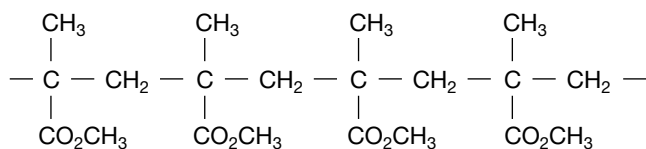
- a
 - b
 - c
 - d
- Enantiomers are:
 - stereoisomers with superimposable mirror images
 - stereoisomers that contain no chiral carbon atoms
 - stereoisomers with non-superimposable mirror images
 - stereoisomers with *cis-trans* isomerism.

- Which properties are generally characteristic of hydrocarbons?
 - Low melting point and soluble in polar solvents
 - High melting point and soluble in polar solvents
 - Low melting point and insoluble in polar solvents
 - High melting point and insoluble in nonpolar solvents
- Which of the following alkanes would you expect to have the lowest melting point?
 - octane
 - propane
 - pentane
 - butane
- The lowest temperature at which a material produces a flammable vapour describes:
 - auto ignition temperature
 - flashpoint
 - fire point
 - ignition temperature.
- Which of the following compounds is likely to have the lowest flashpoint?
 - cooking oil
 - pentane
 - ethanol
 - carbon dioxide
- Which of the following is the most soluble in water?
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 - $\text{CH}_3\text{CH}_2\text{OH}$
 - $\text{CH}_3\text{CH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{Cl}$
- Which of the following has the lowest boiling point?
 - 2,3-dimethylbutane
 - hexane
 - 2,3-dimethylpentane
 - 3-methylpentane
- Which of the following compounds can form hydrogen bonds between its molecules?
 - $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$
 - $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- Which of the following has the greatest solubility in octane?
 - octanol
 - propylamine
 - pentane
 - ethanoic acid
- Which of the following is an *incorrect* statement about amino groups?
 - They form aqueous solutions with a pH greater than 7.
 - They are found in amino acids.
 - They contain nitrogen.
 - They are non-polar.
- When comparing the boiling points of aldehydes and ketones with compounds of similar molecular mass, it can be observed that their boiling points are:
 - higher than those of alcohols and alkanes
 - lower than those of alcohols and alkanes
 - higher than those of alcohols but lower than those of alkanes
 - higher than those of alkanes but lower than those of alcohols.

15. Which of the following is an *incorrect* statement about the properties of carboxylic acids?
- A** The boiling points of carboxylic acids are higher than alcohols of similar size.
B The smaller carboxylic acids are liquids at room temperature.
C Carboxylic acids cannot form hydrogen bonds with water.
D Carboxylic acids ionise only partially in water.
16. The following reaction is an example of:



- A** an addition reaction
B a substitution reaction
C a condensation reaction
D a combustion reaction.
17. Which of the following can be used to convert an alkene to an alkane?
- A** H_2O **C** HCl
B CO_2 **D** H_2
18. 2-bromobutane reacts with KOH in ethanol to produce two products. The type of reaction involved is:
- A** addition **C** oxidation
B acid-base **D** substitution.
19. Which compound is converted to pentanal by acidified potassium dichromate solution?
- A** pentan-1-ol **C** pentanone
B pentan-2-ol **D** pentanoic acid
20. The polymer polymethylmethacrylate:



is formed from the monomer:

- A** $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{CH} \\ | \\ \text{CO}_2\text{CH}_3 \end{array}$
B $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}=\text{CH} \\ | \\ \text{CO}_2\text{CH}_3 \end{array}$
C $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{C}=\text{C} \\ | \\ \text{CO}_2\text{CH}_3 \end{array}$
D $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{CH} \\ | \\ \text{CO}_2\text{CH}_3 \end{array}$

21. If a secondary alcohol is oxidised it produces:
- A** a ketone
B an aldehyde
C a carboxylic acid
D initially an aldehyde that reacts further to form a carboxylic acid.
22. Which of the following statements is incorrect?
- A** Ethanoic acid reacts with magnesium to form magnesium ethanoate and hydrogen.
B Oxidation of ethanol results in ethanoic acid.
C Ethanol dissociates in water to form the ethoxide ion and hydronium ion.
D Ethanoic acid does not dissolve in water.
23. The synthesis of polyester is:
- A** a condensation reaction where water molecules are used up
B a hydrolysis reaction where water molecules are eliminated
C the result of monomers of alcohol and carboxylic acid molecules joined together to form a long chain of ester
D the result of monomers of ringed alcohol and unsaturated hydrocarbon molecules joined together to form a long chain of ester.
24. Complete this sentence by selecting the correct option.
 Carboxylic acids may be prepared by the oxidation of ...
 I: primary alcohols II: secondary alcohols
 III: aldehydes IV: ketones.
- A** I only **C** I and III
B II and III **D** II and IV
25. If the theoretical yield for a reaction to produce propanoic acid is 126 grams and 95.0 grams of the product is actually made, what is the percentage yield?
- A** 132% **C** 32.6%
B 75.4% **D** 24.6%

Review questions

Properties and bonding

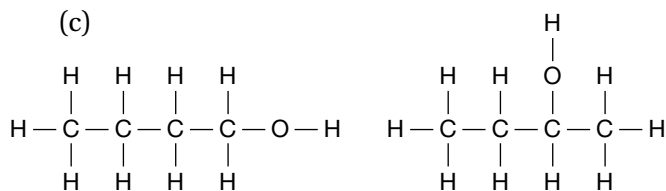
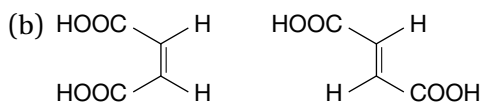
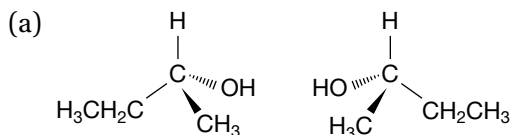
- Describe the main intermolecular forces acting in the following compounds.

(a) CH_3Cl	(e) $\text{H}_2\text{C}=\text{CH}_2$
(b) CH_3OCH_3	(f) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
(c) CBr_4	(g) <i>cis</i> - CH_2Cl_2
(d) $\text{CH}_3\text{CH}_2\text{NH}_2$	(h) HCOOH
- The molar masses of propan-1-ol and butane are similar. Which would you expect to have the higher boiling point? Explain your answer.
- Use a labelled diagram to explain why methanol, CH_3OH , is soluble in water.
- Describe the trends in the following properties as the molar mass of a hydrocarbon increases.

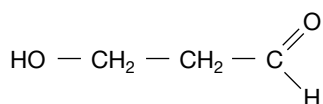
(a) Volatility	(c) Flashpoint
(b) Viscosity	(d) Boiling point

Isomerism

- Draw and label the *cis* and *trans* isomers with the molecular formula $C_2H_2F_2$.
- Draw each of the following structures and place an asterisk (*) at the chiral carbon atom.
 - 2-chlorobutane
 - 2-methylbutan-1-ol
 - butan-2-ol
 - 3-methylhexane
- but-2-ene reacts with HCl to form a pair of optically active isomers.
 - Draw diagrams to show the relationship between the two isomers.
 - State the structural requirement for a molecule to be able to exist as enantiomers.
- Describe the type of isomerism present in each of the following pairs of compounds:



- This compound has three structural isomers: X, Y and Z.



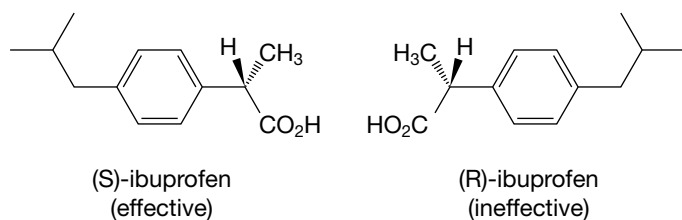
Isomer X is a ketone.

Isomer Y is an ester.

Isomer Z reacts with sodium carbonate to produce carbon dioxide.

Draw the structures of these isomers.

- The enantiomers for the pain-relief medication ibuprofen are shown below.
 - List the functional groups present.
 - Identify and state the chiral carbon atom.



- Name the molecule below, and explain why it can be described as being chiral.



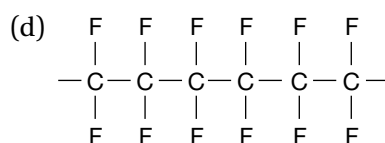
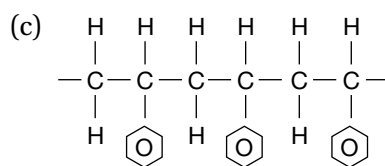
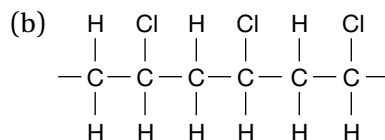
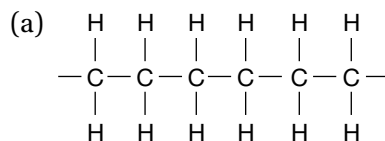
- Explain why H_2NCH_2COOH can react with both an acid and a base.

Cracking

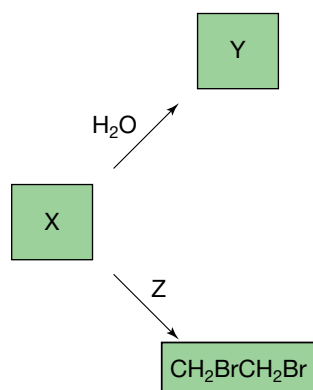
- In a sample of natural gas coming ashore for processing, the ethane content is found to be 2.5%. This ethane may be subsequently separated and sold for cracking to produce ethene. This ethene may then be converted into ethanol — an important industrial solvent.
 - Write an equation for the production of ethanol from ethene.
 - Calculate the theoretical mass of ethanol that may ultimately be made from 10 000 L of natural gas, collected at 10 atm and 15 °C.

Reactions of organic compounds

- What is a substitution reaction? Write the equations of methane reacting with bromine and all the possible products formed.
- Under what conditions can substitution reactions with alkanes occur?
- Write equations for the reactions between:
 - ethene + HI
 - propene and H_2 (Pt catalyst)
 - ethene + Br_2
 - but-1-ene + Cl_2
 - methane + excess O_2
 - ethane + Cl_2
 - ethene + H_2O
 - but-2-ene + H_2 .
- For each of the following polymer backbones, identify the individual monomer.



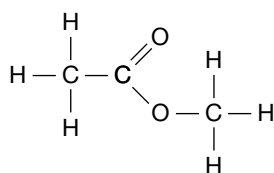
18. Write the formula of each of the substances X, Y and Z that are shown in the diagram below.



19. Write structural formulas for the products formed when the following substances are reacted together under appropriate conditions.

- $\text{H}_2\text{C}=\text{CH}_2$ and H_2O
- $\text{H}_3\text{C}-\text{CH}=\text{CH}_2$ and H_2O
- $\text{H}_3\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ and Br_2
- $\text{H}_2\text{C}=\text{CH}_2$ and HCl
- $\text{H}_3\text{C}-\text{CH}=\text{CH}_2$ with itself

20. (a) Name the following ester.



- (b) Name and draw the structures of the reactants required to produce this ester.

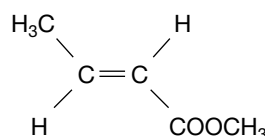
- Describe a simple chemical test that could be used to distinguish an unsaturated hydrocarbon from a saturated one.
- Ethene is an important material, not only for the production of polymers, but also for the manufacture of many other chemicals. Write equations to show the production of three such chemicals from ethene.
- (a) Draw and name the two possible products formed from the reaction between HCl and propene.
(b) Why is only one product formed in the reaction of HCl and but-2-ene?
- Calculate the volume of ethene required to produce 100 kg of polyethene at 25°C and 250 atm pressure.
- Polypropene is produced by the polymerisation of a particular monomer.
(a) What is meant by the term 'monomer'?
(b) What is the name of the monomer used in the above process?
(c) What is the source of this monomer in industry?
(d) Which other very important substance, which can also act as a monomer, is also formed by catalytic cracking?

26. Synthetic rubber uses buta-1, 3-diene and styrene to make styrene-butadiene rubber (SBR).

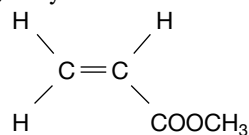
- Draw the structures of buta-1, 3-diene and styrene, and hence explain why both these substances are suitable monomers for this process.
- What is the main industrial source of buta-1,3-diene?
- From what important chemical is styrene made?

27. (a) Draw sections of the polymers that are formed from the following monomers.

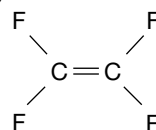
- (i) methyl methacrylate



- (ii) vinyl acetate

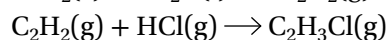
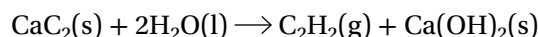


- (iii) tetrafluoroethene.



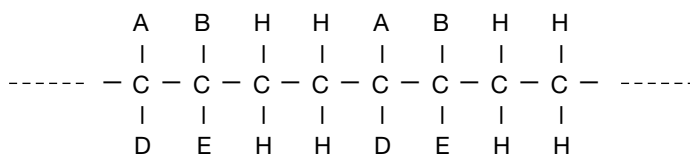
- (b) Suggest a name for each of the polymers above. Try to find out their common names and some uses for each one.

28. One way of manufacturing vinyl chloride (chloroethene) is initially to produce ethyne (acetylene, C_2H_2) and then to react this with hydrogen chloride. The equations are:



- Draw the structural formulas for acetylene and vinyl chloride.
- Calculate the mass of calcium carbide required to make 500 g of vinyl chloride.
- What type of reaction is represented by the second equation above?
- Draw a section of the polymer that vinyl chloride makes.

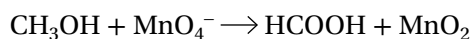
29. Shown below is a small section of a polymer that is made from two different monomers.



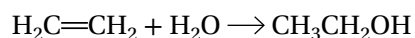
- (a) Could the monomers $\text{DAC}=\text{CBE}$ and $\text{H}_2\text{C}=\text{CH}_2$ have been used to make this polymer?
- (b) Could the monomers $\text{H}_2\text{C}=\text{CBE}$ and $\text{H}_2\text{C}=\text{CAD}$ have been used to make this polymer?
- 30.** What type of reaction is the esterification process? What are the reactants and products?
- 31.** Carboxylic acids can be made from alkanes. Describe the stages and products formed in the conversion of ethane to ethanoic acid. Draw structures and name the products at each stage.

Efficiency of reactions

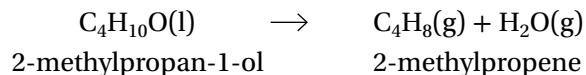
- 32.** When 11.5 g of methanol was treated with excess potassium permanganate, 13.2 g of methanoic acid was obtained. Balance the following equation by first balancing the relevant half-equations, and then calculate the percentage yield.



- 33.** Explain why the atom economy of this reaction is 100%.



- 34.** 2-methylpropan-1-ol can be used to manufacture diesel and jet fuel. The first step in the process is the production of 2-methylpropene.



Calculate the % atom economy for this reaction.



Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Multiple choice questions

- Which of the following statements correctly describes *cis-trans* isomers?
A They have different arrangements around a double bond.
B They have an asymmetric carbon atom that makes them mirror images.
C They have the same physical properties.
D They have different molecular formulas. 1 mark
- Burning ethane in excess oxygen produces carbon dioxide and water in the ratio:
A 1 : 3 **B** 1 : 1 **C** 2 : 3 **D** 2 : 1. 1 mark
- The ester with the formula $\text{CH}_3\text{COOC}_2\text{H}_5$ is made from:
A propanol and ethanoic acid
B ethanol and methanoic acid
C methanol and ethanoic acid
D ethanol and ethanoic acid. 1 mark
- An unknown reactant, X, is oxidised by acidified potassium dichromate solution to produce a substance that does not react with solid sodium carbonate. Which of the following molecules could represent the structure of X?
A $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
B $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
C CH_3OCH_3
D CH_3COOH 1 mark

Extended response questions

- (a) For each of the following monomers, draw the structure of part of a chain comprised of three monomers.
(i) CHClCHCl 1 mark
(ii) CH_2CHCN 2 marks
(b) What type of polymerisation is this? 1 mark
- Pentyl ethanoate has the sweet-smelling aroma of banana. Its semi-structural formula is $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.
(a) In which organic group does this compound belong? 1 mark
(b) Apart from flavourings, what is another use for this type of compound? 1 mark
(c) Reacting ethanoic acid with what other substance can produce pentyl ethanoate? 1 mark
(d) Name the type of reaction that takes place. 1 mark
- Consider the following reaction pathway.
$$\text{but-2-ene} \xrightarrow{\text{Step 1}} \text{CH}_3\text{CHClCH}_2\text{CH}_3 \xrightarrow{\text{Step 2}} \text{substance X} \xrightarrow{\text{Step 3}} \text{butanone}$$

(a) Name substance X and draw its structure. 2 marks
(b) Why does but-2-ene show *cis-trans* isomerism but but-1-ene does not? 2 marks
(c) To which group of compounds does but-2-ene belong? 1 mark
(d) Name the type of reaction occurring in step 1. 1 mark

10 Analysis of organic compounds

We are all familiar with the vibrant colours of a rainbow and the coloured sheen of oil floating on water. These two examples from everyday life demonstrate that light is a spectrum, a mixture of different colours. These different colours are really different types of electromagnetic radiation with different frequencies or wavelengths. Different substances interact with light and radiation in different ways. How can we use these interactions to identify them?

Chromatography, another method of analysis, can be used to separate the components of a mixture and then identify the components.

Finally, in this chapter, the use of volumetric analysis to determine the concentration of solutions is described.

YOU WILL EXAMINE:

- how mass spectrometry can be used to determine the structure of organic compounds
- how infrared spectroscopy can provide information about functional groups
- how structures of organic compounds can be deduced using nuclear magnetic resonance spectroscopy
- the principles of chromatography
- how high-performance liquid chromatography can be used to separate and identify organic compounds
- the use of calibration curves to determine concentrations
- the principles of volumetric analysis involving acid–base and redox reactions
- the roles of primary standards, standard solutions and indicators in volumetric analysis
- the application of volumetric calculations to find concentrations of compounds
- errors that might affect the final results in a titration
- information provided by combined techniques.



Doctors use magnetic resonance imaging (MRI) to see what is inside bodies without having to cut them open. Diagnosis of disorders ranging from torn ligaments and strokes to cancer and brain tumours can be achieved using MRI scans. Images are created by a signal from flipping proton spins (hydrogen nuclei) in water molecules or fat molecules using a magnetic field and radio waves. The patient must lie motionless in a tunnel-like machine with a large magnet. A detailed, three-dimensional image is then produced of the patient's insides. Our bodies are 60 to 70% water and, in an MRI image, water-containing tissue appears white, whereas bones with lower water content are much darker. It is a very sensitive technique that can detect changes in soft tissue. MRI is based on the principles of nuclear magnetic resonance (NMR), a spectroscopic technique often used to obtain information about the structure of molecules.

Chemical analysis

We cannot see atoms and molecules, so how do scientists determine the structures of the organic compounds discussed in chapter 8? Moreover, how do they know that the products of the reactions discussed in chapter 9 are actually the ones described? Analytical chemists provide answers to these questions and many more. Observation of physical properties, including states at room temperature and solubility in water, provides some hints, and chemical tests can offer more information. Simple techniques, such as gravimetric and volumetric analysis, are available in a school laboratory, but more advanced instrumental techniques are available to chemists that are considerably more accurate and often easier and quicker to perform. These techniques include spectroscopy and chromatography. The analysis can be qualitative or quantitative.

Qualitative analysis finds what substances are present. Quantitative analysis measures the quantity of substance present.

In **qualitative analysis**, the chemist is merely interested in *what* is present. In testing a urine sample from a racehorse, for example, the mere presence of a banned drug (or its metabolised products) is all that is necessary. In the confectionery industry, a sample of imported food dye might be tested to see whether it contains chemicals that are banned in this country.

On the other hand, the question of *how much* may need to be answered — this is **quantitative analysis**. Quantitative analysis could determine the level of cholesterol in blood. Health authorities might need to know whether the level of mercury in samples of fish is below the allowed level.

A logical sequence often used in many analytical procedures is to perform a qualitative analysis first to find out what is present, and then to perform a quantitative analysis to find the various amounts of substances present.

Spectroscopy

A mass spectrometer analyses ions formed from atoms and molecules to determine their mass and charge. It does this by analysing the path of the substance through a magnetic field.

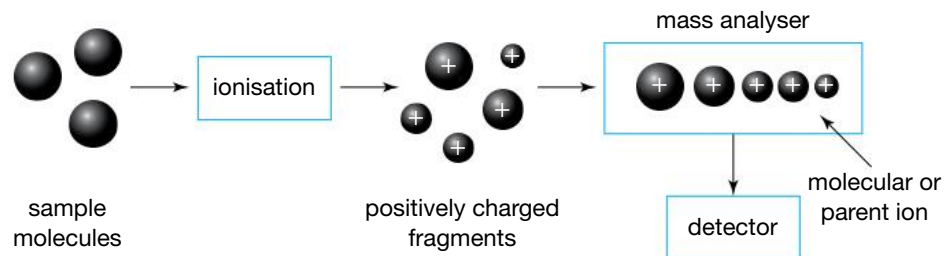
Spectroscopy looks at the interaction of light and matter. It is the study of the absorption, scattering or emission of electromagnetic radiation by particles such as ions, atoms or molecules. In Unit 2, you learned how atomic absorption spectroscopy can provide information about the quantitative and qualitative analysis of metals in a variety of situations. Other forms of spectroscopy tell us about molecular energy levels, structures of molecules and functional groups in organic compounds.

Mass spectrometry

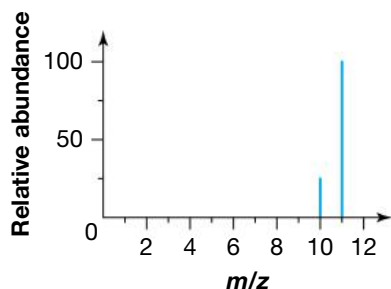
The output of a mass spectrometer is a mass spectrum that generally looks like a column graph. Each bar represents an ion with a specific mass to charge (m/z) ratio. The height of the bar shows the relative abundance.

Mass spectrometry is a technique that can be used to determine the structures of molecules, and its applications are numerous. Besides detecting drugs, mass spectrometry can be used to determine the structures of biomolecules, to detect explosives, toxins in seafood, oil deposits in rocks and impurities in steel, in space exploration and radiocarbon dating of fossils.

It is not strictly spectroscopy because it does not use electromagnetic radiation. Instead, molecules are bombarded by high-energy electrons, and the positive ions formed in this process then undergo fragmentation. The output is a mass spectrum that plots the mass/charge ratio (m/z) versus the abundance of each fragment. The most abundant peak is assigned a value of 100%. Only milligrams of a sample are required for the analysis, but the sample is destroyed in the process.



Fragmentation in a mass spectrometer



A mass spectrometer readout for boron

study on

Unit 4

AOS 1

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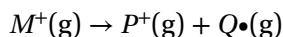
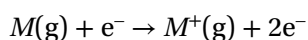
Do more

Interpreting a mass spectrum

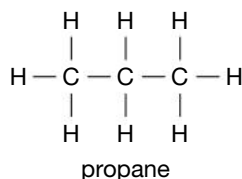
Although the horizontal scale is technically mass/charge, the bulk of the positive ions produced have a single positive charge (+1). This means that the horizontal axis is effectively a mass scale. Mass spectrometry can be used to identify isotopes of an element and to find out molecular structures. The mass spectrum at left shows that boron has two isotopes and that the heavier isotope is more abundant.

Analysing organic compounds

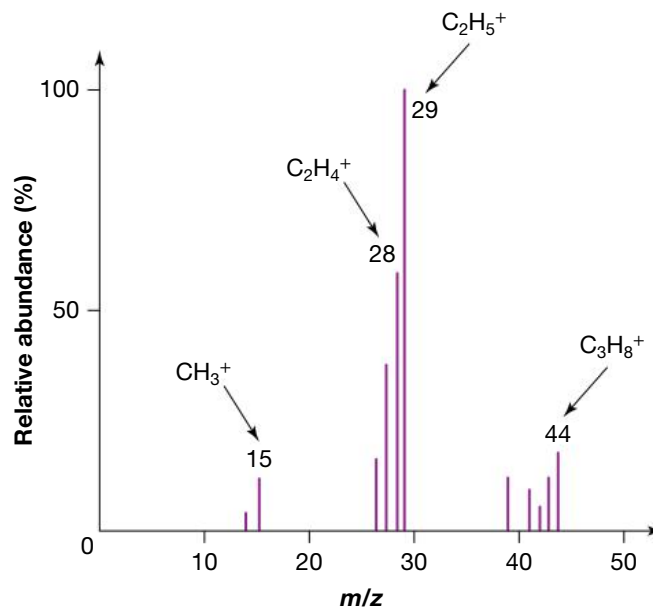
When a compound is analysed in a mass spectrometer, most of the molecule breaks up into smaller fragments, called fragment ions. Identification of the fragment ions can help determine the structure of the original molecule. The few remaining whole molecules produce ions with a peak at the relative molecular mass of the compound, even though this might be small due to extensive fragmentation. The ion represented by this peak is called the parent ion or molecular ion. Each line in the spectrum represents a positive ion with a specific mass/charge (m/z) ratio.



M^+ is the parent or molecular ion, which breaks down to P^+ and $Q\cdot$. The charged fragment, P^+ , is detected in the mass spectrometer. The uncharged (free radical) fragment, $Q\cdot$, is not detected. Mass spectrometers can be used in conjunction with high-performance liquid chromatography (HPLC) to further identify a peak in a chromatogram.



Structural formula and mass spectrum for propane



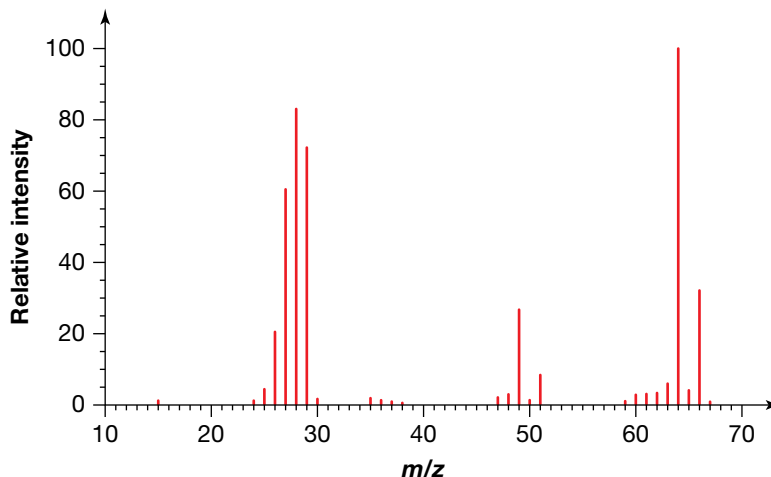
Consider the mass spectrum of propane above. Observe how each fragment ion produces a specific peak. The most abundant ion is known as the **base peak** and is usually assigned a height of 100%. This is the most common fragment, either because it is the most stable or it can be formed in different ways. Note that it is not always required to identify every peak in the spectrum. Table 10.1 shows m/z ratios for some small ions that may be observed in a mass spectrum. Sometimes, it is easier to determine the fragment by subtracting the fragment that is lost; for example, subtracting 15 from the molecular mass suggests that a methyl group, CH₃, was part of the molecule.

TABLE 10.1 m/z values for small ions

m/z	Positively charged fragment
15	CH_3^+
17	OH^+
18	H_2O^+
19	H_3O^+ , F^+
26	C_2H_2^+ , CN^+
27	C_2H_3^+
28	C_2H_4^+ , CO^+
29	C_2H_5^+ , CHO^+
30	CH_2NH_2^+
31	CH_3O^+
35 (37)	$^{35}\text{Cl}^+$ ($^{37}\text{Cl}^+$)

Sample problem 10.1

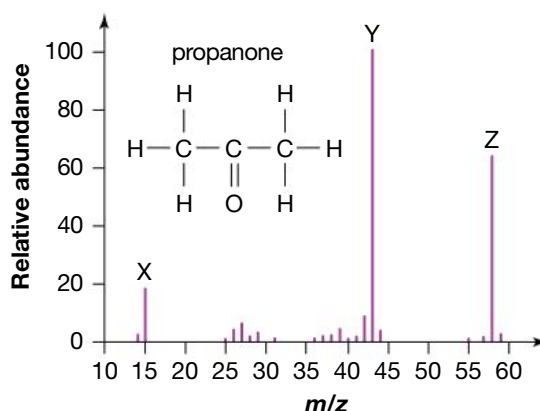
The diagram below shows the mass spectrum for chloroethane, $\text{C}_2\text{H}_5\text{Cl}$. What ions are responsible for the peaks at $m/z = 66$ and 64 , 51 and 49 , and 29 and 28 ?



- Solution:**
- Look for molecular ion peaks, and check for isotope peaks (e.g. for carbon and chlorine).
 - Calculate the molecular mass, remembering that chlorine has two isotopes, ^{35}Cl and ^{37}Cl .
 $[\text{C}_2\text{H}_5^{35}\text{Cl}]^+$ shows a peak at $m/z = 64$ and $[\text{C}_2\text{H}_5^{37}\text{Cl}]^+$ at $m/z = 66$.
 - Identify any other fragments and calculate the masses to confirm the peaks observed. Look for gaps of 15 lost from the molecular ion showing the loss of a methyl group.
 $[\text{CH}_2^{35}\text{Cl}]^+$ shows a peak at $m/z = 49$ and $[\text{CH}_2^{37}\text{Cl}]^+$ at $m/z = 51$.
The peak for $[\text{C}_2\text{H}_5]^+$ occurs at $m/z = 29$, and the peak for $[\text{C}_2\text{H}_4]^+$ occurs at $m/z = 28$.

Revision questions

- The mass spectrum for chlorine atoms shows two peaks: one with $m/z = 35$ and a relative abundance of 3, and another with $m/z = 37$ and a relative abundance of 1.
 - How many isotopes of chlorine are there?
 - Calculate the relative atomic mass of chlorine.
- Consider the structures of butane and methylpropane. Both of these molecules have the molecular formula C_4H_{10} .
 - Draw the two structures.
 - Suggest the possible fragment ions that would remain if only one bond is broken in each molecule.
- Propanone, commonly called acetone, CH_3COCH_3 , is an important solvent in industry. In a mass spectrometer, propanone breaks down into a series of fragment ions.
 - Which peak corresponds to $CH_3-CO-CH_3^+$?
 - Identify which fragment ions correspond to the other labelled peaks.



Infrared spectroscopy

Infrared (IR) spectroscopy identifies the functional groups and single, double and triple bonds in organic molecules. This qualitative analysis method measures the characteristic amount of energy that the bonds between atoms in a molecule absorb when exposed to radiation in the infrared portion of the electromagnetic spectrum.

Infrared (IR) radiation is one way of transferring heat from one place to another. It has longer wavelengths than visible light and extends from the red end of the visible section of the electromagnetic spectrum. All objects emit IR radiation; for example, toasters, heat lamps and even you emit IR radiation. Your TV remote control uses IR to change channels and volume. Infrared radiation is used in chemical analysis because it is emitted or absorbed by molecules when the bonds change their vibrational movements.

Covalent bonds can be likened to springs in that they can bend, stretch and vibrate in a number of different ways. These produce what are called *vibrational energy levels*. Just as the electrons in atoms have a number of allowed electronic energy levels, these vibrations have allowed vibrational energy levels. It is, therefore, possible to talk about 'ground-state' vibrational energy levels and 'excited-state' vibrational energy levels. A molecule can move from a lower to a higher vibrational energy level if it absorbs an amount of energy equal to the difference between levels. The region of the electromagnetic spectrum corresponding to such amounts of energy is the infrared region. All of this is affected by the type of bond. Therefore, the amount of energy required for these transitions, and therefore the frequency (or wavelength), can give clues about the types of covalent bonds present.

One of the important pieces of information needed to identify an unknown organic compound is the types of functional groups within a molecule. Infrared

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See more

Infrared
spectroscopy

spectroscopy can identify the following groups: —CH (alkyl groups), —OH (hydroxyl groups) and C=O (carbonyl groups). Infrared spectroscopy can also be used to determine if double or triple bonds are present in a molecule.

Proteomics is the study of the structures and functions of proteins. Infrared spectroscopy was used to analyse proteins in human DNA as part of the Human Genome Project. The three-dimensional shapes of protein molecules can be easily and cheaply investigated by using infrared spectroscopy to study the C—C bonds, instead of using more complicated NMR spectroscopy.



This infrared photograph of the Trifid Nebula was taken by the Spitzer Space Telescope. The nebula is 5400 light-years away from Earth in the Sagittarius constellation. Visible-light telescopes cannot see into the nebula, but infrared cameras can detect infrared radiation coming from the nebula's interior, allowing us to 'see' what's inside it.

Infrared cameras take pictures using the infrared part of the electromagnetic spectrum. The differences in infrared wavelengths between parts of an object or between objects can be used to show different colours.

A traditional infrared spectrum measures % transmittance on the y -axis and wavenumber (cm^{-1}) on the x -axis. The spectrum runs along the top of the readout when 100% of the light is transmitted and dips down to make an inverted peak when light is absorbed. Different bonds in an organic molecule have characteristic wavenumbers and produce dips or inverted peaks that allow them to be identified.

IR spectra usually change scale at $2000\text{--}4000\text{ cm}^{-1}$.

The infrared spectrum

An IR spectrum looks upside down compared with a UV-visible or AAS spectrum. This is because it measures transmittance, which is the opposite of absorbance, on the vertical or y -axis. Unlike a UV-visible spectrum, which has a base line of zero absorbance running along the base of the graph, the IR spectrum has a base line of 100% transmittance running along the top of the graph, meaning that no light has been absorbed by the sample. A peak occurs in the UV-visible spectrum when energy is absorbed, whereas a dip appears in the IR spectrum when energy is absorbed. The IR spectrum measures wavenumber, which is the inverse of wavelength, on the x -axis; wavenumber is proportional to frequency. As the wavelength increases, the wavenumber decreases. You have previously studied aspects of spectroscopy in Unit 2.

Nearly all molecules absorb IR radiation and it is largely a qualitative technique. The region above 1000 cm^{-1} can be used to identify the functional groups present. Tables exist to help identify peaks in this region and attribute them to certain types of bonds.

study on

Unit 4

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**Do more**

Interpreting IR spectra

The fingerprint region of the spectrum, below 1000 cm^{-1} , is a crowded series of peaks that can be used to identify a substance because it is identical in every analysis of that substance.

The region below 1000 cm^{-1} is caused by 'whole-molecule' vibrations. As a general rule, the more complicated this region, the larger the molecule concerned.

For historical reasons, the wavenumber axis runs backwards and changes scale at 2000 cm^{-1} . Care needs to be taken when reading spectra.

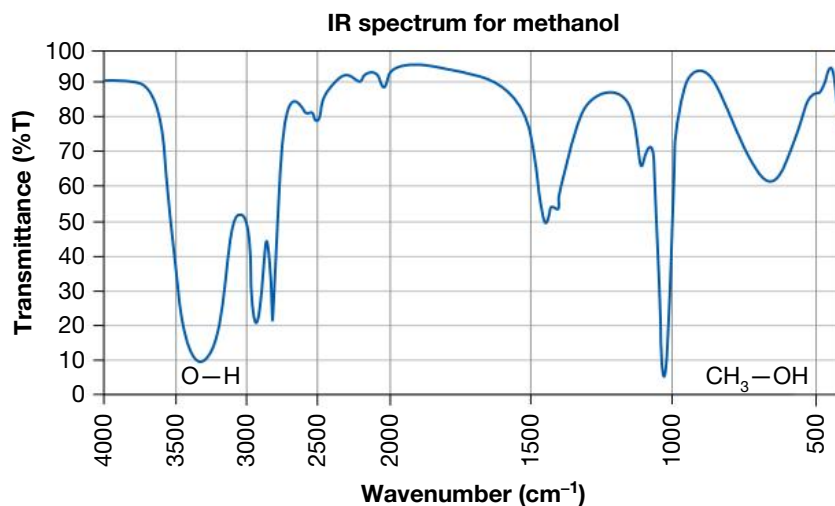
TABLE 10.2 Characteristic range for infrared absorption

Bond	Wavenumber (cm^{-1})
C—Cl	700–800
C—C	750–1100
C—O	1000–1300
C=C	1610–1680
C=O	1670–1750
O—H (acids)	2500–3300
C—H	2850–3300
O—H (alcohols)	3200–3550
N—H (primary amines)	3350–3500

Source: VCAA 2015, *VCE Chemistry Data Book*, VCAA, Melbourne, p. 7.

The IR spectrum for methanol in the graph below shows characteristic peaks at 3300 cm^{-1} for —OH and 2950 cm^{-1} for —CH. The peak at 2950 cm^{-1} , indicating a C—H bond, is almost always present in organic molecules and therefore is less helpful as it is not a characteristic identifier.

The lower end of an IR spectrum often looks like a series of peaks crowded together. This is called the **fingerprint region** of the spectrum. It is difficult to identify individual peaks caused by particular bonds, but the region is still useful in identifying the substance, as the region looks similar in any analysis of that substance.



This IR spectrum for methanol shows characteristic peaks at 3300 cm^{-1} for —OH and 2950 cm^{-1} for —CH; the —CH peak is almost always present in organic molecules and so is less helpful. Nearly every organic molecule has C—H bonds.

Differences between infrared spectra

Most organic spectra contain peaks for C—H bonds in the same area, so how do we tell the different spectra apart?

In general, the more types of atoms there are in a molecule, the more peaks appear on the IR spectrum, as these atoms affect the bonding between each other and absorb at slightly different wavenumbers.

To distinguish between alcohols and carboxylic acids, look at two peaks. Alcohols have a broad peak between 3200 and 3550 cm^{-1} but no peak near 1700 cm^{-1} . Carboxylic acids have a very broad peak between 2500 and 3300 cm^{-1} and a peak near 1700 cm^{-1} .

IR spectra for ethanol and propan-1-ol. The broad peak at $3200\text{--}3550\text{ cm}^{-1}$ in both spectra is characteristic of the —OH group in alcohols. The small peak at 1700 cm^{-1} in the spectrum for ethanol is due to a CH_3CH_2 bond; it should not be confused with the large peak at 1700 cm^{-1} for the carbonyl group (see sample problem 10.2).

Differences can be seen by comparing the spectra below for ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, and propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$. The peaks for O—H at 3300 cm^{-1} and for C—H at 2900 cm^{-1} are clear in each of the spectra. However, there are many more peaks in the $1000\text{--}1100\text{ cm}^{-1}$ region for the longer molecule than the shorter molecule. This is because the C—H bonds adjacent to other C—H bonds, as in $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, affect each other. In addition to this, the electronegative oxygen atom affects the adjacent C—H bond, slightly polarising it towards the oxygen atom. This is because the oxygen atom draws the electrons in the C—O bond towards itself, making the carbon atom take on a slightly positive charge. This positive charge attracts the electrons in the C—H bond towards the C atom, making the C—H bond slightly polar. This alters the bond length and strength, making the bonds absorb and transmit IR at slightly different frequencies, and so there are more peaks. The next C—H bond in the chain does not feel the same electrostatic attraction and so is not as affected.

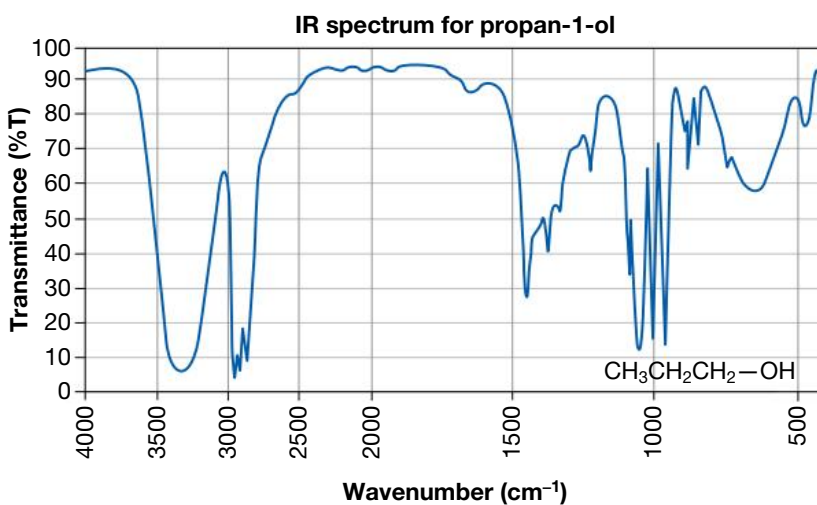
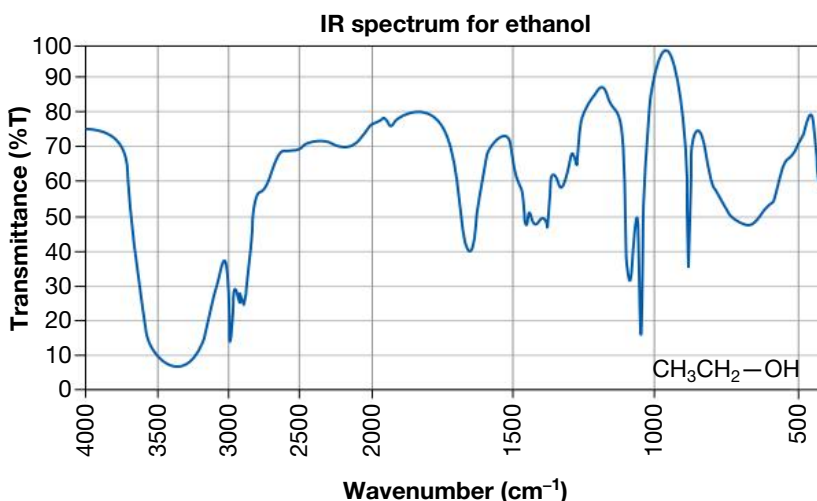
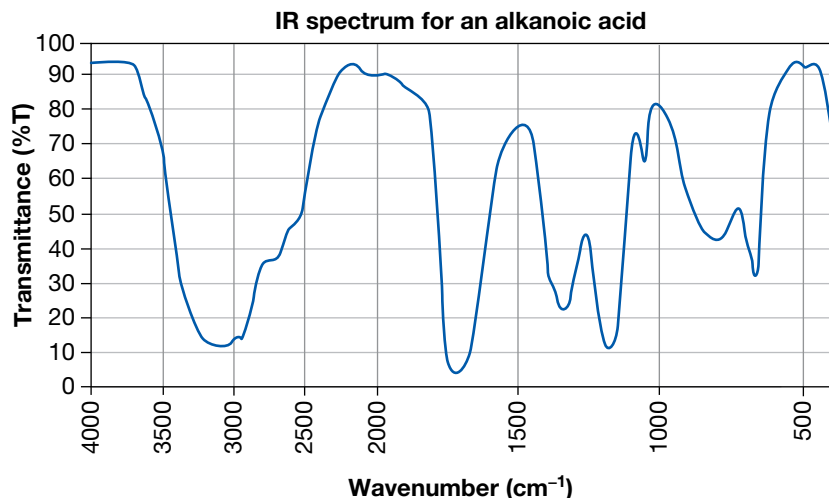


TABLE 10.3 Infrared band positions for alcohols and carboxylic acids

Functional group	—O—H (alcohols)	—O—H (carboxylic acids)	—C=O	—C—O—	—N—H
Infrared band position (cm^{-1})	3200–3550	2500–3300	1670–1750	1000–1300	3350–3500

Sample problem 10.2

Identify the major peaks in this IR spectrum for a molecule that has only one carbon atom in its molecular structure, and so identify the molecule.



Solution: The infrared spectrum shows the following peaks.

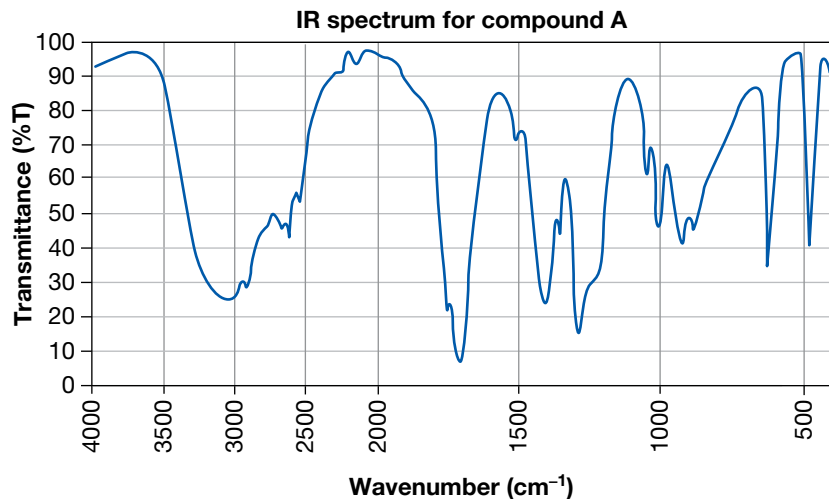
O—H peak at a range of 2500–3300 cm^{-1}

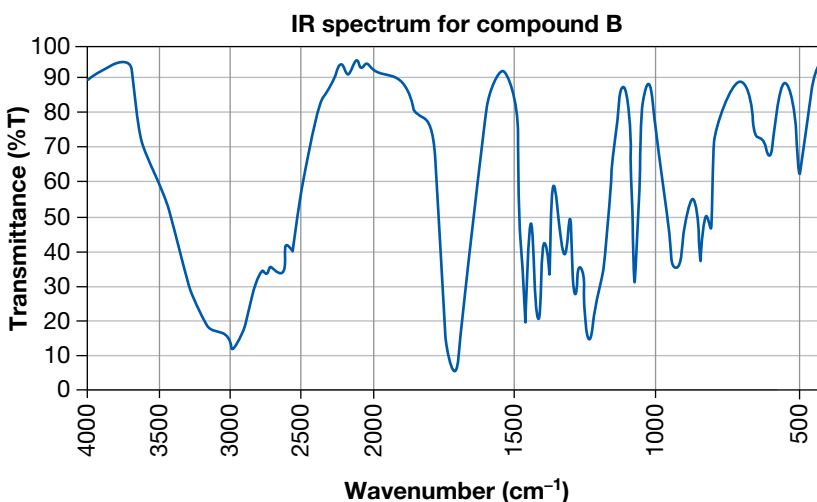
C=O peak at a range of 1600–1750 cm^{-1}

Since there is only one carbon atom, the oxygen atom must be double-bonded to it, so we have C=O. Adding the O—H gives us —COOH but leaves C with one unbonded electron, which could bond to an H since there are no other carbon atoms present. The C—H peak at 2950 cm^{-1} is mostly hidden by the broad O—H peak. The structure could be methanoic acid, HCOOH. For more complicated molecules, further testing to determine the molecular mass, using mass spectrometry, for example, must be carried out to determine the exact structure.

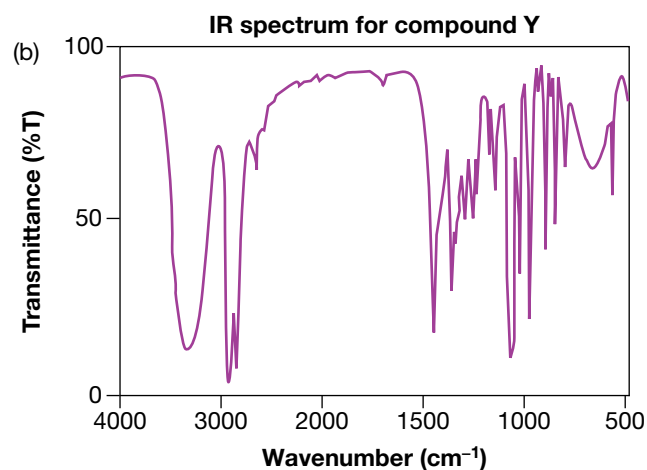
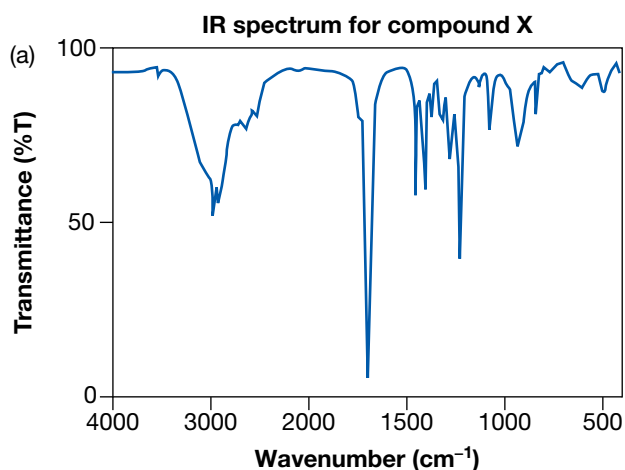
Revision questions

4. Examine the IR spectra below and on the top of the next page.





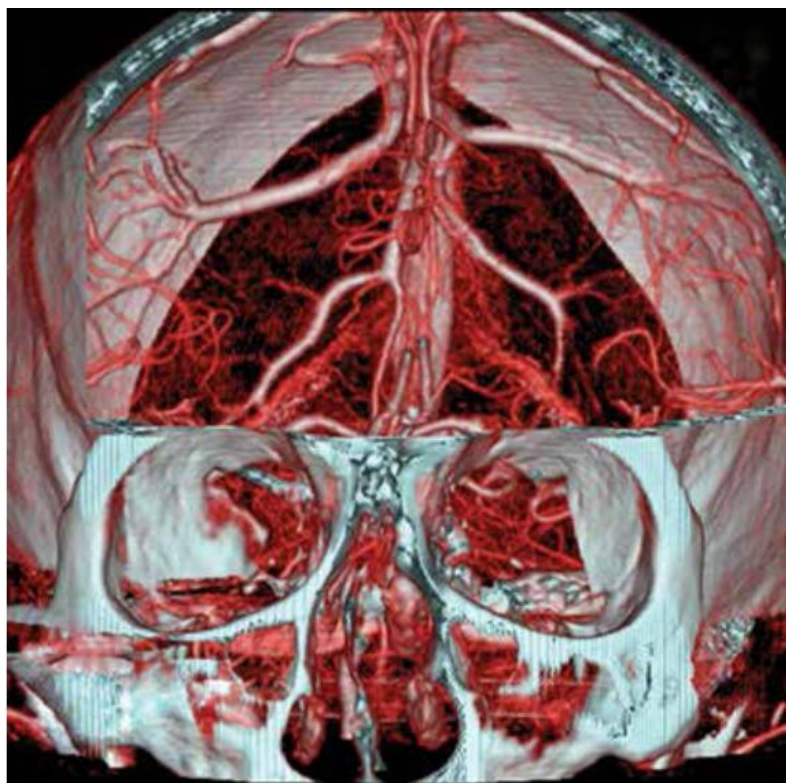
- (a) Using table 10.2 (page 280), identify the bonds responsible for the major peaks on each spectrum.
 - (b) By examining the peaks, determine which spectrum has the most C—H bonds.
 - (c) Both substances were examined by mass spectrometry. The results confirmed that both of the molecules contained only carbon, hydrogen and oxygen. The molecular masses of the molecules were 60 and 74. Determine the possible molecular formulas of the two substances. Hence deduce one possible molecular structure for each of the substances.
5. The following figure shows two infrared spectra for two different compounds, X and Y. Only one is a carboxylic acid; the other is an alcohol. Use table 10.2 on page 280 to identify the spectrum corresponding to a carboxylic acid.



Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) images are often used in medical diagnosis. In medicine, they are called MRI scans (magnetic resonance image scans).

Nuclear magnetic resonance (NMR) images are called MRI scans in the medical field. (MRI stands for magnetic resonance imaging.) These colourful images provide doctors with pictures of the soft tissues of the body. When NMR was introduced, many patients refused to have NMR scans because they thought it had something to do with being bombarded with radiation from a nuclear reactor. However, the word 'nuclear' in this case refers to nucleus of



A magnetic resonance imaging scan showing the blood vessels in the brain

Nuclei with odd total numbers of protons and neutrons (nucleons) have two spin states and can act like magnets.

an atom and how it interacts with a magnetic field. To alleviate patients' fears, NMR scanning is now called MRI.

Particles making up a nucleus exhibit properties called 'spin' and 'magnetic moment'. The combination of particular numbers of protons and neutrons give each nucleus an overall spin and magnetic moment, which responds to an applied magnetic field. NMR measures this response to give an indication of the connectivity of atoms in a molecule. It does this by recording the interaction of C and H nuclei with a magnetic field. NMR is a qualitative analysis method.

Some nuclei have two overall spin states and behave as if they are magnets spinning about their axes. ^1H and ^{13}C are two such nuclei. If a strong, external magnetic field is applied to such nuclei, these spinning magnets either align with the external field (to produce a slightly lower energy level) or align against it (to produce a slightly higher energy level). By absorbing the exact difference in energy between these two states, a nucleus can 'flip' between its lower and higher spin states. It then releases this same amount of

energy when it 'relaxes' back to its lower state. The energy involved in these changes is in the radio frequency section of the electromagnetic spectrum. The energy difference between these two spin states depends on the strength of the external magnetic field that is 'felt' by the nucleus. This is not always the same as the external magnetic field because other atoms that surround a given nucleus can modify it in subtle, but important, ways. Therefore, *the energy required for a nucleus to change its spin state depends on what is around it (its environment)*. The use of NMR can therefore give valuable information about the connectivity of atoms in a molecule.

Common types of NMR spectra

The three main types of NMR spectra are:

- carbon-13 NMR (^{13}C)
- low-resolution proton NMR (^1H)
- high-resolution proton NMR (^1H).

All of these produce spectra that consist of a series of peaks. The horizontal scale is called 'chemical shift' (δ) and reads backwards. For technical and instrumental reasons, a zero reference point is always included. This is obtained by adding a small amount of tetramethylsilane (TMS), $(\text{CH}_3)_4\text{Si}$, to each sample.

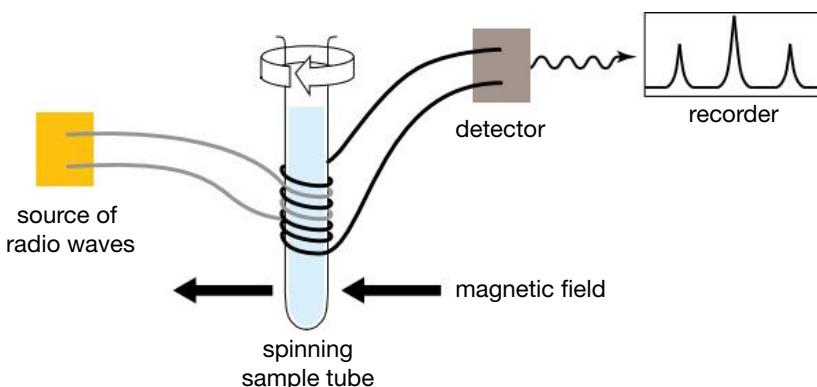
Interpreting NMR spectra

NMR is a qualitative method that gives valuable information about the arrangements of atoms in a molecule. Analysis of an NMR spectrum involves consideration of the following features:

- the number of signals (or peak sets)
- the chemical shift of each signal (or peak set)
- the relative area under each signal (or peak set)
- the splitting of signals into a set or cluster of peaks (for high-resolution proton NMR).

More particularly:

- the number of signals (or peak sets) gives information about the number of unique environments (^1H and ^{13}C)
- the chemical shift gives information about the functional groups involved
- the relative signal or peak areas give information about the number of atoms responsible (^1H)
- in high-resolution proton NMR, peak splitting gives information about the number of hydrogen atoms on adjacent carbon atoms.



A schematic diagram of an NMR spectrometer

Uses of NMR include analysis of products, organic synthesis, quality control of medicines, forensic analysis of proteins, and identification of oil and gas deposits.

NMR is used extensively in organic synthesis. For example, in pharmaceutical manufacturing, NMR is used for quality control of medicines. It ensures that the drug molecule has been made with the correct atom-atom linkages and hence has the desired properties. Other uses are for studying DNA, RNA and similar proteins in forensic analysis, as the technique is not destructive; samples can be studied for weeks. NMR is also used in the petrochemical industry to identify oil and gas deposits, and other features of the rock sample in which deposits are contained. Although the scans seen in medical MRIs are like slices through the body that build up into a three-dimensional picture, simpler scans are effective when analysing most molecules.

Chemical shift

An NMR spectrum is a two-dimensional graph of peak height versus chemical shift, δ (in ppm).

The two particles most commonly used in NMR analysis are carbon-13 atoms, ^{13}C , and protons, ^1H . Other atoms within an organic molecule can be analysed, but examining the environments of the carbon atoms and protons reveals valuable information about the structure of the molecule under investigation.

The electrons around a particular carbon atom or proton partially block the external magnetic field, and thus change the energy gap between the aligned and anti-aligned nuclear spin states. This effect is very small, which is why the horizontal scale is measured in ppm.

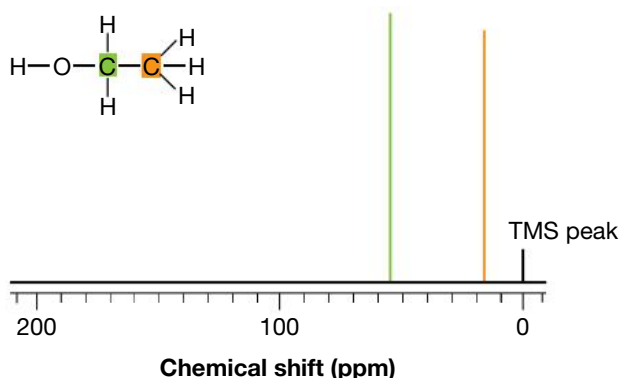
An NMR spectrum is a two-dimensional graph of peak height versus chemical shift, δ (in ppm). The number of signals on the x-axis of the graph indicates the number of types of protons or carbons. The chemical shift or position of the peaks on the x-axis of the graph indicates the types of protons or carbons. The NMR graph starts from zero on the right and reads backwards. The zero reference point is taken from the chemical shift peak produced by tetramethylsilane, $(\text{CH}_3)_4\text{Si}$ or TMS, which is added to every sample; without this zero point, it would be impossible to know where to start the horizontal scale.

Different functional groups are found at different characteristic chemical shifts on the NMR spectrum. Comparison with a table of the chemical shifts enables identification of the group. Either carbon or hydrogen may be the subject of the NMR scan, and each set of data lends different information to the analysis. Depending on the solvent used in the analysis, a signal may also be found for the carbon or hydrogen atoms in that solvent.

Note that the following NMR spectra are called low-resolution NMR spectra. The difference between high- and low-resolution proton NMR spectra is discussed on page 290.

Identifying groups using ^{13}C analysis

This type of NMR analyses the ^{13}C atoms in molecules. It gives us information about the different chemical environments around each carbon atom.



The ^{13}C NMR spectrum for ethanol has two peaks that reflect the different environments of the two carbon atoms in the $\text{CH}_3\text{CH}_2\text{OH}$ molecule.

The ^{13}C NMR spectrum for ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, above has two signals that correspond to the two different carbon atoms in the molecule. One carbon atom is bonded to hydrogen atoms only; the other is bonded to hydrogen and oxygen atoms. Oxygen is much more electronegative than hydrogen, which affects the bonding. This has a small but significant effect on the resonance that the protons in the carbon nuclei produce in the NMR instrument. The difference in resonance can be measured as a difference in chemical shift for the two carbon atoms. The chemical shifts in ^{13}C NMR are measured on a scale from 0–250 ppm.

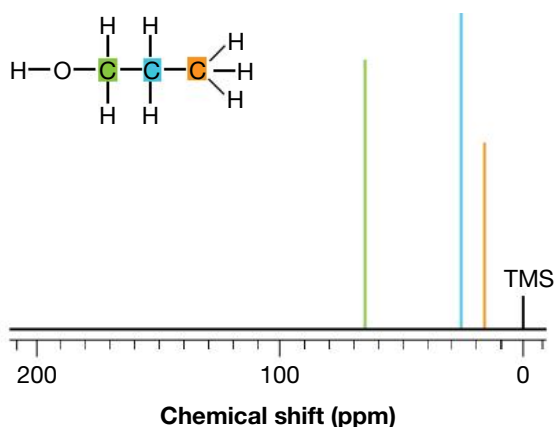
TABLE 10.4 ^{13}C NMR data

Type of carbon	Chemical shift (ppm)
$\text{R}-\text{CH}_3$	8–25
$\text{R}-\text{CH}_2-\text{R}$	20–45
R_3-CH	40–60
R_4-C	36–45
$\text{R}-\text{CH}_2-\text{X}$	15–80
$\text{R}_3\text{C}-\text{NH}_2$	35–70
$\text{R}-\text{CH}_2-\text{OH}$	50–90
$\text{RC}\equiv\text{CR}$	75–95
$\text{R}_2\text{C}=\text{CR}_2$	110–150
RCOOH	160–185

Source: VCAA 2015, *VCE Chemistry Data Book*, VCAA, Melbourne, p. 7.

Chemical shifts in ^{13}C NMR correspond to a carbon atom in a particular environment within a molecule.

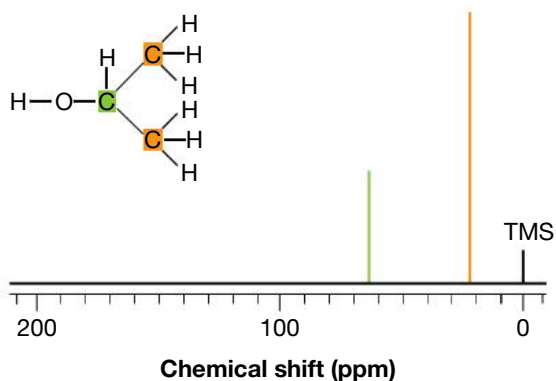
The NMR spectrum of propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, at the top of the next page shows three signals. The three carbon atoms in propan-1-ol are in three different chemical environments, so they produce three separate signals. The first signal at 10 ppm corresponds to the $\text{R}-\text{CH}_3$ group, the second signal at 20–30 ppm corresponds to R_2CH_2 , and the third signal at 65 ppm corresponds to the alcohol group, $\text{C}-\text{OH}$.



The three signals in this NMR spectrum reflect the three different chemical environments of the three C atoms in propan-1-ol.

Although propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, also has three carbon atoms, the two signals on this NMR reflect the two different chemical environments of the three C atoms in this molecule. The central carbon atom is bonded to the oxygen atom, while the two carbon atoms either side of it are in an equivalent chemical environment.

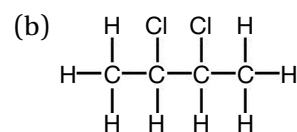
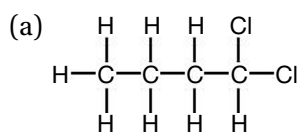
The low abundance of ^{13}C nuclei means that there is no statistical link between the signal intensity and the number of ^{13}C nuclei in a particular chemical environment. Hence, there is no significance attached to the signal heights in ^{13}C NMR.



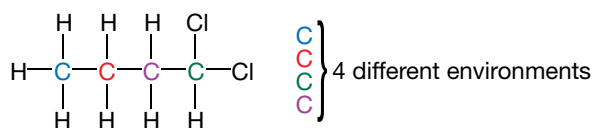
Although propan-2-ol has three carbon atoms, two of the carbon atoms in the methyl groups are identical. Imagine a three-dimensional model of this molecule; clearly the methyl groups are the same. The two signals on this NMR reflect the two different chemical environments of the three carbon atoms in the molecule.

Sample problem 10.3

How many different environments for the carbon atoms are there in each of the following isomers of $\text{C}_4\text{H}_8\text{Cl}_2$?

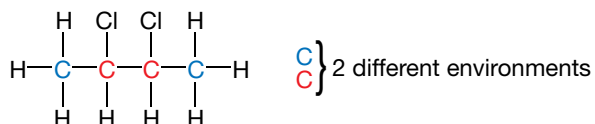


Solution: (a)



1,1 dichlorobutane contains carbon atoms in four non-equivalent environments.

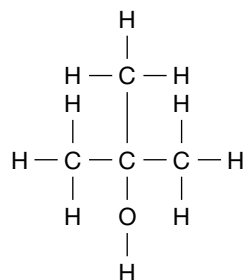
(b)



2,3 dichlorobutane contains carbon atoms in two non-equivalent environments.

Revision questions

- The molecule C₄H₁₀ has two isomers. Sketch the isomers and examine the chemical environment of each carbon atom. Decide how many signals each isomer would produce in a ¹³C NMR spectrum.
- Draw the structural formulas of the two isomers of bromopropane, and explain how ¹³C NMR spectrometry could be used to identify each.
- How many different carbon environments are present in the compound 2-methylpropan-2-ol?



¹H is different from ¹³C NMR in that the height of the signal is significant and the horizontal scale is different.

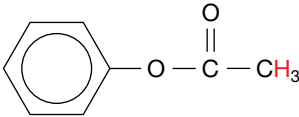
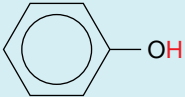
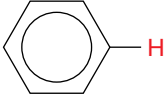
Identifying groups using proton analysis

The other element that is commonly used in NMR analysis is hydrogen, in the form of protons, ¹H. ¹H NMR analysis considers the different environments that each hydrogen atom experiences in a molecule. The *x*-axis scale for ¹H NMR has a scale of 0–13 ppm, whereas the scale for ¹³C NMR has a scale of 0–250 ppm. This is a measure of how different nuclei in various bonding environments respond to an external magnetic field.

In ¹H NMR, the signal intensity (height) is statistically linked to the number of atoms for that signal. This is similar to the calibration graphs in other instrumental methods such as gas chromatography, HPLC, colorimetry, UV-visible spectroscopy and atomic absorption spectroscopy. An integral trace provides the relative area under each signal in ¹H spectra and indicates how many hydrogen atoms contribute to that signal. It is often indicated by a numeral written at the top of the integration curve (peak); for example, (3) indicates three H atoms.

The bonding electrons of each atom in a molecule experience a small but significant effect caused by the other atoms around them. A highly electronegative element, such as a halogen, affects the electrons of neighbouring atoms by slightly attracting their electrons towards it. An oxygen atom in an alcohol group not only affects the hydrogen atom bonded to it, but also affects the hydrogen atom bonded to the adjoining carbon atom. The distribution of electrons affects the magnetic field around each nucleus, enabling slight changes in electron distribution to be measured by NMR.

TABLE 10.5 Chemical shifts for proton analysis

Type of proton	Chemical shift (ppm)
$R-\text{CH}_3$	0.8–1.0
$R-\text{CH}_2-R$	1.2–1.4
$R\text{CH}=\text{CH}-\text{CH}_3$	1.6–1.9
$R_3-\text{CH}$	1.4–1.7
$\text{CH}_3-\text{C}(=\text{O})\text{OR}$ or $\text{CH}_3-\text{C}(=\text{O})\text{NHR}$	2.0
$\text{R}-\text{C}(=\text{O})\text{CH}_3$	2.1–2.7
$R-\text{CH}_2-X$ ($X = \text{F}, \text{Cl}, \text{Br}$ or I)	3.0–4.5
$R-\text{CH}_2-\text{OH}$, $R_2-\text{CH}-\text{OH}$	3.3–4.5
$\text{R}-\text{C}(=\text{O})\text{NHCH}_2\text{R}$	3.2
$R-\text{O}-\text{CH}_3$ or $R-\text{O}-\text{CH}_2\text{R}$	3.3
	2.3
$\text{R}-\text{C}(=\text{O})\text{OCH}_2\text{R}$	4.1
$R-\text{O}-\text{H}$	1–6 (varies considerably under different conditions)
$R-\text{NH}_2$	1–5
$\text{RHC}=\text{CH}_2$	4.6–6.0
	7.0
	7.3
$\text{R}-\text{C}(=\text{O})\text{NHCH}_2\text{R}$	8.1
$\text{R}-\text{C}(=\text{O})\text{H}$	9–10
$\text{R}-\text{C}(=\text{O})\text{O}-\text{H}$	9–13

Source: VCAA 2015, VCE Chemistry Data Book, VCAA, Melbourne, pp. 5–6.

Sample problem 10.4

How many signals or sets of peaks for the hydrogen atoms would be expected on a proton NMR of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$? List where these signals would occur.

Solution: There should be three signals or sets of peaks: one signal for the CH_3 group at $\delta = 0.9$ ppm, one signal or set of peaks for the CH_2 at δ between 1.2 and 1.4 ppm, and one signal or set of peaks for OH at δ between 1 and 6 ppm.

Revision questions

9. Using table 10.5, sketch the proton NMR of propane, $\text{CH}_3\text{CH}_2\text{CH}_3$.
10. How many peaks for hydrogen atoms would be expected for a proton NMR of propyl ethanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$?

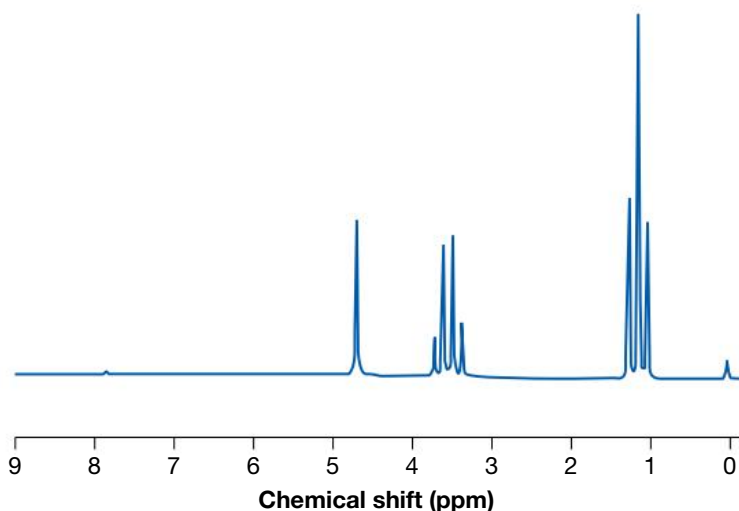
Low- and high-resolution ^1H NMR spectra

The NMR spectrum of ethanol below has its three signals split into three groups of peaks. This is a high-resolution spectrum.

There are two different types of NMR spectrum: high resolution and low resolution. A low-resolution spectrum shows the unique types of environments of the hydrogen atom in the molecule; the ratio of the areas under the peaks shows the number of hydrogen atoms in that environment, and the chemical shift tells you important information about the type of bond involved. A high-resolution spectrum contains the same information as the low-resolution spectrum, but each signal in the low-resolution spectrum appears to have been split into several peaks. The number of peaks in the high-resolution spectrum tells you about the number of hydrogen atoms next to the hydrogen atom that has produced that signal. For simple molecules, the number of peaks is one more than the number of hydrogen atoms on the carbon atom next to that hydrogen atom and chemically different from that hydrogen atom.

In the high-resolution spectrum of ethanol below, the signal of three peaks indicates that there are two hydrogen atoms attached to the carbon atom next in line in the molecule under investigation. This splitting of peaks is due to spin coupling, as discussed in the following section.

Proton NMR spectrum of ethanol



High-resolution ^1H NMR spectrum of ethanol. The $\text{R}-\text{CH}_3$ signal (0.9 ppm) is split into three peaks; this means there is an adjacent CH_2 group.

A signal in a low-resolution spectrum can be split into a set of peaks in the high-resolution spectrum. The number of peaks in the high-resolution spectrum tells you about the number of hydrogen atoms next to the hydrogen atom that has produced that signal. For simple molecules, the number of peaks is one more than the number of hydrogen atoms on the carbon atom adjacent to that hydrogen atom ($n + 1$ rule).

study on

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See more
High-resolution
proton NMR

For the high-resolution NMR spectrum of ethanol, even though the —OH and —CH₂ groups are separated by four bonds, under most conditions the —OH signal does not show splitting, for chemical reasons that are beyond this VCE course.

How nuclei affect each other: coupling

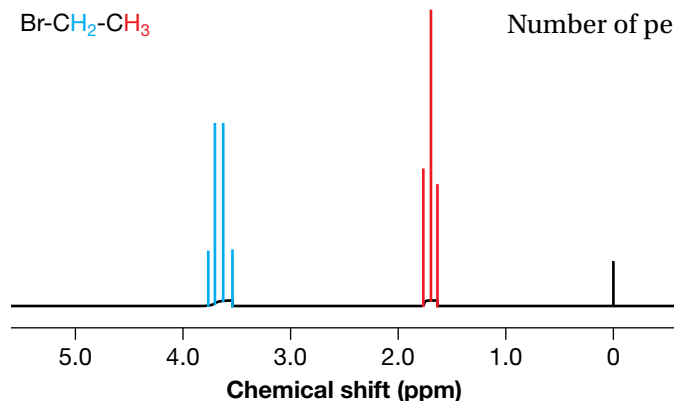
¹H nuclei can interact with other ¹H nuclei near them. If the neighbours are chemically different, that interaction splits the NMR signal into a number of peaks. For example, each proton in ethane, CH₃CH₃, has three neighbouring protons on the adjacent CH₃ group, but there is no splitting of the NMR signal since neighbours are chemically equivalent to the first set of protons.

Consider the CH₃ NMR signal in the 2-methylpropane, CH₃CH(CH₃)₂, spectrum. Each CH₃ proton has the same one proton neighbour on the adjacent central carbon atom. The CH₃ signal is split into two peaks, with height ratio 1 : 1. The CH signal is split into a large number of peaks because there are 9 neighbouring CH₃ protons. This is called the *n* + 1 rule:

$$\text{Number of peaks} = (\text{number of neighbouring protons}) + 1$$

For the molecule CH₃CH₂Br, bromoethane, let us look at the signal for the CH₃ group at 1.7 ppm. The next group is CH₂, which has two protons. This creates three peaks within the CH₃ signal on the NMR spectrum, with height ratio 1 : 2 : 1.

In the same molecule, CH₃CH₂Br, bromoethane, we can also look at the signal for the CH₂ group at 3.4 ppm. The next group is a methyl group, —CH₃, which has three protons. This creates four peaks within the CH₂ signal on the NMR spectrum, with height ratio 1 : 3 : 3 : 1.



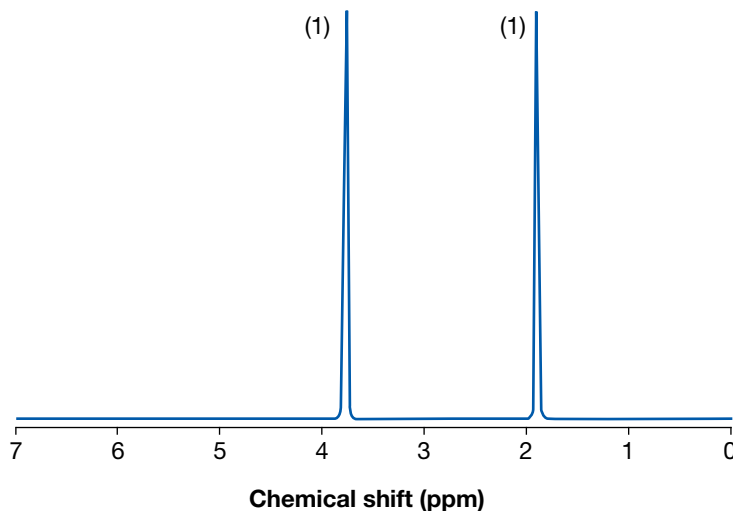
¹H nuclei can interact with other ¹H nuclei near them, and the effect can be measured by the number of peaks in the NMR spectrum.

Revision question

- 11.** Consider the signal or peak cluster near 3.5 ppm on the ethanol NMR spectrum on page 290. Explain why this is a set of four peaks.

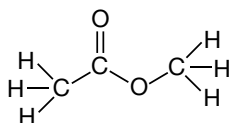
Sample problem 10.5

Analyse the proton NMR spectrum below and use table 10.5 to identify the structure of the molecule. The empirical formula for the molecule is C₃H₆O₂. Mass spectrometry reveals that the molecular mass of the molecule is 74.



Solution: Since the molecular mass of the molecule is 74 and $M(\text{C}_3\text{H}_6\text{O}_2)$ is 74, the empirical formula must also be the molecular formula.

The integration trace of the NMR shows the relative areas are 1 and 1. This means the six hydrogen atoms must be in two groups, CH_3 and CH_3 . But since there are two peaks, we know these groups are in different environments. The signals are not split into triplets or quartets, which indicates that the groups are not next to each other. The chemical shift $\delta = 1.95$ indicates that the CH_3 group is next to a slightly electronegative group, such as a carboxyl group. This could mean a $\text{CH}_3\text{COO}-$ structure.

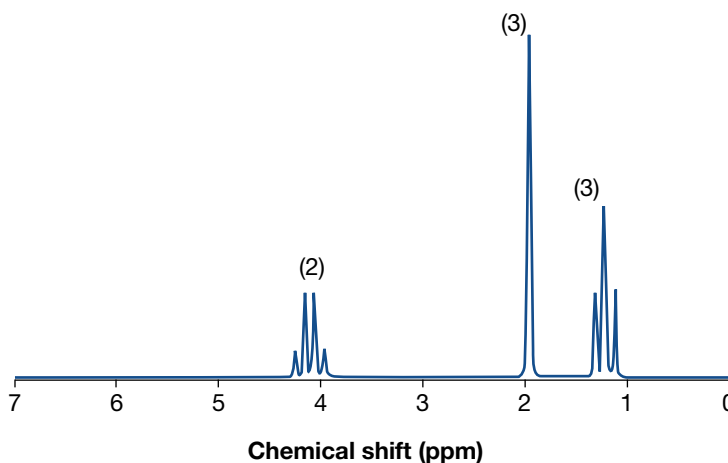


The other peak at $\delta = 3.9$ indicates that the CH_3 group is next to a strongly electronegative group, i.e. the oxygen atom. This could mean a $\text{CH}_3-\text{O}-$ structure.

Putting this information together indicates that the structure (shown at left) is methyl ethanoate.

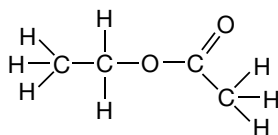
Sample problem 10.6

Analyse the proton NMR spectrum below and use table 10.5 to identify the structure of the molecule. The molecular formula for the molecule is $\text{C}_4\text{H}_8\text{O}_2$.



Solution: The triplet at $\delta = 1.2$ indicates a simple alkyl group, and the integration curve (3) shows that there are 3 hydrogen atoms present; therefore, this is a CH_3 group. The fact that it is a triplet, following the $n + 1$ rule, indicates that it is next to a CH_2 group.

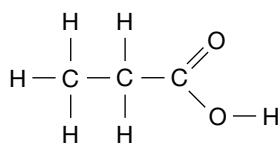
The single peak at $\delta = 2.0$ indicates a CH_3 group; this chemical shift indicates that it is next to an electronegative group, possibly a carboxyl group. The fact that the signal is not split into a series of peaks implies that there are no hydrogen atoms on the next group.



The quartet at $\delta = 4.1$ shows that this CH_2 is next to a CH_3 group and next to an oxygen atom. Therefore, the structure is ethyl ethanoate.

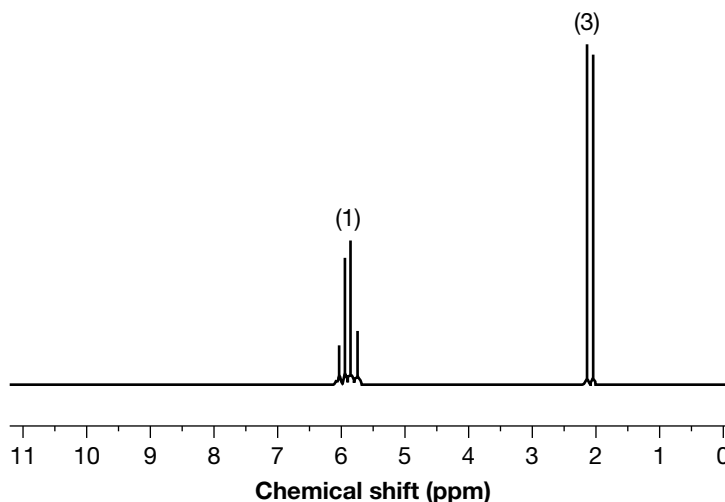
Revision questions

12. Propanoic acid (shown at left) is used as a preservative and anti-mould agent for animal feed and also in packaged food for human consumption. Complete the table on the next page showing each hydrogen environment, splitting patterns, relative peak height and the chemical shifts for each type of hydrogen atom in this molecule.



Hydrogen set or atom	Splitting pattern	Relative peak height	Chemical shift (ppm)
CH ₃			

13. Draw the structures of the isomers represented by the formula C₂H₄Cl₂. Explain which isomer has the following proton NMR spectrum.



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Experiment 10.1 Separation of food dyes using chromatography

doc-18823

Chromatography

The analysis techniques described so far have been useful in finding what is in the sample. You may remember other techniques from Unit 2 that allow us to also find the concentration of the substance that is present; these include chromatography and volumetric analysis.

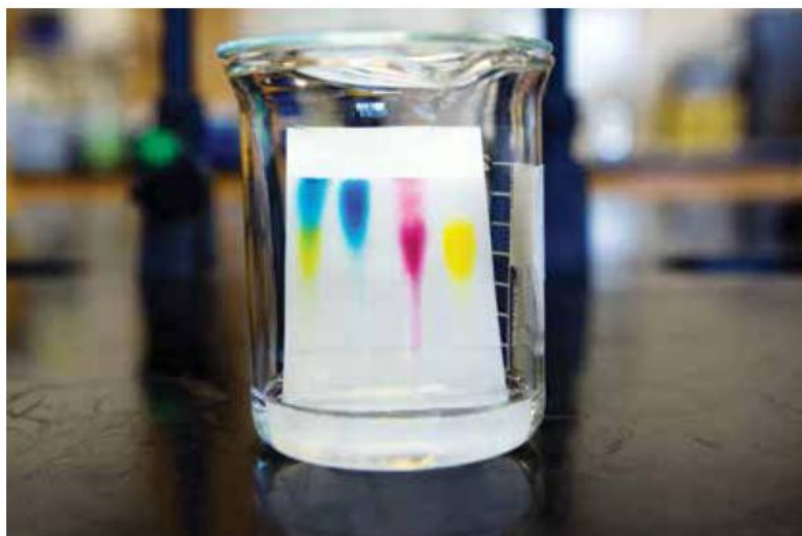
High-performance liquid chromatography, **HPLC**, can be used to separate components of a mixture, and then structural information about the components can be obtained by analysis using NMR or mass spectra. HPLC can be used to separate and also identify and quantify each component in any sample that can be dissolved in a liquid. It is extremely sensitive and a valuable tool in a wide variety of fields.

Principles of chromatography

In all forms of chromatography, a **mobile phase** passes over a **stationary phase**. The stationary phase is either a solid with a high surface area, or a finely divided solid coated with liquid. The mobile phase moves over or through the stationary phase and carries the mixture to be separated with it.

As the mixture being analysed is swept along in the mobile phase, some of its components 'stick' more strongly to the surface of the stationary solid phase than others. They then 'unstick' and move on. Therefore the components travel at different speeds, and so they separate.

Chromatography can be very simple (as in paper chromatography and thin-layer chromatography (TLC)) or very sophisticated (as in high-performance liquid chromatography (HPLC) and gas chromatography (GC)). In paper



Thin-layer chromatography — the red and yellow dyes are more strongly attracted to the stationary phase than the blue dye as they have not travelled as far up the paper (stationary phase).

In high-performance liquid chromatography (HPLC), a liquid (eluent) is pumped at high pressure through a column that is packed with a finely divided solid. Many organic substances can be separated, identified and quantified using this method.

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Experiment 10.2 Separating mixtures using column chromatography
doc-18824

A high-performance liquid chromatography instrument

chromatography, the stationary phase is made up of cellulose fibres that are naturally coated with a thin layer of water. In thin-layer chromatography, a finely divided adsorbent material is coated onto either a glass slide or aluminium foil to form this phase. Liquids for the mobile phase can be any of a wide range of mixtures of solvents (including water). If you have ever seen ink separating into coloured bands as it rises up filter paper or chalk, you have witnessed chromatography.

The nature of the interactions that occur between the stationary and mobile phases can vary. However, a common interaction involves the processes of **adsorption** and **desorption**. The components of the sample adhere to the material in the stationary

phase to differing extents. These interactions are then broken in the desorption process, allowing the substances to move on. The stronger these interactions, the slower a substance moves.

High-performance liquid chromatography (HPLC)

You may recall from Unit 2 that HPLC is an adaption of the simple methods described previously. Invented in the early 1960s, advances in technology have developed this into an extremely sensitive and widely used technique. Detection of concentrations in parts per million and parts per billion levels is routine. Advanced instruments are now capable of detecting parts per trillion! Applications of HPLC include research, medicine, pharmaceutical science, forensic analysis, food analysis, drug detection in sport and environmental monitoring.

In HPLC, the most common stationary phase is a narrow diameter tube, called a column, that is packed tightly with a finely divided powder. This provides the large surface area required for the process. Particle sizes in the range of a few micrometres are typically used, although these are now becoming even smaller and, when coupled with the higher pressure pumps now becoming available, are leading to what is being called ultra-performance liquid chromatography (UPLC).



Columns containing a wide range of powders are available and can be chosen to give optimal results for a particular scenario. Columns packed with finely divided alumina or silica are common examples. Likewise, a wide range of liquids that can be pumped through the column are available. The particular liquid chosen for this purpose is called the **eluent** and can be either a pure liquid or a mixture of liquids.

Separation by HPLC occurs due to interactions between the substances in the mobile phase and the stationary phase. The weaker these interactions with the stationary phase, the faster a substance moves through the column.

study on

Unit 4

AOS 1

Topic 5

Concept 2



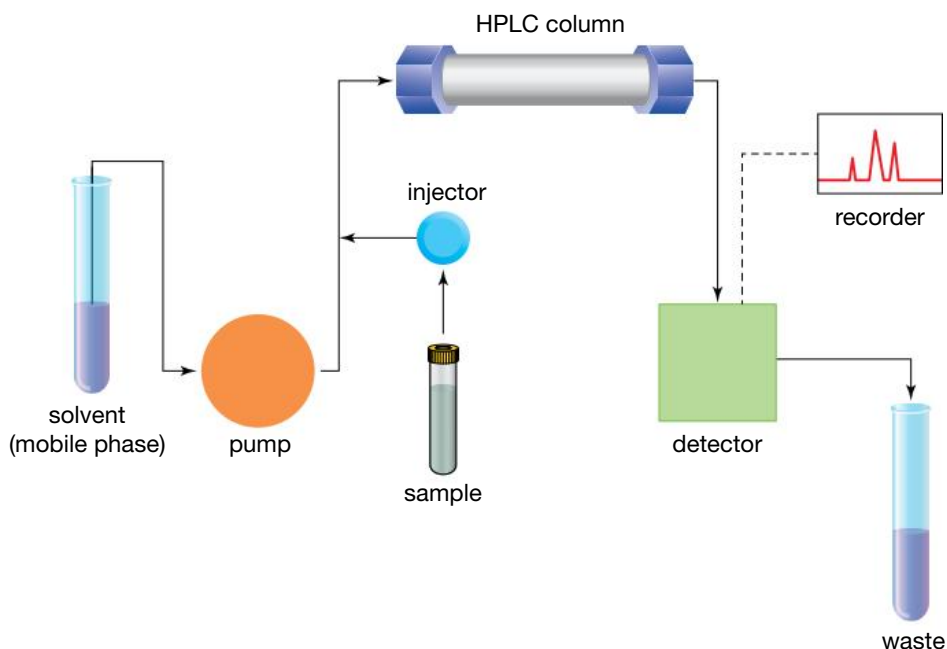
See more

High-performance liquid chromatography (HPLC)

A schematic diagram of a high-performance liquid chromatography instrument

In operation, the substance to be analysed (called the **sample**) is injected onto the start of the column as a liquid. The eluent is then pumped through the column, taking the sample with it. As the mobile phase moves through the column, the process of adsorption and desorption results in the components of the sample (referred to as **analytes**) moving at different speeds and thus being separated from each other.

After passing through the column, the components in the sample exit the column and are detected by a suitable device. This is then recorded on a chart as a series of peaks (this chart is called a **chromatogram**). In many modern instruments, a computer can also present this information in tabular form, showing the **retention time** and area of each peak. The data can then be fed into programs for graph drawing or for further mathematical evaluation.



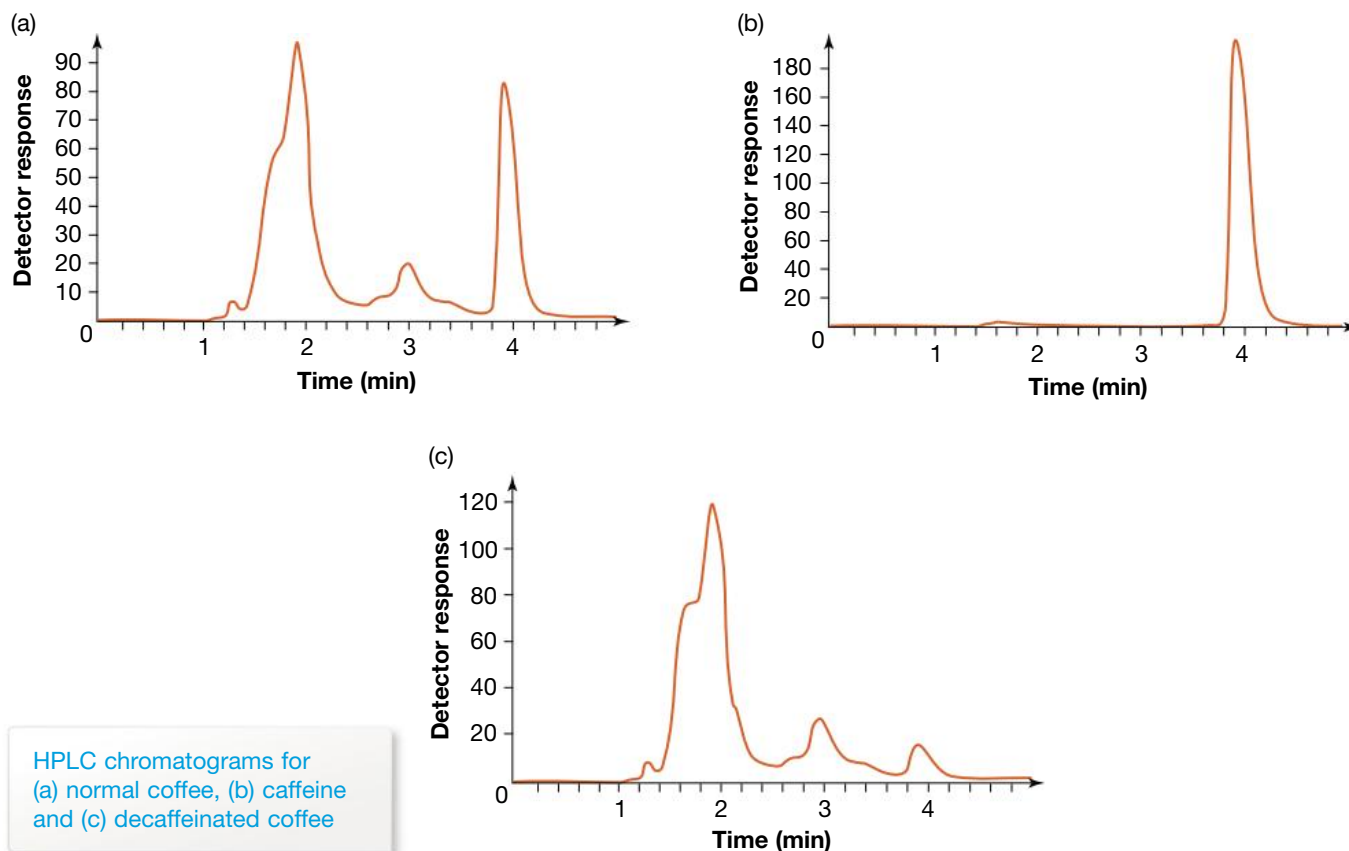
Two important features of a chromatogram are:

1. *the positions of its peaks.* The time taken for each component of the sample to travel from the injection port to the end of the column where it is detected is referred to as its retention time, t_R . This corresponds to the position of the peak on the chromatogram. Retention time can be used to identify a component — the retention time for an unknown substance is compared with retention times for known substances under the same operating conditions.
2. *the area underneath each peak.* The greater the amount of a component, the greater the area under the corresponding peak. This measurement can therefore be used to quantitatively measure a substance. The quantitative use of HPLC is discussed later in this chapter. It should be noted that, when the peaks produced are narrow, the area measurement can be replaced by a measurement of the peak height.

Shown on the next page are some results obtained from testing a brand of decaffeinated coffee. Note that a caffeine standard has been run through the instrument so that the potential caffeine peak on the chromatogram of the sample can be identified. Therefore, the reduction in the height of the peak due to caffeine becomes obvious when normal and decaffeinated coffee results are compared.

For a quantitative measurement of the amount of caffeine remaining in the sample, the height (or the area under the peak) could be measured and

compared with a set of caffeine standards of known concentrations. Quantitative use is discussed in more detail in the next section.



HPLC chromatograms for (a) normal coffee, (b) caffeine and (c) decaffeinated coffee

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HPLC

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Unit 4

AOS 1

Topic 5

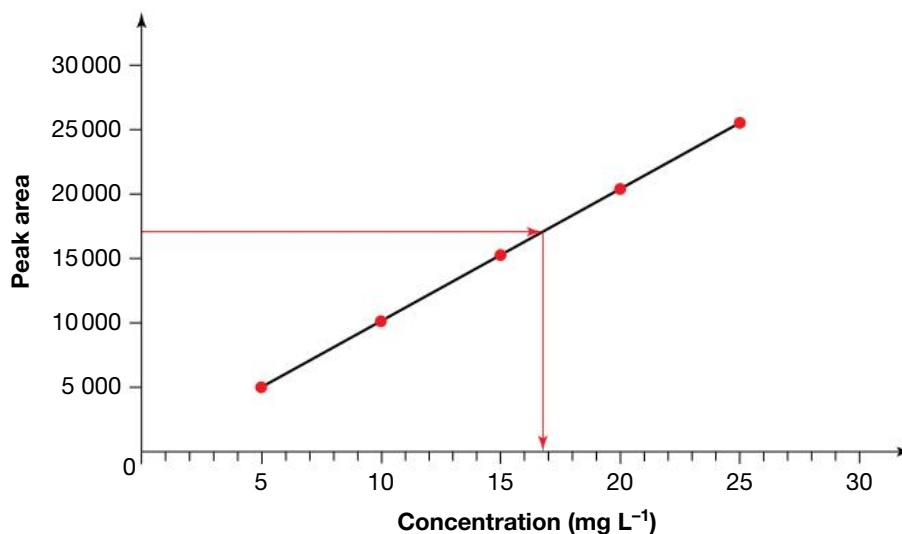
Concept 3

See more
Calibration curves

Using the calibration curve, the concentration of the unknown sample (shown by the red arrow) can be estimated as 16.8 mg L^{-1} .

Quantitative analysis using HPLC

Instruments must be accurately **calibrated**, using a set of standards, before any meaningful quantitative results can be obtained. This involves running a set of standards of *known concentration* through the instrument and noting the readings (usually either peak height or peak area). From these results, a graph of reading versus concentration can be drawn. It is then a matter of running the sample to be tested through the instrument and noting the reading. The calibration graph can then be used to obtain its concentration.



The position of a peak, also called its retention time, can be used to identify a substance. The area underneath a peak is related to the amount of the component present.

Most modern instruments are programmed to do this automatically. They use statistical algorithms to determine the *equation of the line of best fit* using the calibration data. The test result for the unknown is then simply fed into this equation and the result displayed.

Types of HPLC

High-performance liquid chromatography is often categorised according to the nature of stationary and mobile phases used. The two most common types are:

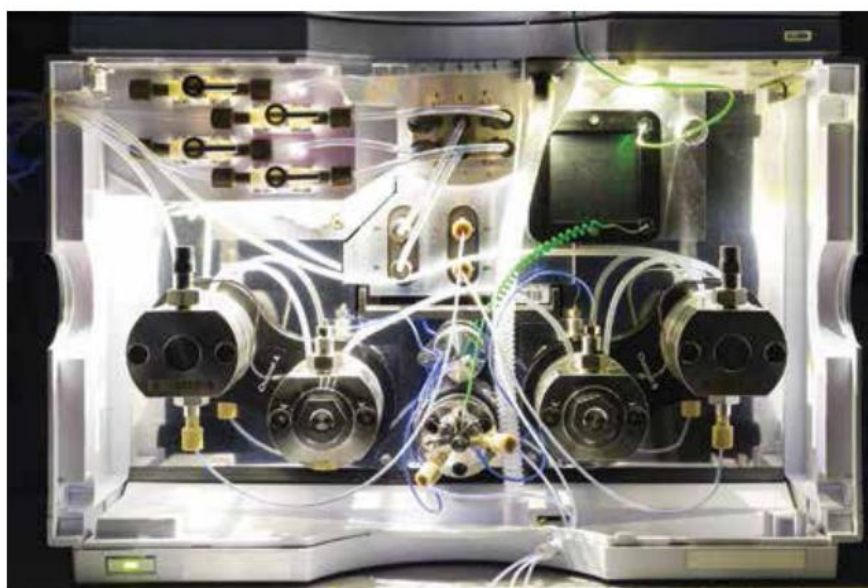
1. Normal-phase liquid chromatography (NPLC). Here, the material in the column is more polar than the mobile phase. Because of this, the more polar components in the sample adsorb more strongly to the column material and move more slowly through the column. Therefore, they have a longer retention time.
2. Reverse-phase liquid chromatography (RPLC). This is the opposite of NPLC, where the material inside the column is less polar than the liquid being pumped through it. The columns used often contain silica particles that have been coated with long hydrocarbon chains (C_8 and C_{18} are commonly used) to achieve a level of 'non-polarity'. This has the opposite effect on retention times. The more polar molecules in the sample are not as strongly adsorbed to the column material and therefore move through it more quickly, thus displaying shortened retention times. RPLC is the most commonly used form of HPLC.

Besides the two types mentioned above, there are other forms of HPLC that can be used in appropriate circumstances. These include ion-exchange chromatography and size-exclusion chromatography.

Detectors

A range of detectors may be used in HPLC, depending on the circumstances of the analysis. Examples include UV-visible detectors, diode array detectors (which use either visible or ultraviolet light to detect substances in the liquid as they exit from the column) and refractive index detectors (which measure changes in refractive index as substances elute). The increased absorbance of the light as substances leave the column is detected and creates an electrical signal that subsequently produces a peak on the chromatogram.

It is also possible to use a mass spectrometer as a detector. This option is considerably more expensive but has the advantage of being able to positively identify the different substances in the sample as they elute.



The essential components of a high-performance liquid chromatograph

Sample problem 10.7

Although it is usually done using gas chromatography (GC), the level of ethanol in wine may be determined using HPLC.

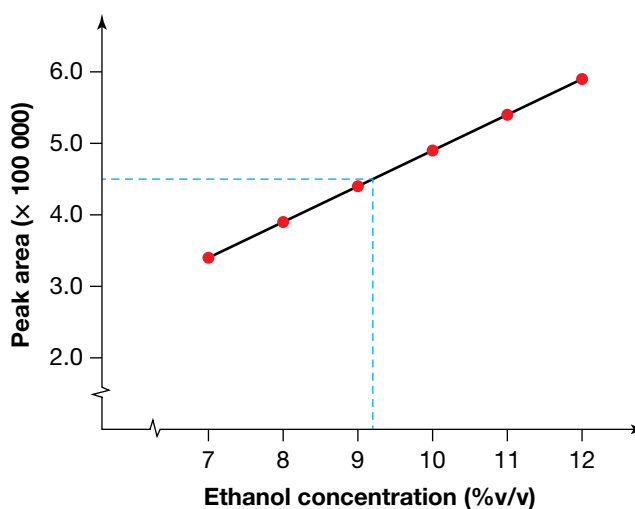
In one such analysis using HPLC, a set of six reference samples of known ethanol concentration were run through the instrument for the purpose of calibration. A sample of wine was then analysed under exactly the same conditions as the reference samples. A much more complicated chromatogram was obtained, from which the ethanol peak was identified.

The results obtained are shown in the table below.

Standard concentration, %(v/v)	Peak area
7	342 401
8	391 318
9	440 230
10	489 136
11	538 058
12	586 970
sample	450 012

- (a) Using these results, plot a calibration curve of concentration versus peak area.
- (b) Use the graph to deduce the ethanol content in the sample of wine.
- (c) How is the ethanol peak identified from the complicated pattern produced by the wine sample?
- (d) Explain why only one peak is produced in the chromatogram for each standard analysed.

Solution: (a) Plotting these results yields the following graph:



- (b) Reading from the calibration graph, the sample of wine gives an ethanol concentration of 9.2%.
- (c) Each ethanol standard produces a peak at the same position on the chromatogram; in other words, they all have the same retention time. So it is just a matter of finding the peak from the chromatogram of the wine sample that corresponds to this retention time.
- (d) Ethanol is the only substance present (apart from the solvent).

Revision questions

14. The ester methyl butanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$, is used as a flavour additive and in perfumes. It has both a pleasant odour and taste. However, butanoic acid, from which it is made, has an extremely unpleasant odour. It is therefore desirable that residual butanoic acid levels be kept to a minimum in methyl butanoate preparations that are used for the above purposes.

HPLC was used to measure the level of butanoic acid in a sample of food-grade methyl butanoate. A number of standards were run through the instrument, together with a sample of the methyl butanoate. The results are shown in the following table.

Concentration of butanoic acid (mg L^{-1})	Peak area
4.0	640
6.0	958
8.0	1280
10.0	1605
sample	1150

- Besides butanoic acid, what other organic compound is required to make methyl butanoate?
 - Plot the calibration curve for the above data.
 - Hence determine the concentration of butanoic acid in the sample tested.
 - Draw the structural formula for butanoic acid.
15. A sample of fuel oil was analysed for its pentadecane, $\text{C}_{15}\text{H}_{32}$, content, using a newly developed HPLC procedure.

To test this procedure, standards of 120, 140, 160 and 180 $\mu\text{g L}^{-1}$ of pentadecane (dissolved in hexane) were made up in 10.0 mL volumetric flasks by diluting a pentadecane solution of known concentration equal to 240 $\mu\text{g L}^{-1}$. As an additional check on the accuracy of these dilutions, two additional 'verification' standards were also analysed. These were certified to be 150 and 170 $\mu\text{g L}^{-1}$ respectively. The results are tabulated below.

Pentadecane concentration ($\mu\text{g L}^{-1}$)	Peak area
120	48 003
140	56 005
160	64 015
180	72 012
verification standard 1	
verification standard 2	

- To what class of compounds does pentadecane belong?
- Why is the pentadecane not dissolved in water?
- Describe how each of the standard solutions is prepared, giving the necessary volumes of pentadecane solution and hexane required.
- Draw the calibration curve from this data.
- What peak area readings would be produced by the two verification standards?

study on

Unit 4

AOS 1

Topic 4

Concept 8

See moreCombining
spectroscopies**eBook plus****Digital document**

Experiment 10.3 Spectroscopy

doc-18822

Combining techniques

Each of the techniques described so far is a powerful tool in its own right. The analysis and subsequent identification of a compound, however, is often the result of information gleaned from a number of such techniques. In the same way that a crime might be solved using clues from different sources, an unknown compound may be identified using clues from many different techniques. Such techniques often involve the instruments described in this chapter but may also use clues from some of the more traditional methods of analysis.



A combination of analytical techniques is sometimes used to determine the identity and concentration of a substance.

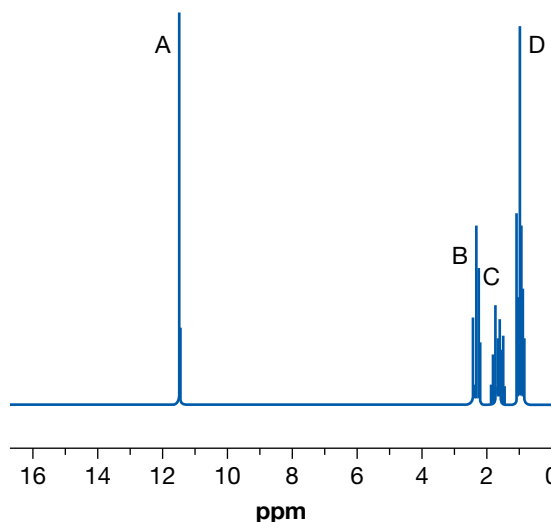
A possible sequence of steps might be as follows:

- Consider any traditional clues. For example, if the compound evolves hydrogen gas when mixed with magnesium, it would quickly be suspected of being a carboxylic acid. Other typical acid properties could be quickly checked to confirm this.
- Use HPLC to see if the sample is a mixture of compounds and to separate it into the components. Once the sample is identified by comparison of retention times or using other techniques, the concentration can be found by comparison of peak heights with known standards. Additional information about the structures of individual components can be found using mass spectrometry, infrared spectroscopy or nuclear magnetic resonance.
- Look at the mass spectrum and identify the parent peak. This indicates the relative molecular mass. Also, check other peaks. These may give clues to functional groups and alkyl groups that are present.
- Examine the IR spectrum. This should allow the types of bonds, and, from this, the functional group to be identified. This can be related back to any clues from the previous step.
- Look at the NMR spectrum noting features such as the number of different environments and the number of atoms within each environment. Also note any splitting patterns if this is appropriate. This is particularly useful in confirming alkyl groups and, in particular, distinguishing between alkyl groups for which there is more than one possible structure.

At this stage, a suggested structure should be emerging. This can be rechecked against all the clues deduced so far. In addition, the chemical shifts from the NMR spectrum could now be examined as extra confirmation.

Sample problem 10.8

Analysis of an unknown compound has revealed that it has an empirical formula C_2H_4O . Its MS has its parent peak at 88. The IR has significant peaks at 1700 cm^{-1} and a broad peak at 3000 cm^{-1} . The NMR spectrum is shown below.



Peak set	Number of split peaks	Relative area of peak set
A	1	1
B	3	2
C	multiple	2
D	3	3

Solution: The IR spectrum indicates the presence of carbon-oxygen double bonds and oxygen-hydrogen bonds. This indicates that the compound is likely to contain the COOH group and is most likely a carboxylic acid.

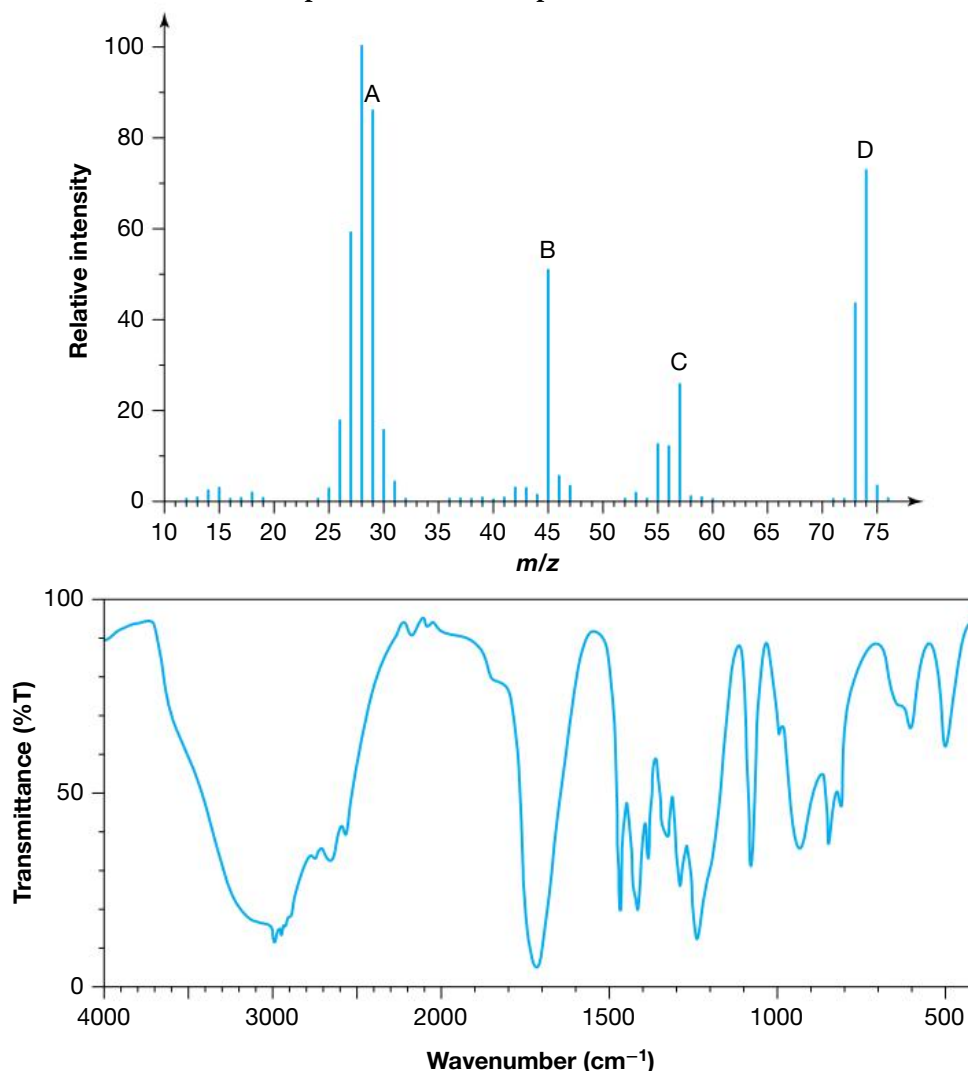
From the relative molecular mass and empirical formula, it can quickly be deduced that the molecular formula is $C_4H_8O_2$. Subtracting the COOH group from this leaves C_3H_7 for the rest of the molecule. Examination of the NMR spectrum indicates four different environments for the hydrogen atoms. One of these, signal A, is not split and is therefore the one that forms part of the COOH group. The remaining peak sets are all consistent with the C_3H_7 part of the molecule being $CH_3CH_2CH_2$.

Note: One of the CH_2 groups (signal C) has two sets of neighbouring protons (CH_3 and CH_2). It is expected to have $4 \times 3 = 12$ peak splitting. It would be difficult to see all 12 peaks and usually this is mistaken as 6 peaks.

The compound is therefore butanoic acid, $CH_3CH_2CH_2COOH$.

Revision question

16. An organic compound has the empirical formula $\text{C}_3\text{H}_6\text{O}_2$. When sodium carbonate is added to this compound bubbling is observed. The mass spectrum and infrared spectrum of the compound are shown below.



- Determine the molecular formula of this compound.
- Suggest the formulas of the fragments labelled A, B, C and D.
- Identify the bonds responsible for the peaks at:
 - 3000 cm^{-1}
 - 1720 cm^{-1}
 - 1230 cm^{-1} .
- Suggest a possible structure for this compound, giving reasons based on the above spectra.
- Name the compound.

Volumetric analysis

Volumetric analysis uses standard solutions and accurately measured volumes. A standard solution is one whose concentration is known to a high level of accuracy.

Volumetric analysis is a quantitative technique that involves reactions in solution. The accurate concentration of a solution is usually determined by reacting it with another solution whose concentration is known accurately or, in some cases, by making it up directly from a primary standard (see page 303).

The procedure usually involves measuring an accurate volume of one of the solutions with a **pipette** (this volume is called an **aliquot**) and pouring it into



Volumetric flasks, conical flasks, pipettes, burettes and various beakers are used in volumetric analysis.

a conical flask. The other solution (called a **titrant**) is then added carefully from a **burette** until the reaction is just complete (as predicted by the stoichiometry of the equation). By knowing the volumes involved and the concentration of one of the solutions, the concentration of the other solution may be determined. This procedure is called **titration**. The volume of the titrant delivered is known as the **titre**.

Two common types of reactions encountered in volumetric analysis are acid-base reactions and redox reactions.

The correct use of burettes and pipettes, as well as other important aspects of volumetric analysis has already been covered in Unit 2. Some of the more important points of this technique are revisited in this chapter.

Standard solutions

A **standard solution** is one whose concentration is accurately known. There are usually two methods by which a solution may have its concentration determined accurately:

1. by reacting it with another solution whose concentration is known accurately. This is called standardisation.
2. by taking a substance called a **primary standard** and dissolving it in a known volume of water. Primary standards are pure substances that satisfy a special list of criteria.

To qualify as a primary standard, a substance must have a number of the following properties:

- It must have a high state of purity.
- It must have an accurately known formula.
- It must be stable. In other words, its composition or formula must not change over time, which can happen, for example, as a result of storage or reaction with the atmosphere.
- It should be cheap and readily available.
- It should have a relatively high molar mass so that weighing errors are minimised.

Note that this means that not all substances are suitable for use as primary standards. Sodium hydroxide, for example, is unsuitable for use as a primary standard for the following reasons.

1. It absorbs moisture from the atmosphere (is *deliquescent*) as it is being weighed out. Hence, the precise mass of sodium hydroxide is uncertain because of the absorbed water.
2. As a typical hydroxide, it reacts with carbon dioxide in the atmosphere to produce sodium carbonate. Thus, there are doubts about its purity.

Hydrated sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, is also unsuitable, but for a different reason. This substance is *efflorescent*; that is, it loses water to the atmosphere as it is being weighed out. This water comes from the crystal structure and is known as 'water of crystallisation'. As a result, the precise formula is unknown.

However, if hydrated sodium carbonate is heated, these weakly bonded water molecules may be driven off. Eventually, anhydrous sodium carbonate, Na_2CO_3 , is formed, which makes an excellent primary standard.

To prepare a primary standard, chemists use special flasks called *volumetric flasks*. These flasks are filled to a previously calibrated etched line on their necks, so that the volume of their contents is accurately known.

A primary standard is a substance that can be used to produce solutions with precisely known concentrations. Primary standards must have certain important properties. A secondary standard can be prepared by standardising it (measuring its concentration) against a primary standard.

Both hydrated sodium carbonate and sodium hydroxide are unsuitable for use as primary standards because they react with the atmosphere.

study on

Unit 4

AOS 1

Topic 6

Concept 1



See more

Primary standards and standard solutions

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Experiment 10.4 Standardisation of hydrochloric acid

doc-18825

study on

Unit 4

AOS 1

Topic 6

Concept 2

See more
Volumetric
techniques

Sample problem 10.9

Prior to checking the ethanoic acid content of some vinegar, a quality control technician prepared a standard solution of sodium carbonate by weighing out 1.29 g of anhydrous sodium carbonate, dissolving it, and making the total volume of solution up to 250.0 mL in a volumetric flask.

Calculate the concentration of the solution produced.

Solution:

$$\begin{aligned} n(\text{Na}_2\text{CO}_3) &= \frac{m}{M} \\ &= \frac{1.29}{106.0} \\ &= 0.0122 \text{ mol} \\ c &= \frac{n}{V} \end{aligned}$$

$$\begin{aligned} c(\text{Na}_2\text{CO}_3) \text{ solution} &= \frac{0.0122}{250.0} \times 1000 \\ &= 0.0487 \text{ M} \end{aligned}$$

Making up solutions and measuring their volumes requires care and precision. Therefore, it is very important that correct procedures are followed.

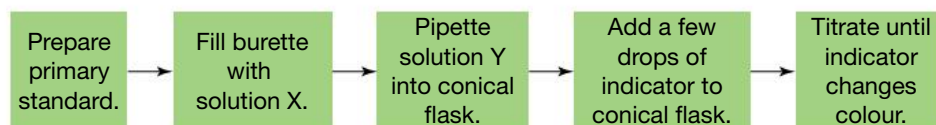
Revision questions

17. The substance potassium hydrogen phthalate, $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$, is frequently used as a primary standard for acid-base determinations. Calculate the concentration of a solution that is made by weighing out 10.19 g of this substance and accurately dissolving it in 500 mL of water.
18. A student standardised a solution of sodium hydroxide as follows: 20.00 mL of the hydroxide solution was titrated with 0.0921 M hydrochloric acid, using methyl orange as indicator. Titres of 18.67 mL, 18.73 mL and 18.64 mL were obtained.
 - (a) Write the equation for the reaction occurring during this titration.
 - (b) Calculate the molarity of the sodium hydroxide solution from the given data.
 - (c) Why is the methyl orange indicator necessary in this experiment?
 - (d) Once its concentration is determined, can the sodium hydroxide solution be called a standard solution? Explain.

How do we know when to stop a titration?

In volumetric analysis, the calculations require that a titration be stopped when one substance has *just finished* reacting with the other one. This point is called the **equivalence point**. Detection of this point is, therefore, critical to the success of a volumetric procedure.

The equivalence point of a titration occurs when the exact molar ratio of reactants is present, as shown in the equation. The end point occurs when experimental evidence (often a change in colour of an indicator) tells you to stop the titration.



Some typical steps in a volumetric procedure



Phenolphthalein is used as an indicator in some acid–base titrations.

For a particular titration, the equivalence point is fixed. The end point, however, may depend on the choice of indicator.

study on

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Concept 3



See more
Simple (direct)
titration

In acid–base titrations, the solutions and their products are usually colourless, and identification of the equivalence point would therefore be quite difficult. To overcome this problem, a few drops of a suitable acid–base **indicator** are usually added. Such indicators work because they are either weak acids or bases themselves, and, when they change into their conjugate form, a distinct colour change occurs. The pH at which such colour changes occur varies from one indicator to another. A key step in a particular titration is therefore to choose an indicator that changes colour at the pH of the equivalence point.

In some situations, a reaction may be self-indicating. This is often true in redox titrations where a substance involved in the analysis may have conjugate forms that display distinctly different colours. An example is in a titration involving the permanganate ion, MnO_4^- , which is bright purple, because an indicator is not required due to the reduced form, Mn^{2+} , being almost colourless.

In either type of titration, we therefore usually depend on a colour change to tell us when to stop. This is called the **end point**. As this occurs only after a slight excess is added, we often do not have the true equivalence point. Thus, we can say that the *end point is an approximation to the equivalence point*. However, in a carefully designed procedure with a carefully chosen indicator, these two points should be very close together.

Choosing a suitable indicator

As we have seen, the equivalence point of a titration occurs when the correct stoichiometric amounts are present. At this point, the pH of the solution is not always 7, due to the acid–base properties of the conjugate products that might be formed. It is therefore important to choose an indicator that changes colour close to the correct pH value for the titration concerned.

A further consideration is how quickly the pH changes around the point at which the indicator changes colour. This determines whether the end point is sharp and therefore easily detected. Table 10.6 shows the pH values at which various indicators change colour.

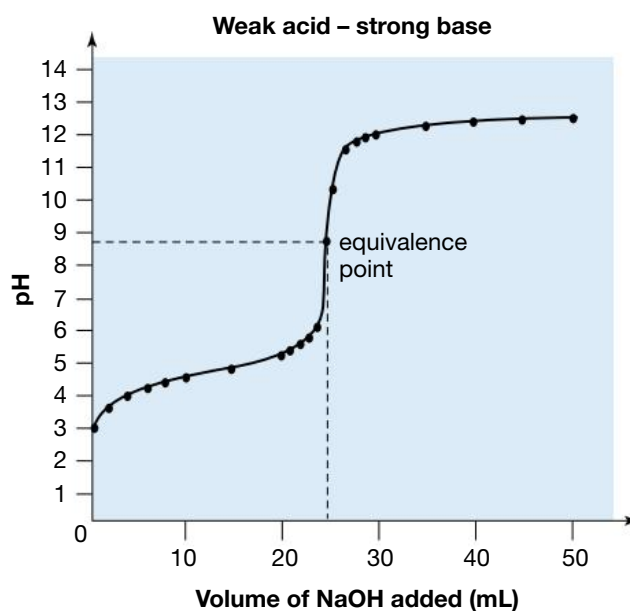
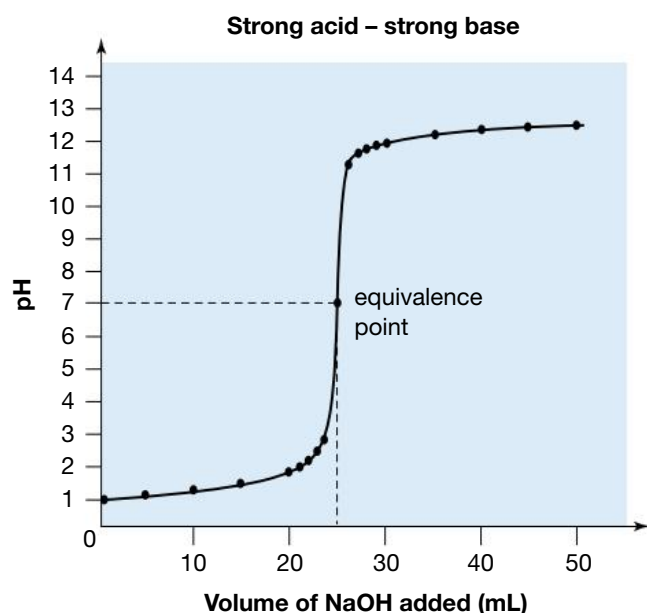
TABLE 10.6 Some common acid–base indicators

Indicator	Colour at lower pH	Colour at higher pH	pH range for colour change
methyl orange	red	yellow	3.1–4.4
methyl red	red	yellow	4.2–6.3
litmus	red	blue	5.0–9.0
bromothymol blue	yellow	blue	6.0–7.6
phenolphthalein	colourless	crimson	8.3–10.0

Titration curves

A **titration curve** is a graph of the volume added from a burette versus the pH of the solution in the titration flask. The graphs below show titration curves for three different scenarios:

- a solution of strong acid being reacted with a solution of strong base
- a solution of strong base being reacted with a solution of weak acid
- a solution of strong acid being reacted with a solution of weak base.



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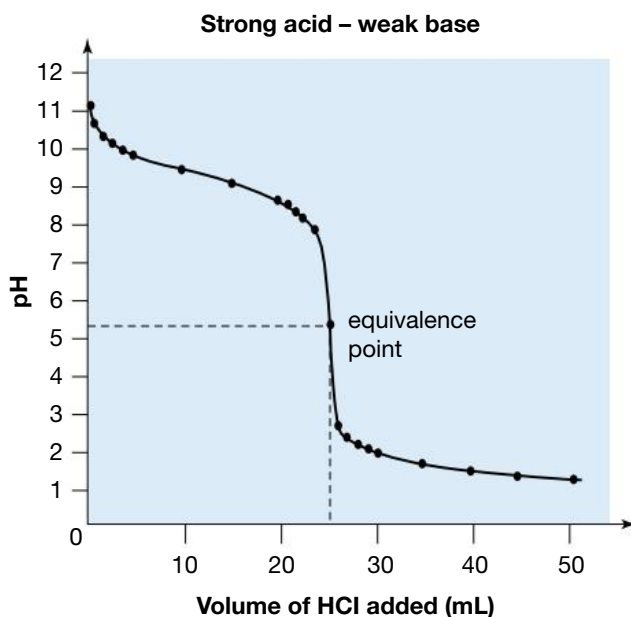
Concept 4



Do more

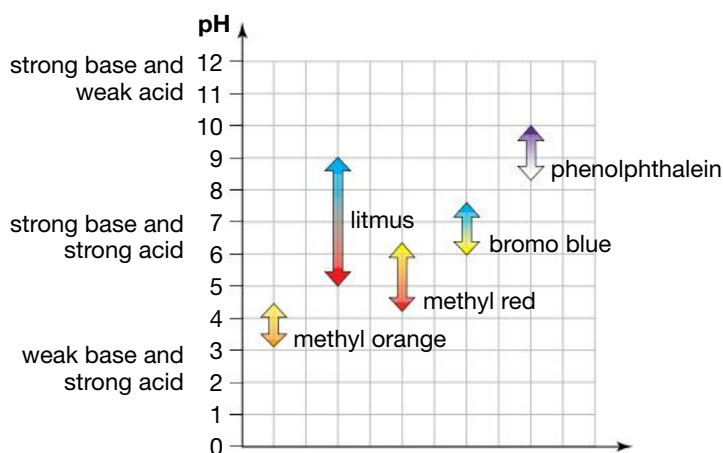
Acid–base titration

Three titration curves



In the first graph above, note that all the indicators from table 10.6 change colour in the steep portion of its graph. The steepness of this section is such that the volume over which it occurs could be as little as one drop. Therefore, there is a wide choice of indicators that might be used, each one giving a sharp end point that is close to the correct pH.

In the other two cases, the situation is more complicated. In both cases, some indicators do not even change colour at the correct pH. In the second graph, for example, methyl red does not change colour at the correct pH. Litmus would also be unsuitable because it begins to change colour before the steep section of the graph. The end point therefore occurs over a volume range that is too wide. In other words, it is not 'sharp'. A good choice of indicator for this case would be phenolphthalein. Methyl red would be a good choice in the third graph.



Indicator colour changes

Due to the colourless solutions used in many acid–base reactions, indicators are necessary to know when to stop an acid–base titration. For accurate results, the choice of indicator may be very important in a volumetric procedure.

More about these titration curves

Examination of the titration curves referred to earlier also yields the following important points:

- The pH at the start of the titration depends on what is present in the flask at the start. Likewise, the pH at the end of the titration depends on what is present in excess at the end of the titration.
- The pH at the equivalence point for the strong acid/strong base combination is 7. This is because the conjugate species present at this point are weak species and cancel each other out anyway.
- When there is a weak species involved, the conjugate is appreciably stronger and this affects the pH at the equivalence point. For example, if a weak acid is involved, its (stronger) conjugate base is present at equivalence, thus raising the pH at this point.

As mentioned previously some redox reactions are self-indicating but there are occasions where an indicator is required. An example of an indicator used in redox titrations is starch. Starch is used to detect the presence of iodine, I_2 , which is formed in titrations from the oxidation of iodide ions, I^- . Starch is dark blue in the presence of iodine. Another indicator suitable for redox titrations is methylene blue, which is blue in the presence of an oxidising agent and colourless in the presence of a reducing agent.

Concordant titres

Although it may appear tedious and time consuming to produce the required solutions and to prepare the necessary equipment, a big advantage of volumetric analysis is that it is subsequently very easy to perform repeat titrations. Such repetition reduces the effect of random errors.

When performing repeat titrations, one usually aims for **concordant** titres. Concordant titres are titres that are within a defined volume of each other, with 0.10 and 0.05 mL being commonly accepted values; 0.05 mL is an exacting standard and requires very careful attention to detail and excellent technique as it represents approximately one drop. However, in many situations, including school laboratories, titres within ± 0.10 mL of each other is a more realistic standard. On this basis, if a titration produces results of 19.25, 19.20,

19.40 and 19.20 mL, for example, all except the third value may be considered concordant. Note that the volume of a titre is rounded to the nearest 0.05 mL.

Stoichiometry and volumetric analysis

As is to be expected, solution stoichiometry plays a central role in the processing of experimental results from volumetric analysis. As will be seen in the examples to follow, the basic steps of any stoichiometric calculation are present at some stage in this procedure:

- writing a balanced chemical equation
- converting the known information into amounts (in moles)
- calculating amounts (in moles) of a second substance
- changing amounts (in moles) of this substance to the type of information required.

Note that, as solutions are involved, the formula $n = cV$ is used frequently. Also note that, due to the necessities of experimental procedure, dilution often takes place and subsequent calculations need to take this into account, so the formula $c_1V_1 = c_2V_2$ is useful here.

Some examples of volumetric analysis

As mentioned earlier in this chapter, volumetric analysis is a method ideally suited to analysing acids and bases, as well as oxidising agents and reducing agents. We would therefore expect that organic compounds showing distinct acid–base properties, such as carboxylic acids and amines, as well as those that have redox properties, such as alcohols and aldehydes, can be analysed using this technique.

Volumetric analysis is a tried-and-true technique that has been around for many years. A number of variations to the basic method have evolved, all aimed at taking into account the properties of the substances involved. As a result, volumetric analysis may be performed using simple (or direct) titration where one reactant is simply added to the other until the correct stoichiometric proportions are present, as well as by more sophisticated variations such as back titrations (not part of the VCE course).

Sample problems 10.10 to 10.12 all illustrate the use of volumetric analysis by simple (or direct) titration.

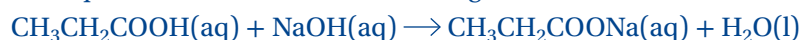
Sample problem 10.10

Propanoic acid is used as a preservative in animal feeds. It is sold as a range of solutions that contain between 10–100%(m/v) propanoic acid.

In the analysis of one such solution, a 25.00 mL sample was carefully diluted to 250.0 mL in a volumetric flask. 25.00 mL aliquots of this diluted solution were then reacted with 0.2500 M sodium hydroxide. The average of the concordant titres obtained was 32.10 mL.

Calculate the percentage (%m/v) of propanoic acid in the original solution.

Solution: The equation for the reaction occurring is:



$$n(\text{NaOH})_{\text{used}} = cV = 0.25 \times \frac{32.10}{1000} = 0.008\,03 \text{ mol}$$

From the equation:

$$n(\text{NaOH})_{\text{used}} = n(\text{CH}_3\text{CH}_2\text{COOH})_{\text{diluted}}$$

$$\therefore n(\text{CH}_3\text{CH}_2\text{COOH})_{\text{diluted}} = 0.008\,03 \text{ mol}$$

$$\therefore c(\text{CH}_3\text{CH}_2\text{COOH})_{\text{diluted}} = \frac{n}{V} = \frac{0.008\,03}{0.2500} = 0.321 \text{ M}$$

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Experiment 10.5 Analysis of vitamin C
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Find c_1 , the concentration of the original solution, given that $V_1 = 25.00$ mL.

$$c_1 V_1 = c_2 V_2$$

$$\therefore c_1 = \frac{c_2 V_2}{V_1}$$

$$\therefore c(\text{CH}_3\text{CH}_2\text{COOH})_{\text{undiluted}} = \frac{0.321 \times 250.0}{25.00} = 3.210 \text{ M}$$

Change to percentage:

$$\begin{aligned} 3.210 \text{ M} &= 3.210 \times 74.0 = 237.5 \text{ g L}^{-1} \text{ (convert moles to mass)} \\ &= 23.75 \text{ g/100 mL (express as mass per 100 mL solution)} \\ &= 23.8\% \end{aligned}$$

Sample problem 10.11

Ethylamine is widely used as a precursor to many herbicides. A chemist investigating the production of herbicides wished to check the claim on a newly purchased bottle that it contains between 68–72%(m/v) ethylamine dissolved in water.

After carefully diluting 10.00 mL of the amine solution to 1000 mL in a volumetric flask, 20.00 mL aliquots of this diluted solution were taken and titrated against a 0.197 M hydrochloric acid solution. Using methyl orange as the indicator, an average titre of 15.80 mL was obtained.

Do the contents of the bottle fall within the specifications shown on the label?

Solution: The equation for the reaction occurring is:



$$n(\text{HCl})_{\text{used}} = cV = 0.197 \times \frac{15.80}{1000} = 0.00311 \text{ mol}$$

From the equation:

$$n(\text{HCl})_{\text{used}} = n(\text{CH}_3\text{CH}_2\text{NH}_2)_{\text{diluted}}$$

$$\therefore n(\text{CH}_3\text{CH}_2\text{NH}_2)_{\text{diluted}} = 0.00311 \text{ mol}$$

$$\therefore c(\text{CH}_3\text{CH}_2\text{NH}_2)_{\text{diluted}} = \frac{n}{V} = \frac{0.00311}{0.02000} = 0.156 \text{ M}$$

$$c_1 V_1 = c_2 V_2$$

$$\therefore c_1 = \frac{c_2 V_2}{V_1}$$

$$\therefore c(\text{CH}_3\text{CH}_2\text{NH}_2)_{\text{undiluted}} = \frac{0.156 \times 1000}{10.00} = 15.6 \text{ M}$$

Change to percentage:

$$\begin{aligned} 15.6 \text{ M} &= 15.6 \times 45.0 = 700 \text{ g L}^{-1} \\ &= 70.0 \text{ g/100 mL} \\ &= 70.0 \text{ g/100 g} \\ &= 70.0\%(\text{m/m}) \end{aligned}$$

Therefore, the claim on the label is correct.

Sample problem 10.12

The ethanol content in wine may be determined by a redox titration using potassium dichromate. The ethanol in the wine is oxidised to ethanoic acid,

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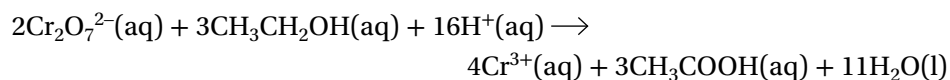
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Concept 6

Do more
Redox titrations
revised

while the orange dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$, are reduced to green Cr^{3+} ions. The reaction is therefore self-indicating. The equation for the reaction is:



In a particular analysis, a 25.00 mL sample of wine was poured into a volumetric flask and carefully diluted to 250.0 mL. 20.00 mL aliquots were then titrated against 0.150 M potassium dichromate solution. The average titre obtained was 17.50 mL.

- Calculate the concentration of ethanol (in M) of the tested wine.
- Ethanol levels are usually quoted as % (v/v). Given that the density of ethanol is 0.789 g mL^{-1} , convert your answer from (a) into a percentage.

Solution: (a) From the equation:

$$n(\text{Cr}_2\text{O}_7^{2-})_{\text{used}} = cV = 0.150 \times \frac{17.50}{1000} = 0.00263 \text{ mol}$$

$$\frac{n(\text{Cr}_2\text{O}_7^{2-})}{2} = \frac{n(\text{CH}_3\text{CH}_2\text{OH})}{3}$$

$$\therefore n(\text{CH}_3\text{CH}_2\text{OH})_{\text{diluted}} = 0.00263 \times \frac{3}{2} = 0.00394 \text{ mol}$$

$$\therefore c(\text{CH}_3\text{CH}_2\text{OH})_{\text{diluted}} = \frac{n}{V} = \frac{0.00394}{0.0200} = 0.197 \text{ M}$$

$$\therefore c_2 = \frac{c_1 V_1}{V_2}$$

$$\therefore c(\text{CH}_3\text{CH}_2\text{OH})_{\text{undiluted}} = 0.197 \times \frac{250.0}{25.00} = 1.97 \text{ M}$$

$$\begin{aligned} \text{(b)} \quad 1.97 \text{ M} &= 1.97 \times 46.0 = 90.7 \text{ g L}^{-1} \\ &= 9.07 \text{ g/100 mL} \end{aligned}$$

$$\text{Since density} = \frac{\text{mass}}{\text{volume}}$$

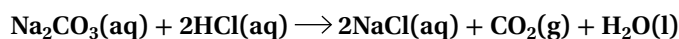
$$\begin{aligned} V(\text{ethanol}) &= \frac{m}{d} \\ &= \frac{9.07}{0.789} \\ &= 11.5 \text{ mL/100 mL} \\ &= 11.5\%(\text{v/v}) \end{aligned}$$

Note: Other methods for determining the ethanol content are gas chromatography, high-performance liquid chromatography and density measurements.

Revision questions

- A student standardised a hydrochloric acid solution as follows: 20.00 mL of a 0.0592 M sodium carbonate solution was pipetted into a conical flask. When the acid was added from the burette, 19.15 mL was required to reach the end point.

Given that the equation for the reaction is:



calculate the accurate concentration of the hydrochloric acid.

- To analyse a sample of vinegar for its ethanoic acid content, a student began by accurately diluting a 20.00 mL sample of the vinegar to 250.0 mL in a

volumetric flask. The student then placed 20.00 mL samples of this diluted vinegar in conical flasks and titrated them against a 0.0500 M solution of sodium hydroxide. The average titre obtained was 21.55 mL.

Assuming that ethanoic acid is the only acid present in the vinegar, calculate the concentration of the ethanoic acid in the vinegar (in g L⁻¹).

Sources of error

Volumetric analysis involves a number of steps, a number of different skills and a number of different measurements. Mistakes, uncertainties and poor technique throughout this process can accumulate to produce errors and uncertainties in the final result. Due care and diligence must therefore be applied throughout all stages. Hence, it is important not only to understand the method and to practise the technical skills involved, but also to be able to predict the effect that a particular error will have on the final result. In this way, the cause of unexpected results can be traced and subsequently rectified to improve the accuracy of the analysis.

Table 10.7 shows some general areas in which mistakes could be made and what effects these mistakes have on the final result.

TABLE 10.7 Effect on the calculated result of some possible mistakes during volumetric analysis

Situation	Effect if substance under analysis is in the ...		Comments
	burette	titration flask	
rinsing water left in burette	underestimated	overestimated	The burette solution is diluted with water, so more is used.
rinsing water left in pipette	overestimated	underestimated	The solution aliquot in the titration flask is diluted.
indicator chosen changes colour too soon	overestimated	underestimated	The choice of indicator can be critical.
water in titration flask	no effect	no effect	All necessary measurements are made before the chemicals are mixed with this water.
concentration of standard solution lower than calculated	overestimated	overestimated	Fewer moles of the standard solution than expected will be used; the substance being analysed will appear to have a higher concentration.
concentration of standard solution higher than calculated	underestimated	underestimated	More moles of the standard solution than expected will be used; the substance being analysed will appear to have a lower concentration.
random errors	variable	variable	Random errors can be minimised by repetition. It is easy to obtain multiple results with volumetric analysis.

Chapter review

Summary

- Qualitative analysis finds what substances are present. Quantitative analysis measures the quantity of substance present.
- A mass spectrometer (MS) analyses compounds to determine their mass/charge ratio. It does this by analysing the path of ionic fragments of molecules through a magnetic field.
- The output of a mass spectrometer is a mass spectrum that generally looks like a column graph. Each column represents an ion with a specific mass to charge (m/z) ratio. The height of the bar shows the relative abundance of the ion. The highest peak is known as the base peak and is assigned a value of 100%. Most ions formed have a single positive charge, and so the m/z value is usually equivalent to the mass.
- Another important peak in a mass spectrum of an organic compound is the parent peak (also called the molecular ion peak). This is the peak that represents the ion formed when an electron is knocked from the original molecule, leaving it with a positive charge. The relative molecular mass of the compound is therefore the same as this m/z value.
- Infrared (IR) spectroscopy identifies the functional groups and single, double and triple bonds in organic molecules. This qualitative method measures the characteristic amount of energy that the bonds in molecules transmit when exposed to radiation in the infrared portion of the electromagnetic spectrum.
- The infrared spectrum measures % transmittance on the y-axis (vertical axis) and wavenumber (cm^{-1}) on the x-axis (horizontal axis). Wavenumber is the reciprocal of the wavelength. The spectrum runs along the top of the readout when 100% of the light is transmitted and dips down to make an inverted peak when light is absorbed. Different bonds in an organic molecule have characteristic wavenumbers and produce dips or inverted peaks that allow them to be identified.
- IR spectra usually change scale at 2000 cm^{-1} , and the scale runs backwards.
- The fingerprint region of the spectrum, below 1000 cm^{-1} , is a crowded series of peaks that can be used to identify a substance because it is identical in every analysis of that substance.
- In general, the more types of atoms there are in a molecule, the more peaks appear on the IR spectrum, as these atoms affect the bonding between each other and absorb at slightly different wavenumbers.
- To distinguish between alcohols and carboxylic acids, look at two regions. Alcohols have a peak between 3200 and 3550 cm^{-1} but no peak near 1700 cm^{-1} . Carboxylic acids have a very broad peak between 2500 and 3300 cm^{-1} and a strong narrow peak near 1700 cm^{-1} .
- To distinguish between esters and carboxylic acids, an ester has only one peak at 1700 cm^{-1} , but a carboxylic acid has two peaks, as mentioned above.
- Uses of NMR include organic synthesis, quality control of medicines, forensic analysis of proteins, and identification of oil and gas deposits.
- An NMR spectrum is a two-dimensional graph of peak height versus chemical shift, δ (in ppm).
- Chemical shifts in ^{13}C NMR correspond to a carbon-13 atom in a particular environment within a molecule.
- Chemical shifts in ^1H NMR correspond to a hydrogen atom in a particular environment within a molecule.
- A signal in a low-resolution ^1H spectrum can be split into a set of peaks in the high-resolution spectrum. The number of peaks in the high-resolution spectrum indicates the number of hydrogen atoms adjacent to the hydrogen atom that has produced that signal. For simple molecules, the number of peaks is one more than the number of hydrogen atoms attached to the adjacent carbon atom of that hydrogen atom. This is often called the $n + 1$ rule.
- For the high-resolution ^1H NMR spectrum of ethanol (and other alcohols), even though the $-\text{OH}$ and $-\text{CH}_2$ groups are separated by four bonds, under most conditions the $-\text{OH}$ signal does not show splitting (for chemical reasons that are beyond this VCE course).
- ^1H nuclei can interact with other ^1H nuclei near them, and the effect can be measured by the number of peaks in the NMR spectrum.
- In all forms of chromatography, separation is achieved when a mobile phase (consisting of the mixture to be analysed and a solvent) is made to move over a stationary phase. The stationary phase has a large surface area. Separation occurs due to interactions between the substances in the mobile phase and the stationary phase. The weaker these interactions, the faster a substance moves through the column.
- High-performance liquid chromatography (HPLC) is an instrumental technique that is based on the principles of chromatography.
- In HPLC, a high-pressure liquid (eluent) is pumped through a column that is packed with a finely divided solid. Many organic substances can be separated, identified and quantified using this method.
- Separation on HPLC occurs due to interactions between the substances in the mobile phase and the stationary phase. The weaker these interactions with

- the stationary phase, the faster a substance moves through the column.
- Retention time (of a component) is an important term associated with HPLC. It is the time from injection of the sample until the component is detected leaving the column. Components in a mixture can be identified by their retention times.
 - When HPLC is used for quantitative analysis, it is necessary to use standards of known concentration. The readings produced by these standards are then graphed against their concentrations so that a graph called a calibration curve can be drawn. The concentration of an unknown sample can then be deduced from this graph by interpolation.
 - HPLC can be used for both qualitative and quantitative analysis.
 - Volumetric analysis is a quantitative technique that uses standard solutions and accurately known volumes to determine the concentration of a solution accurately.
 - Common reactions in volumetric analysis are acid-base reactions and redox reactions.
 - A standard solution is one whose concentration is accurately known.
 - A primary standard is a substance with certain properties that enable it to be weighed and made up into a solution whose concentration is precisely known.
 - A secondary standard is a solution that has been standardised using another standard.
 - Titration is the process by which burettes and pipettes are used in the procedure of volumetric analysis.
 - The equivalence point of a titration occurs when the correct stoichiometric amounts of the reactants involved are mixed in the titration vessel.
 - The end point of a titration is the stage at which the chosen indicator changes colour. An indicator is selected so that its endpoint approximates the equivalence point of the reaction.
 - The properties of a material have an important bearing on the method chosen to analyse it.

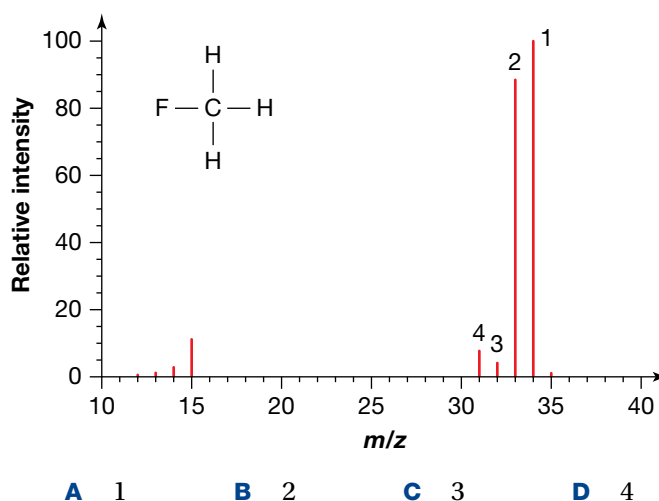
Summary of the applications of instrumental analysis

Instrument	Type of radiation	Basis of analysis	Method of analysis	Type of analysis
mass spectrometer	—	mass/charge ratio of atoms or groups of atoms	mass spectrum analysis	identification of molecular mass, molecular fragments and structures
IR spectrometer	infrared light	change in vibration of molecules when they absorb IR radiation	infrared absorption spectrum analysis	identification of double bonds, triple bonds and functional groups in organic molecules
NMR spectrometer	radio waves	change in nuclear spin of nuclei of some atoms when they absorb or emit radio waves	NMR spectrum analysis	identification of structural relationships within organic molecules
HPLC	—	adsorption to stationary phase and solubility in mobile phase	chromatogram	separation, identification and quantification of organic compounds

Multiple choice questions

- The information obtained from the analysis of organic compounds using mass spectrometry includes:
 - the number of protons in a compound as determined by the absorption of radio waves in a magnetic field
 - the kinds of functional groups present in the molecule
 - the interaction of compounds with a stationary phase
 - the molecular masses and fragments formed by a compound.
- The tallest peak in a mass spectrum is called the:
 - molecular ion
 - parent peak
 - base peak
 - calibration peak.

- In the following spectrum, which peak corresponds to the $[\text{CH}_2\text{F}]^+$ fragment?



4. To determine the relative molecular mass of an organic molecule, you would look at its:
 - A infrared spectrum
 - B HPLC chromatogram
 - C mass spectrum
 - D proton NMR spectrum.
5. The difference between the infrared spectra of an alcohol and a carboxylic acid is that the alcohol spectrum:
 - A has a peak near $3200\text{--}3500\text{ cm}^{-1}$ and a peak near 1700 cm^{-1}
 - B has a peak near $3200\text{--}3500\text{ cm}^{-1}$ but no peak near 1700 cm^{-1}
 - C has a peak near 1700 cm^{-1} but no peak near $3200\text{--}3500\text{ cm}^{-1}$
 - D does not have a peak near $3200\text{--}3500\text{ cm}^{-1}$ or near 1700 cm^{-1} .
6. Which one of the following pieces of information cannot be obtained from an infrared spectrum?
 - A The number of different H environments
 - B The presence of C=O bonds
 - C The presence of O—H bonds
 - D The identity of a compound through comparison with other spectra
7. Which of the following statements about tetramethylsilane, $(\text{CH}_3)_4\text{Si}$, is *incorrect*?
 - A It is soluble in organic solvents.
 - B It produces a strong signal at 0 because it has 12 equivalent hydrogen atoms.
 - C It is assigned a chemical shift of 0 in infrared spectroscopy.
 - D It is used to provide a reference against which other peaks are measured.
8. The proton NMR spectrum of chloroethane consists of:
 - A a singlet and a doublet
 - B a doublet and a triplet
 - C a triplet and a quartet
 - D a doublet and a quartet.
9. How many signals does the carboxylic acid $(\text{CH}_3)_2\text{CHCOOH}$ have in its ^1H NMR and ^{13}C NMR spectra?
 - A Three ^1H signals and three ^{13}C signals
 - B Three ^1H signals and four ^{13}C signals
 - C Four ^1H signals and four ^{13}C signals
 - D Five ^1H signals and three ^{13}C signals
10. The splitting pattern observed in ^1H NMR spectrum of propane is:
 - A triplet, doublet, triplet
 - B sextet, doublet
 - C septet, triplet
 - D quartet, triplet, quartet.
11. All forms of chromatography involve:
 - A a solid phase moving over a liquid phase
 - B a solid phase moving over a stationary phase
 - C a liquid phase moving over a mobile phase
 - D a mobile phase moving over a stationary phase.
12. Which of the following instrumental techniques would be most helpful to identify and quantify the presence of a known impurity in an illegal drug?
 - A MS
 - B IR
 - C NMR
 - D HPLC
13. Which feature of a chromatogram is most useful in qualitatively analysing the components of a mixture?
 - A The time after injection at which the peaks occur
 - B The heights of the peaks
 - C The wavelengths at which the peaks appear
 - D The widths of the peaks
14. Which feature of a chromatogram is most useful in quantitatively analysing the components of a mixture?
 - A The time after injection at which the peaks occur
 - B The area under the peaks
 - C The wavelengths at which the peaks appear
 - D The widths of the peaks
15. In performing a volumetric analysis, a student fills his burette with a 0.300 M solution. He then titrates this against 20.00 mL of a second solution, whose concentration is unknown. A titre of 21.55 mL is required.
When the concentration of the second solution is calculated, the number of significant figures allowed is:
 - A 1
 - B 2
 - C 3
 - D 4.
16. Sodium hydroxide is unsuitable for use as a primary standard because:
 - A it is not readily available in pure form
 - B it is difficult to handle because of its caustic properties
 - C it absorbs water from the atmosphere and reacts with carbon dioxide as it is being weighed out
 - D it is only slightly soluble and cannot therefore produce solutions that are concentrated enough for volumetric analysis.
17. Some typical steps for part of a volumetric analysis are shown below in jumbled order.
 - A Fill burette with required solution.
 - B Rinse burette with water.
 - C Perform titration and record final volume.
 - D Rinse burette with a small amount of the solution that it is to contain.
 - E Take an initial reading.

The only correct order for these steps is:

- A** D, A, E, C, B
- B** B, D, A, E, C
- C** D, B, A, E, C
- D** B, D, E, A, C.

Use the following information to answer questions 18 and 19.

In a titration to determine the concentration of some hydrochloric acid, a student pours the acid into a burette and titrates it against some standardised sodium carbonate solution.

- 18.** If a small amount of water was left in the titration flask before the aliquot of sodium carbonate solution was added, what effect would this have on the calculated concentration of the hydrochloric acid solution?
- A** The answer would depend on the amount of water left in the flask.
 - B** The concentration would appear to be higher.
 - C** The concentration would appear to be lower.
 - D** There would be no effect on the calculated concentration.
- 19.** After completing this experiment, the student compares her result with those obtained by other members of her class. She discovers that her result is significantly higher.
- A possible reason for this is that:
- A** there was still some water in the burette when she filled it with the hydrochloric acid solution
 - B** she mistakenly used hydrated sodium carbonate instead of anhydrous sodium carbonate to prepare the standard solution
 - C** she mistakenly wrote down an initial burette reading of 10.09 mL instead of 10.90 mL
 - D** she used too many drops of the indicator solution.

- 20.** A student wishes to design an experiment to exactly measure the level of ethanoic acid in vinegar. It is known that the concentration should be about 4.0 g per 100 mL.

The proposed method requires that a sample of the vinegar be first diluted by a factor of 10 and then reacted with a solution of standardised sodium hydroxide. A 20.00 mL pipette will be used to deliver the diluted vinegar, and it is desired that a titre between 20 and 30 mL be obtained.

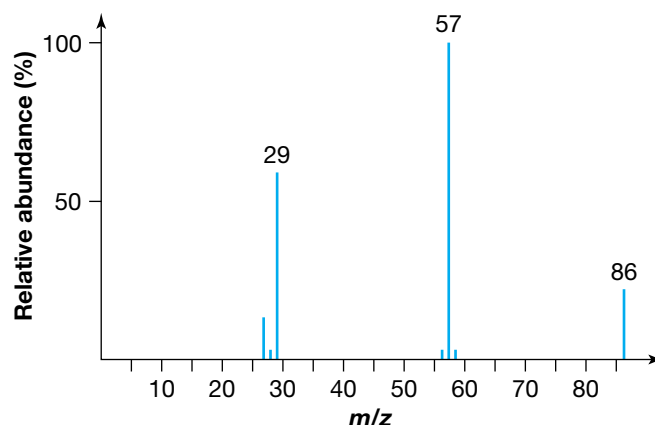
The concentration of sodium hydroxide that should be chosen is:

- A** 0.0200 M
- B** 0.0500 M
- C** 0.100 M
- D** 0.200 M

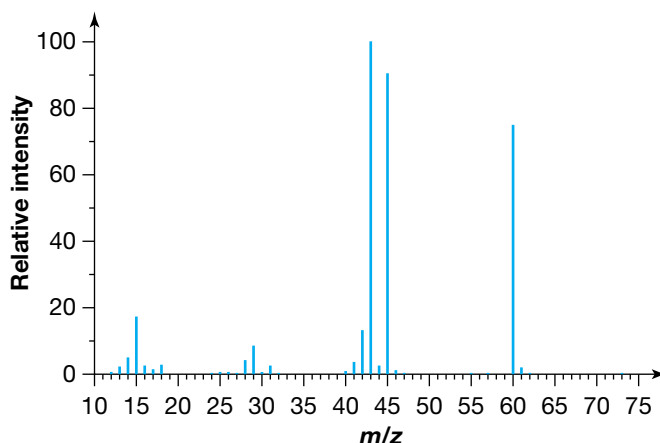
Review questions

Mass spectrometry

- 1.** Consider the following mass spectrum of a ketone, and answer the following questions.



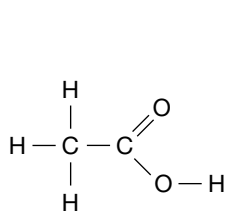
- (a) What is the m/z value for the parent ion?
 - (b) What is the m/z value for the base peak?
 - (c) The peak at $m/z = 57$ represents the loss of what possible fragment from the molecule?
 - (d) Suggest a possible structure for the compound.
- 2.** The empirical formula of an unknown compound is CH_2O . The mass spectrum of this compound is shown below. Identify the compound.



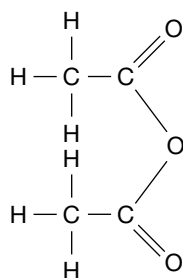
Spectroscopy

- 3.** The production of the painkiller aspirin involves the reaction of a hydroxyl group in salicylic acid with ethanoic acid. However, because this reaction is so slow, another compound, ethanoic anhydride, is used. The structures of ethanoic acid and ethanoic anhydride are shown below. Explain by referring to particular bonds and wavenumbers how these

two compounds could be distinguished using IR spectroscopy.

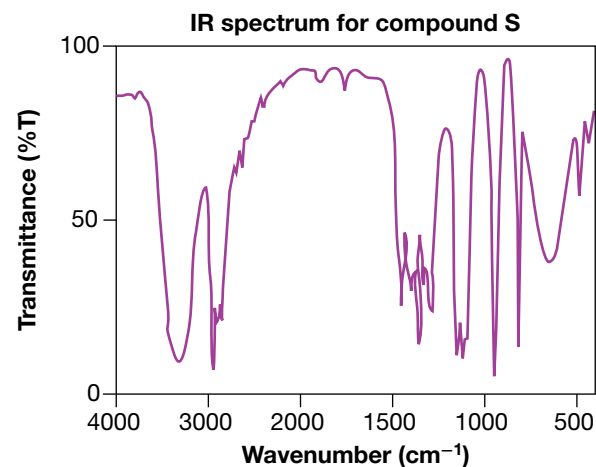
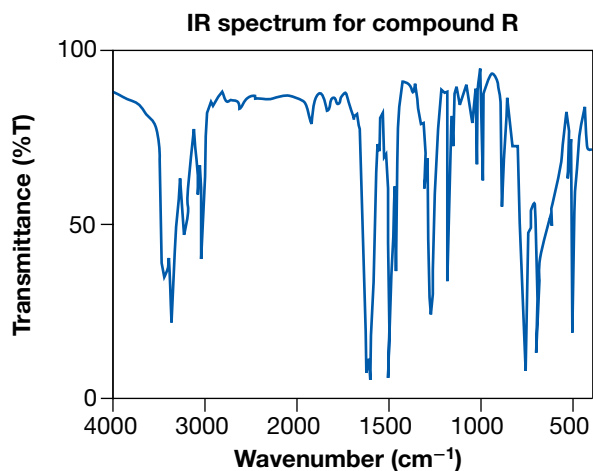


ethanoic acid

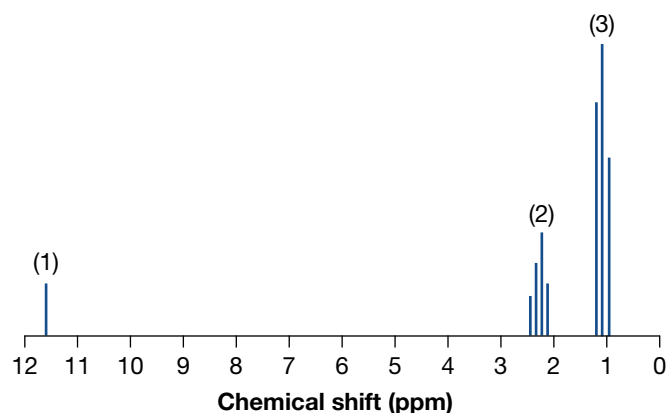


ethanoic anhydride

4. (a) How would an infrared spectrum of butanoic acid differ from that of butan-1-ol?
- (b) How would an infrared spectrum of butanoic acid differ from that of ethanoic acid?
5. Forensic chemists often use infrared spectra to identify organic bases such as amines, which have an —NH_2 group. The —N—H functional group produces peaks at $3350\text{--}3500\text{ cm}^{-1}$ and at $1560\text{--}1650\text{ cm}^{-1}$. Which of the following spectra, R or S, is the amine?

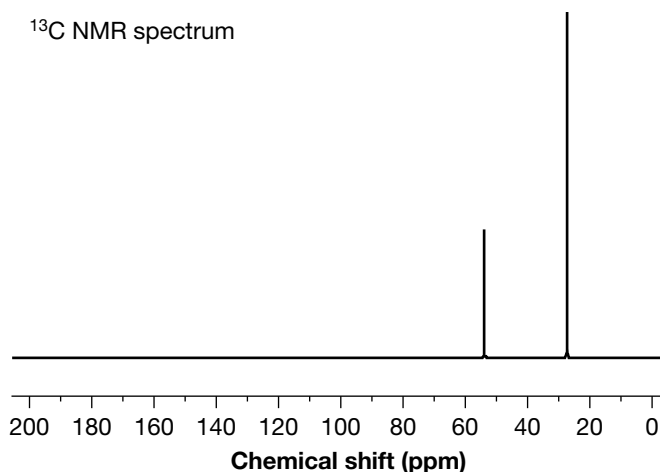


6. List the differences between the analytical methods IR spectroscopy and NMR spectroscopy.
7. NMR is a method of instrumental analysis used to determine the connectivity of atoms in a molecule. Describe how the connectivity is determined by this method.
8. Shown below is an NMR spectrum of a molecule with the molecular formula $\text{C}_3\text{H}_6\text{O}_2$.

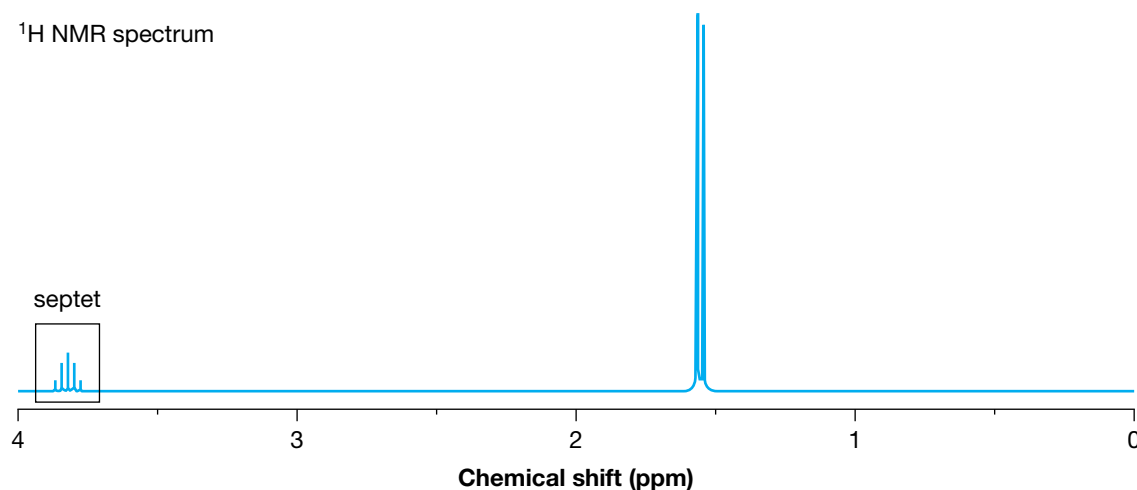


- (a) Identify the peaks using the table of chemical shifts (table 10.5).
- (b) How many peaks would you most likely find in the set of peaks for the CH_2 group?
- (c) Sketch the structure of the molecule.
9. An unknown isomer of $\text{C}_3\text{H}_7\text{Cl}$ has the ^{13}C NMR and ^1H NMR spectra shown below and on the next page. Draw the structure of the possible isomers and identify with reasons which isomer is represented by these spectra.

^{13}C NMR spectrum



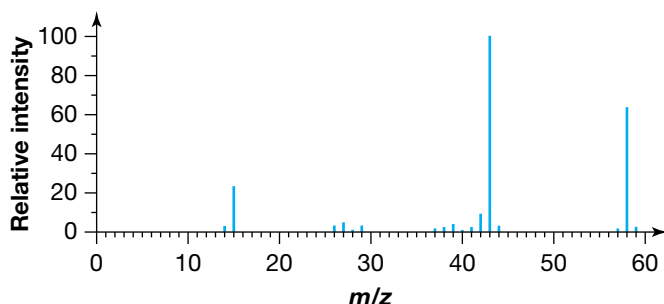
^1H NMR spectrum



10. Compound A has molecular formula $\text{C}_3\text{H}_8\text{O}$.

- (a) Draw the structural isomers represented by this formula.

Compound A reacts with acidified potassium dichromate solution to form compound B, which has molecular formula $\text{C}_3\text{H}_6\text{O}$. The proton NMR spectrum of compound B shows only 1 peak, and its mass spectrum is shown below.



- (b) Name and draw the structure of compound B. Justify your answer by referring to the NMR information and mass spectrum.
- (c) Identify the fragment with $m/z = 43$.
- (d) Write an equation showing the formation of the fragment at $m/z = 15$.
- (e) How many peaks would you expect in the ^{13}C NMR spectrum of compound B?

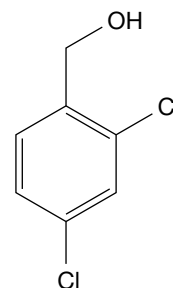
High-performance chromatography

11. Define each of the following terms.

- Mobile phase
- Stationary phase
- Solvent
- Retention time
- Column
- Calibration curve
- Chromatogram

12. In chromatography, why is it important that the stationary phase has a large surface area?

13. A sample containing a complex mixture of substances is analysed using HPLC. A peak of interest appears at retention time 5.3 minutes. When a control sample of substance X is injected, a peak appears at 5.3 minutes. Can we say for certain that the original mixture contains substance X? Explain why or why not.
14. A new brand of throat lozenges called 'Throat Eze' makes the claim that each lozenge contains 1.2 mg of dichlorobenzyl alcohol.



dichlorobenzyl alcohol

To test this claim, a government analyst dissolved the lozenge in a solvent made from water and ethanol and made it up to 500 mL. A small sample was then injected into a high-performance liquid chromatograph. A chromatogram containing a large number of peaks was obtained.

The operator then ran a series of dichlorobenzyl alcohol standards of known concentration through the instrument. Chromatograms for each standard were obtained, as well as a measure of the area under each of the reference peaks.

- Explain how the standards would allow the dichlorobenzyl alcohol peak from the original chromatogram to be identified.
- What is the purpose of using a set of standards as described and subsequently obtaining the area under their peaks?

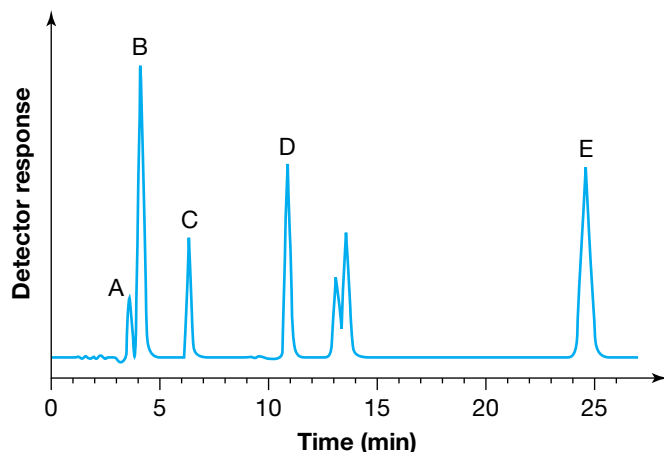
- (c) Shown in the table below are the results from the standards, together with a measurement for the area under the peak that was identified as dichlorobenzyl alcohol from the original chromatogram.

Is the claim made by the manufacturer true?

Results from HPLC analysis of dichlorobenzyl alcohol

Concentration of standard (mg L ⁻¹)	Area under peak (arbitrary units)
1.0	83
2.0	160
3.0	241
4.0	315
lozenge extract	193

15. The following HPLC was obtained when a sample of a mixture was analysed.



- (a) Which compound spent the most time in the stationary phase?
(b) Which compound was the least concentrated?

Volumetric analysis

16. A 0.0500 M solution of sodium oxalate, Na₂C₂O₄, is required for a particular analysis. Calculate the mass that would be required to make 250 mL of such a solution and describe the steps in your preparation of this solution.
17. Distinguish between the following terms:
(a) burette and pipette
(b) aliquot and titre
(c) end point and equivalence point
(d) primary standard and standard solution
(e) deliquescence and efflorescence
(f) quantitative analysis and qualitative analysis.
18. Refer to the list of requirements for a primary standard from earlier in this chapter.
(a) List them in what you consider to be their order of importance.

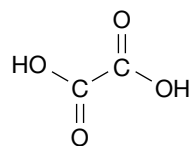
- (b) Do you think that all these requirements would be met every time a primary standard was chosen? Explain.

19. A solution of potassium permanganate can be standardised using pure iron wire. In a particular experiment, 0.317 g of iron wire was dissolved so that Fe²⁺ ions were formed, and the resulting solution was made up to 250.0 mL. Suppose 20.00 mL aliquots of this solution were then taken, with 11.70 mL of the permanganate solution being required.
- (a) Write a half-equation for the oxidation of Fe²⁺ to Fe³⁺.
(b) Write a half-equation for the reduction of MnO₄⁻ to Mn²⁺.
(c) Hence, derive the overall balanced equation for this titration.
(d) Calculate the molarity of the permanganate solution.
(e) Why is an indicator not required for this reaction?
20. Aspirin, CH₃COOC₆H₄COOH, is also known as acetylsalicylic acid. It is a medication used to treat pain and fever.
- (a) Write the equation for its reaction with sodium hydroxide.
(b) A sample of aspirin is analysed using standardised 0.105 M sodium hydroxide using phenolphthalein as an indicator. Calculate the mass of aspirin required to give a titration of 22.80 mL of sodium hydroxide.
21. In a titration to determine the concentration of an ethanal (acetaldehyde) solution, a 25.00 mL aliquot required 14.30 mL of 0.100 M acidified potassium permanganate solution to reach the end point. The equation for the reaction is:
- $$2\text{MnO}_4^-(\text{aq}) + 5\text{CH}_3\text{CHO}(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow 2\text{Mn}^{2+}(\text{aq}) + 5\text{CH}_3\text{COOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
- Calculate the concentration of the ethanal solution.
22. The level of vitamin C (ascorbic acid) in citrus fruits can be determined by titration. The preferred method involves a redox titration using iodine. Acid-base titration is not used due to the presence of other acids, most notably citric acid. The reaction involved produces dehydroascorbic acid and iodide ions as its products, and starch is used as an indicator. The equation for this reaction is:
- $$\text{C}_6\text{H}_8\text{O}_6(\text{aq}) + \text{I}_2(\text{aq}) \longrightarrow \text{C}_6\text{H}_6\text{O}_6(\text{aq}) + 2\text{I}^-(\text{aq}) + 2\text{H}^+(\text{aq})$$
- In an experiment to determine the level of vitamin C in oranges, the juice from a 210 g orange was carefully collected and strained into a 100.0 mL volumetric flask. It was then made up to the mark with water. 20.00 mL aliquots of

this solution were titrated against a standardised 0.005 00 M iodine solution. The average titre required was 24.80 mL.

- (a) Calculate the concentration (in M) of vitamin C in the diluted orange juice.
- (b) Calculate the mass of vitamin C in the volumetric flask.
- (c) Calculate the level of vitamin C in the orange tested. Express your answer as mg/100 g of fruit.

- 23.** Oxalic acid (ethanedioic acid) is a carboxylic acid that contains two carboxyl functional groups. It has the formula $\text{H}_2\text{C}_2\text{O}_4$, and its structure is shown below.



One of its uses is as a spot remover for carpet stains. A student was given the challenge of volumetrically analysing a solution of commercially available carpet stain remover, in which it was known that oxalic acid was the only acid present.

At her disposal she had some anhydrous sodium carbonate, solutions of hydrochloric acid and sodium hydroxide, both of approximately 0.1 M concentration, as well as a wide range of equipment typically needed for volumetric analysis.

After much thought, she decided on a three-step procedure, the method and results of which were as follows.

- Step 1. 1.280 g of anhydrous sodium carbonate was dissolved in water and made up to 250.0 mL in a volumetric flask. 20.00 mL aliquots of this solution were titrated against the hydrochloric acid solution. An average titre of 18.75 mL was obtained.
 - Step 2. 20.00 mL aliquots of the sodium hydroxide solution were titrated against the hydrochloric acid solution from step 1. The average titre obtained for this step was 20.80 mL.
 - Step 3. The spot removal solution was diluted by pipetting 20.00 mL into a 250.0 mL volumetric flask and making it up to the mark with water. This was then poured into the burette and titrated against 20.00 mL aliquots of the sodium hydroxide solution from step 2. The average titre was 24.05 mL.
- (a) Write the equation for the reaction occurring in step 1 and hence calculate the accurate concentration of the hydrochloric acid solution.
 - (b) Write the equation for the reaction occurring in step 2 and hence calculate the accurate concentration of the sodium hydroxide solution.
 - (c) Write the equation for the reaction occurring in step 3 and hence calculate the accurate concentration of oxalic acid (M) in the spot removal solution.



Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

1. Instrumental analysis can be used to separate and identify particular proteins that could be disease markers in our bodies. Which of the techniques could be used to:

(a) separate the molecules

1 mark

(b) determine their molecular mass

1 mark

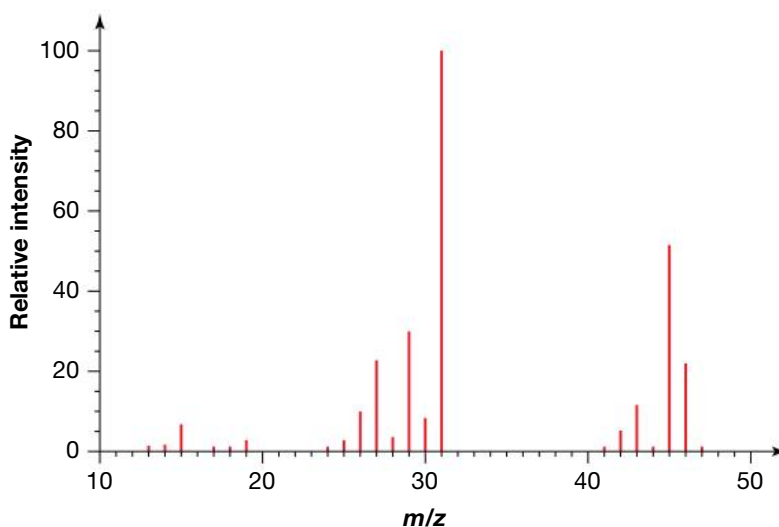
(c) determine the structure of the molecules?

1 mark

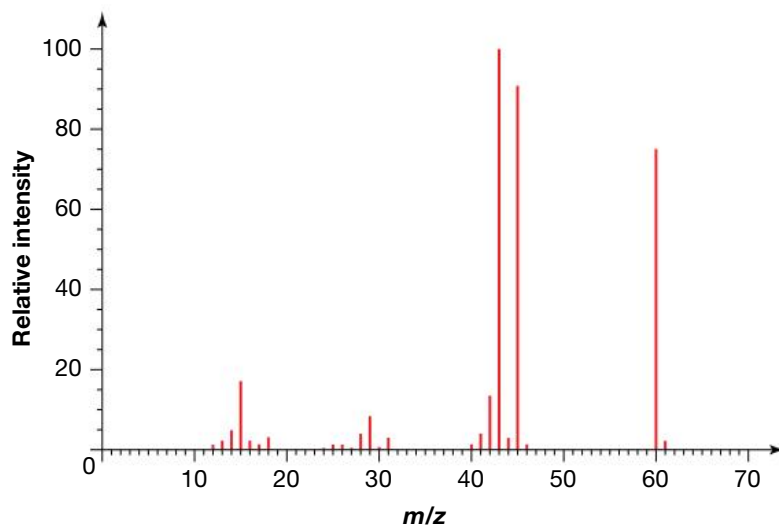
2. The mass spectra below are of ethanoic acid and ethanol.

Identify each spectrum and give reasons for your answer based on the fragments present.

Spectrum A



Spectrum B



3 marks

3. Propene reacts with HCl to form two isomers. Draw the structures of the two isomers, and explain how proton NMR could be used to distinguish between these two isomers.

4 marks

4. On a planet many light-years from Earth, intelligent beings called Troglodols live. A special feature of their diet is that they must eat food that contains a substance they call biparthin. However, the level of

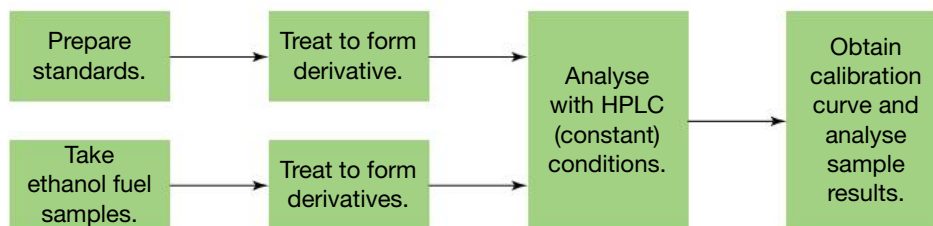
this substance must be carefully monitored as there is a critical concentration above which it becomes a poison. This concentration is 4.5 dramans.

As part of their regular checks, an analyst has recently analysed two food samples with a suitable instrument. This instrument was first calibrated by using standards of known concentration and noting the reading produced by the instrument. The readings produced by the two samples were then also noted. The results are shown in the table below.

Biparthin concentration (dramans)	Instrumental reading
2.0	25.0
3.0	37.8
4.0	50.1
5.0	62.9
food sample no. 1	47.7
food sample no. 2	57.8

- (a) Plot a calibration graph of these results. **2 marks**
- (b) From this graph, estimate the biparthin concentration in each of the two samples tested. **1 mark**
- (c) What recommendations should be made to the inhabitants of this planet regarding these two samples? **2 marks**
5. Ethanol, when used as a fuel, often contains small amounts of aldehydes and ketones. These may be analysed using HPLC by stoichiometrically converting them to a derivative (compound created from a similar compound) and then analysing this derivative. Contaminant levels of butanal, propanone (acetone) and butanone (methyl ethyl ketone) can be analysed this way.

The following diagram summarises how this is done.



- (a) Draw the structures of butanal, propanone and butanone. **3 marks**

A sample of ethanol fuel was analysed for its butanal content as described above, after first being diluted by a factor of 100. The table below shows the results for a set of butanal standards and the diluted fuel.

Concentration of butanal derivative ($\mu\text{g L}^{-1}$)	Peak area
120	2760
140	3220
160	3680
180	4140
200	4600
diluted fuel sample	3059

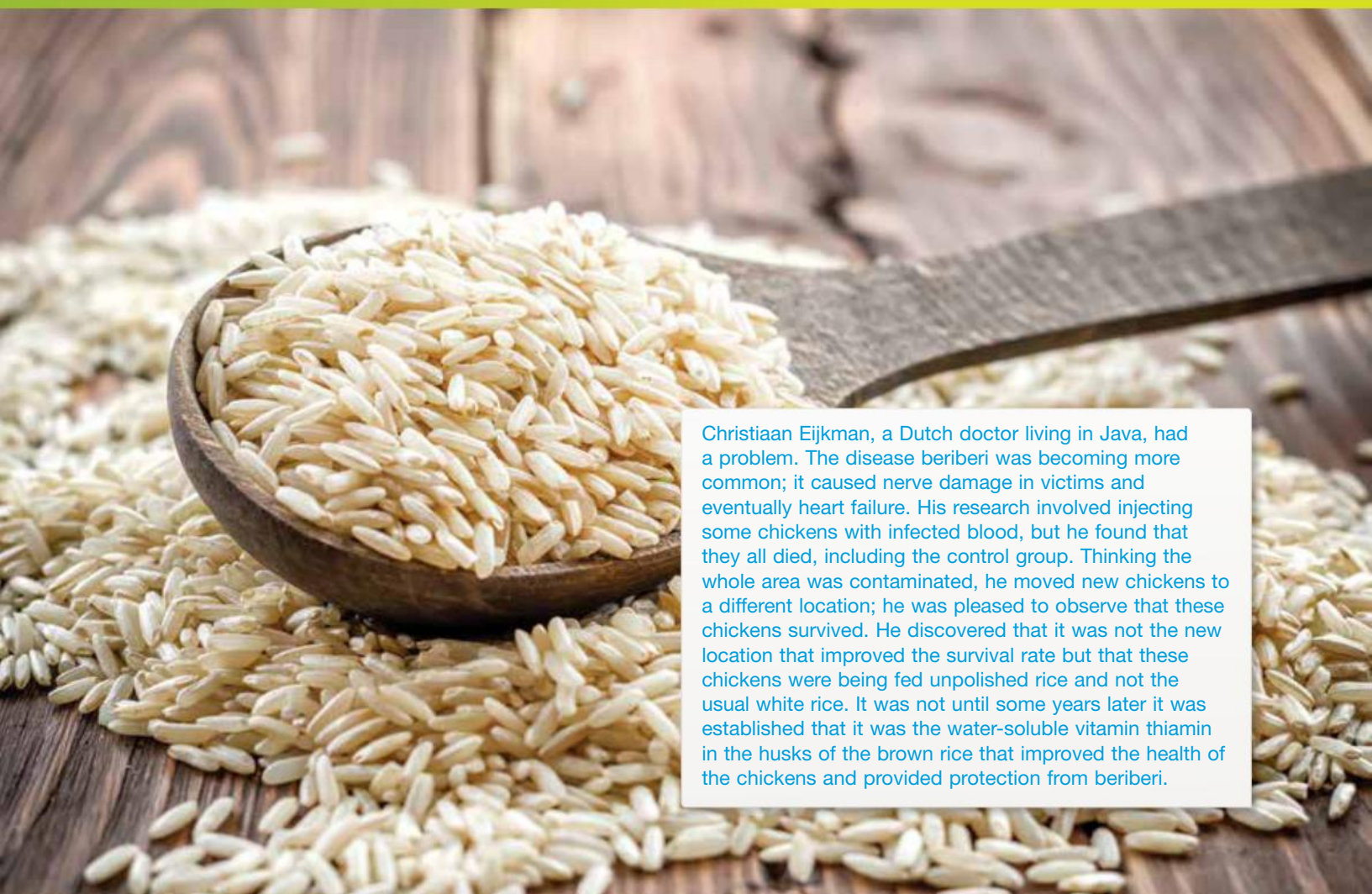
- (b) Estimate the concentration of butanal in the diluted fuel from the table above. **1 mark**
- (c) Draw the calibration curve for these results, and hence determine the exact level of butanal in the diluted sample. **4 marks**
- (d) Hence determine the level of butanal (in mg L^{-1}) in the undiluted fuel. **1 mark**
- (e) The operating conditions of the HPLC are now altered in preparation for the analysis of propanone. Why is it now appropriate to do this? **1 mark**

Vitamins and proteins

Our bodies rely on proteins as essential building blocks of an enormous number of compounds. They are the raw materials for growth and repair of cells and, if required, energy. The thousands of proteins in our body are polymers made up of just 20 different amino acids. This chapter examines the properties and structures of amino acids and proteins, together with the role played by vitamins in protein function. It also discusses how the structures of vitamins affect their properties, in particular their solubility in water or oil.

YOU WILL EXAMINE:

- examples and structures of water-soluble and fat-soluble vitamins
- why vitamins are essential for a healthy diet
- structures of amino acids, polypeptides and proteins
- differences between essential and non-essential amino acids
- the formation of proteins
- functions of proteins
- how enzymes act as protein catalysts
- how coenzymes assist enzymes
- factors affecting the catalytic properties of enzymes
- hydrolysis reactions in the digestion of proteins.



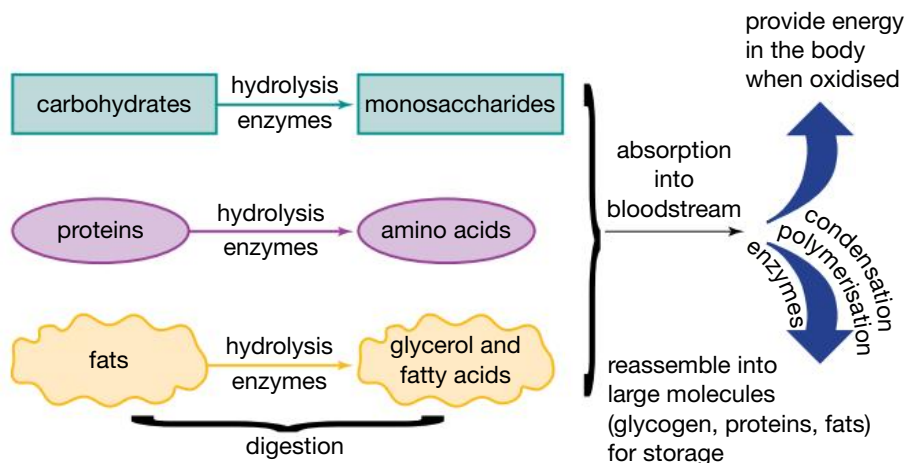
Christiaan Eijkman, a Dutch doctor living in Java, had a problem. The disease beriberi was becoming more common; it caused nerve damage in victims and eventually heart failure. His research involved injecting some chickens with infected blood, but he found that they all died, including the control group. Thinking the whole area was contaminated, he moved new chickens to a different location; he was pleased to observe that these chickens survived. He discovered that it was not the new location that improved the survival rate but that these chickens were being fed unpolished rice and not the usual white rice. It was not until some years later it was established that it was the water-soluble vitamin thiamin in the husks of the brown rice that improved the health of the chickens and provided protection from beriberi.

Eating chemicals

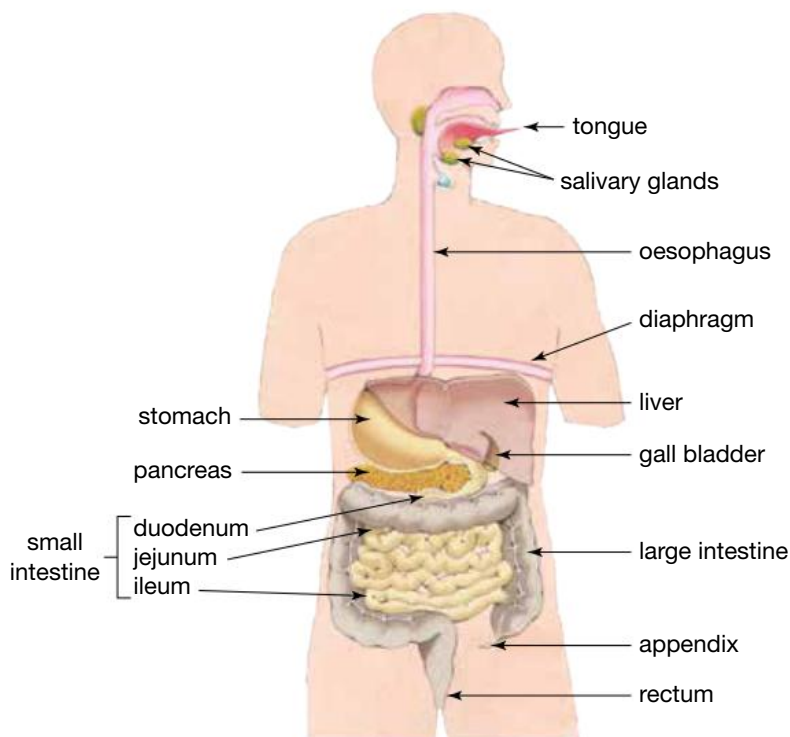
Sharing food with family and friends is one of the joys of life. But what are we eating? Everything we eat is a chemical, but which of these foods is actually useful for our bodies and what happens to the food when we eat it? A balanced diet enables us to stay active and healthy. The major food groups that contribute to a nutritious diet will be discussed in this chapter and chapter 12. The structure of compounds in these food groups has a significant effect on how food is digested, the products formed and how they are used in the body. Everyone knows that food is essential for our survival; it provides nutrients for energy, growth, repair and regulation of body processes. The chemical processes that involve breaking down and building different substances are known as **metabolism**.

Chemical processes that involve breaking down and building different substances in the body are known as metabolism.

Metabolism of food in the body



The many reactions that occur between these organic compounds depend on how the various functional groups interact and the conditions in the particular part of the body. Food is a fuel that provides energy for daily activity, and also at night, to enable our heart, lungs and other organs to keep working effectively.



The human digestive system

The major food groups that our bodies need are proteins, carbohydrates, fats and oils, vitamins and minerals. **Minerals** are inorganic substances required in various amounts for normal body functions. Calcium, for example, is essential for the development of bones and teeth as well as many other roles including muscle contraction, blood clotting and regulation of blood pressure. Iron is an essential part of the haemoglobin protein present in red blood cells. Haemoglobin carries oxygen around the body for respiration. This study of food chemistry focuses on the organic food groups.

TABLE 11.1 Nutrient groups for the body

Food group	Main function in the body
vitamins	small amounts for regulating most metabolic processes including producing energy, growth and development, supporting the immune system and strengthening bones
proteins	for growth and repair of cells, immunity and transport of molecules, and as enzymes, hormones and structural components
carbohydrates	to store and provide energy, for functioning of the central nervous system, and, as fibre, to aid in removing waste from the body
fats and oils	to store some vitamins, to provide energy and insulation, and to maintain cell membranes

Vital vitamins

Vitamins are a group of organic compounds that are essential for growth and nutrition and are required in small quantities in the diet because they cannot be synthesised by the body.

Vitamins can be fat soluble or water soluble.

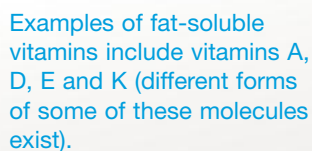
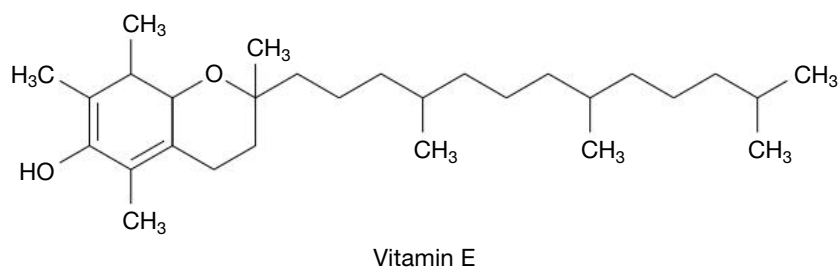
Fat-soluble vitamins include vitamins A, D, E and K.

Vitamins are organic compounds that are needed in minute quantities on a regular basis as part of a healthy diet. Thirteen vitamins are required but they generally cannot be synthesised by humans, except for vitamin D. If, however, vitamins are present in excess or are deficient, diseases such as beriberi, scurvy, anaemia, rickets and skin disorders may occur. Some vitamins can act as coenzymes, which enable a particular enzyme to catalyse a reaction. This will be discussed later in the chapter. Vitamins can be divided into two groups: fat soluble and water soluble.

Fat-soluble vitamins include vitamins A, D, E and K. They can be absorbed in the intestines and moved via the lymphatic system. They are stored in fat deposits and within the liver and may accumulate there. The body converts the antioxidant beta-carotene from orange or dark green vegetables into vitamin A, or it can be obtained from dairy products, fish or liver. Vitamin D is made by the enzyme-catalyzed action of sunlight on cholesterol. Vitamin K can also be produced in small amounts in the intestine by the action of bacteria. Fat-soluble vitamins mainly consist of the elements carbon and hydrogen and consequently form non-polar molecules. This means they contain few if any polar groups and are thus more soluble in non-polar solvents such as fats and oils. The structures on the next page show that vitamins A, D, E and K, with just a few hydroxyl groups, are largely non-polar molecules.

TABLE 11.2 Functions and sources of fat-soluble vitamins

Vitamin	Function	Sources
A	important for vision and immunity	sweet potatoes, carrots, spinach, pumpkin, liver, fish
D	helps the body absorb calcium and phosphorus	sunshine, cod liver oil, salmon, sardines, milk, tuna, mushrooms
E	cell membrane protection	sunflower seeds, almonds, spinach, asparagus, avocado, peanuts, tofu
K	helps blood clot	kale, spinach, spring onions, Brussels sprouts, broccoli, parsley



Water-soluble vitamins dissolve because of the presence of polar functional groups.

Water-soluble vitamins include eight different B-group vitamins and vitamin C. They are absorbed directly into the bloodstream and generally operate in cells to help catalyse cellular reactions. These vitamins do not remain in the body and are excreted through the kidneys in urine if excessive amounts are consumed. They are also more easily destroyed than fat-soluble vitamins by

heat, oxygen and light or just lost in water when boiled. Water-soluble vitamins must therefore be obtained from food on a regular basis, as they cannot be stored. Water-soluble vitamins have functional groups containing oxygen and nitrogen. This causes them to be polar molecules and explains their solubility in water. Other elements that may be present include sulfur, and vitamin B12 contains cobalt.

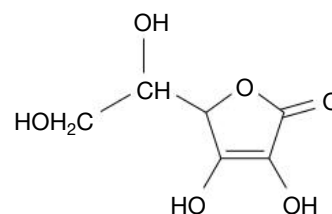
The B-group vitamins assist in breaking down and releasing energy from food. They are required for healthy skin, hair, eyes and liver. The nervous system relies on B-group vitamins to function effectively. Chemical and various refining processes reduce the amount of these vitamins in food, which explains why brown sugar, rice and flour are more nutritious than their white forms. Vitamins play an essential part in metabolism in the body, often by combining with enzymes (protein catalysts), but more about this later.

TABLE 11.3 Functions and sources of water-soluble vitamins

Vitamin	Function	Sources
B1, thiamin	assists in breaking down and releasing energy from food; supports nerve function	wholegrain cereals, seeds, nuts, pork
B2, riboflavin	assists in releasing energy from food and red blood cell formation; supports healthy skin, eyes and nervous system	dairy products, wholegrain breads and cereals, egg white, leafy vegetables, meat, yeast, liver and kidney
B3, niacin	assists in energy production; supports skin health and nervous and digestive systems	meats, fish, poultry, milk, eggs, wholegrain breads and cereals, nuts, mushrooms
B5, pantothenic acid	metabolises food; assists in production of red blood cells and hormones	liver, meats, milk, kidney beans, corn, legumes
B6, pyroxidine	metabolises food; assists in production of red blood cells and hormones; supports nervous system and immunity	poultry, meats, fish and shellfish, seeds and nuts, fish, liver, beans and legumes
B7, biotin	assists in energy production; involved in metabolism of fat	peanuts, leafy vegetables, egg, liver, chicken, yeast, mushrooms
B9, folic acid	assists in production of red blood cells, development of foetal nervous system and DNA synthesis	leafy vegetables, legumes, seeds, liver, poultry, eggs
B12, cyanocobalamin	supports nervous system and production of DNA and red blood cells	meat, liver, fish, cheese, eggs
C, ascorbic acid	maintains healthy immune system; assists in wound healing; helps production of collagen (protein in skin, cartilage, tendons, ligaments, teeth and blood vessels)	red peppers, citrus fruits, kiwi fruit, cantaloupe, broccoli and Brussels sprouts



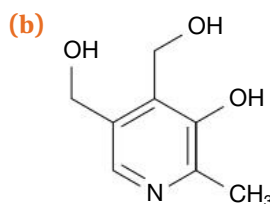
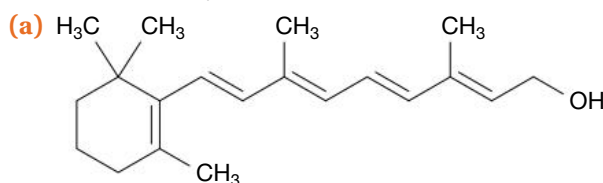
Some sources of vitamin C



Structure of vitamin C (ascorbic acid)

Revision questions

1. Why is it necessary to eat foods containing water-soluble vitamins every day, but this is not the case with fat-soluble vitamins?
2. Explain why it is more likely that an excess of fat-soluble vitamins rather than water-soluble vitamins will cause health problems.
3. Describe whether the following vitamins are water soluble or fat soluble. Give reasons for your answers.

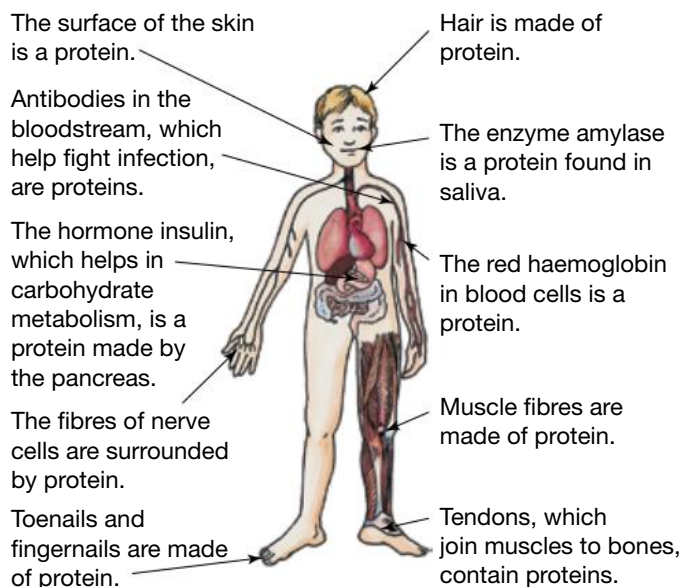


4. What is the molecular formula of vitamin C?

Proteins in the body

Proteins have many roles in the body besides acting as catalysts (as shown in the diagram on the next page). Some are antibodies to prevent infection; some assist with the formation of new molecules by interpreting the genetic information stored in DNA; others act as hormones and transmit signals to coordinate biological processes between different cells, tissues and organs. Proteins provide structural components for cells, assist in movement, and carry atoms and small molecules around the body.

Examples of proteins in the body



All protein molecules contain carbon, hydrogen, oxygen and nitrogen. Some also contain phosphorus and sulfur. Plants can make proteins from inorganic compounds such as nitrates, water and carbon dioxide. Animals cannot make their own proteins directly from the same inorganic starting materials that plants do. They depend on plants or other animals in their food supply for organic compounds that enable them to obtain or synthesise their own protein.

Amino acids — building blocks of proteins

Protein molecules contain C, H, O, N and sometimes P and S. They are present in all cells.

Proteins are polymers built from monomers called **amino acids**. Amino acids are compounds that contain amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) functional groups. Most amino acids have four groups bonded to a central carbon atom: a carboxyl group, an amino group, an *R* group (the amino acid side chain) and a hydrogen atom.

study on

Unit 4

AOS 2

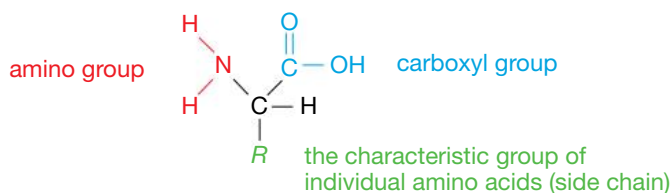
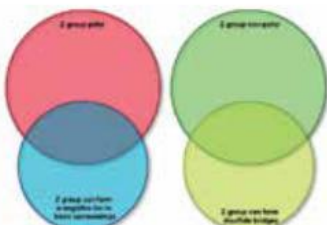
Topic 1

Concept 1



Do more

Properties of amino acids

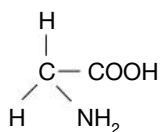


General structure of an amino acid. The functional groups and the characteristic *R* group are all attached to the same carbon atom. Amino acids that are used by cells to synthesise proteins are known as 2-amino acids or α -amino acids.

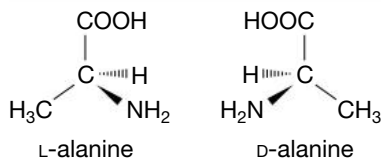
The difference between these amino acids is in the structure of the *R* group. These 2-amino acids can be classified according to the properties of the functional groups in the *R* side groups:

- non-polar: for example, alkyl groups
- polar: for example, alcohols
- acidic: for example, carboxylic acids
- basic: for example, amines.

The simplest 2-amino acid is glycine. Hundreds of other amino acids are known, but only 20 have been found in proteins in the human body. These 2-amino acids are the building blocks of thousands of proteins and are shown in table 11.4.



Structure of glycine



Almost all plant and animal proteins are formed from L-amino acids.

Some amino acids found in proteins are known as **essential amino acids**. These amino acids cannot be synthesised by animals from the other materials in their diets and therefore must be supplied directly in the diet. Essential amino acids vary from species to species. High-protein food is therefore necessary in animal diets so that all of the amino acids necessary for the body to manufacture protein may be obtained.

Except for glycine, amino acids are enantiomers due to their chiral centres, meaning that they are either the L or D form, according to the arrangement of groups around the chiral carbon atom. The molecule synthesised from naturally occurring (+)-glyceraldehyde is considered the D form. It is remarkable, and as yet unexplained, that almost all plant and animal proteins are L-amino acids. This means that enzymes, which are proteins, catalyse reactions only between molecules with the appropriate stereoisomerism. The D form is found in simple organisms such as bacteria and also in some antibiotics that can destroy bacteria by interfering with the proteins required by the bacteria.

TABLE 11.4 Amino acids found in proteins

Name	Abbreviation	Formula	Name	Abbreviation	Formula
alanine	ala	$\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$	leucine ^e	leu	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
arginine	arg	$\text{H}_2\text{NCNHC}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	lysine ^e	lys	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
asparagine	asn	$\text{H}_2\text{NCOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$	methionine ^e	met	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
aspartic acid	asp	$\text{HOOCCH}_2\text{CH}(\text{NH}_2)\text{COOH}$	phenylalanine ^e	phe	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
cysteine	cys	$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$	proline	pro	$\text{C}_5\text{H}_7\text{NO}_2$
glutamic acid	glu	$\text{HOOCCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	serine	ser	$\text{HOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
glutamine	gln	$\text{H}_2\text{NCOCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	threonine ^e	thr	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$
glycine	gly	CH_2COOH $ $ NH_2	tryptophane ^e	trp	$\text{C}_8\text{H}_7\text{NO}_2$
histidine ^e	his	$\text{C}_6\text{H}_7\text{N}_3$ $ $ $\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	tyrosine	tyr	$\text{HO-C}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
isoleucine ^e	ile	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COOH}$	valine ^e	val	$(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$

^e Essential amino acid: one of the 9 amino acids required by humans

Amino acids may exist in different forms depending on the pH of the solution.

study on

Unit 4

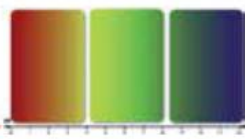
AOS 2

Topic 5

Concept 3

Do more

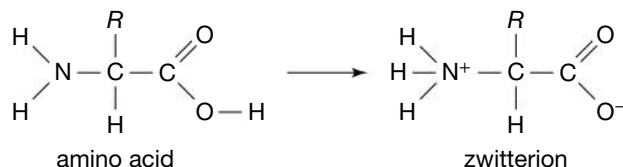
Effect of pH on amino acids



Zwitterions — the dipolar nature of amino acids

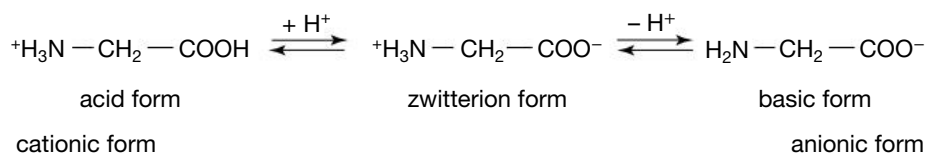
Although amino acids are commonly shown as containing an amino group and a carboxyl group, $\text{H}_2\text{NCH(R)COOH}$, certain physical and chemical properties, including melting points, solubilities and acid-base properties, are not consistent with this structure.

The acid-base properties of carboxyl and amino groups have an effect on amino acid structure. The weakly acidic proton of the carboxyl group easily transfers to the amino group, forming a **zwitterion** or **dipolar ion**. In the pure solid state and in aqueous solutions with an approximately neutral pH, the amino acids exist almost completely as zwitterions.



An amino acid and its corresponding zwitterion

Since amino acids may behave as both acids and bases (that is, they are **amphoteric**), they may exist in several forms, depending on the pH of the solution. Consider glycine, for example — it can lose or gain an H^+ ion. The form of glycine shown in the middle of the figure below is a zwitterion, because it has equal numbers of positive and negative groups, although its net charge is zero.



Glycine in solution

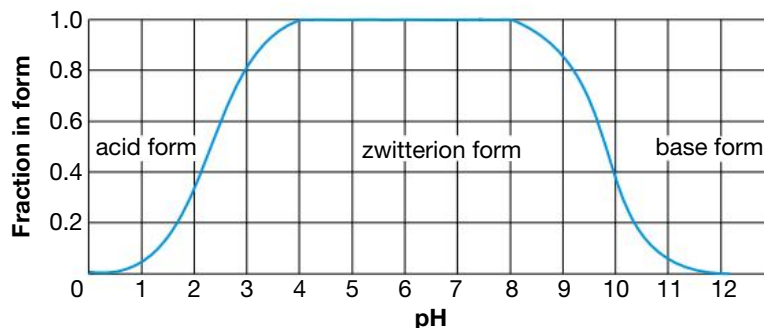
An amino acid may be cationic in an acidic environment, a zwitterion at an approximately neutral pH, or anionic in a basic environment.

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Glycine — amphoteric behaviour
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In an acidic environment, the zwitterion behaves as a base because the carboxyl groups combine with the increasing concentrations of H^+ to form uncharged $-\text{COOH}$ groups. The remaining ammonium group then gives the molecule a net positive charge (cationic form). In a basic environment, the zwitterion behaves as an acid because the ammonium group loses H^+ when the concentration of H^+ is lowered, leaving an uncharged amino group. The molecule then has a net negative charge from the remaining carboxyl group (anionic form).



The form of an amino acid varies with pH. This graph shows the fraction of glycine present as the zwitterion plotted against pH values. The fraction not present as a zwitterion exists as a cation in acidic solutions (left) and as an anion in basic solutions (right).

Revision questions

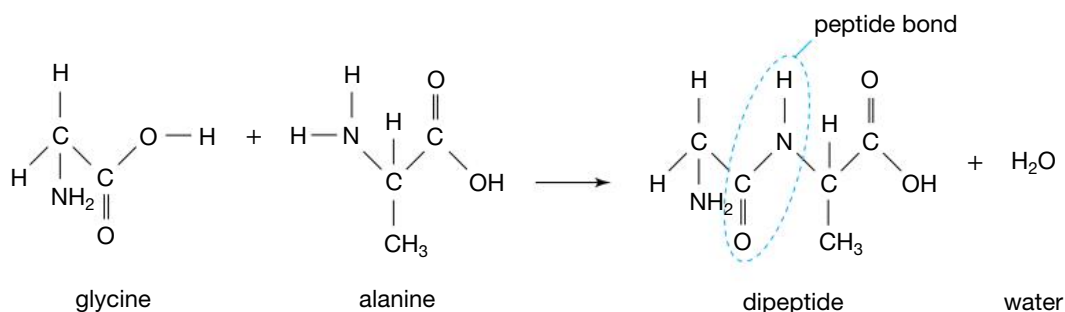
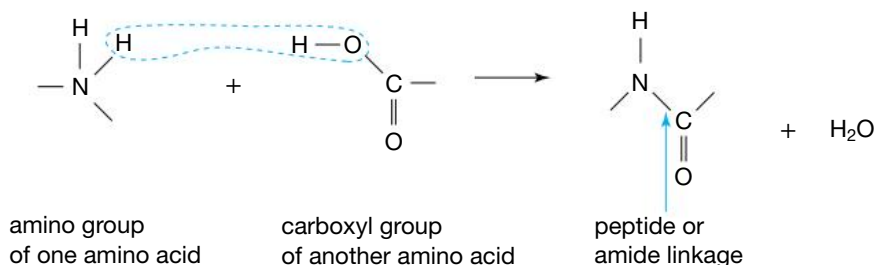
5. Name and draw the two functional groups present in amino acids.
6. Explain why glycine does not form a stereoisomer.
7. Draw the structure of the amino acid serine in a basic solution.
8. State two examples of amino acids with acidic side chains.

Formation of proteins

Amino acids combine to form peptides in a condensation reaction.

Amino acids react to form peptides. The carboxyl group of one molecule reacts in a polymerisation reaction with the amino group of another amino acid molecule to form a **peptide**, or **amide, linkage** between them.

Formation of an amide linkage, also known as a peptide linkage when part of a peptide or protein



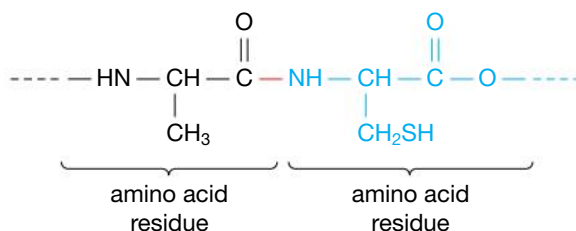
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Experiment 11.1 Investigating proteins
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Since water is produced when a peptide link is formed, this reaction between amino acids to form peptides is an example of a condensation reaction. When two or more amino acids combine to form a peptide, what remains of each amino acid is called an amino-acid residue.

Depending on the number of amino acid residues per molecule, the peptides formed from the condensation reactions of amino acids are known as dipeptides, tripeptides and so on, and finally **polypeptides**, which are the result of condensation polymerisation reactions. Note that, when drawing segments of proteins, it is necessary to show the open bonds at each end by using dashes where the next amino acid residue would be attached. Peptides of molar mass up to about 5000 g mol⁻¹ (about 50 amino acid units) are known as polypeptides; even larger peptides are called **proteins**.

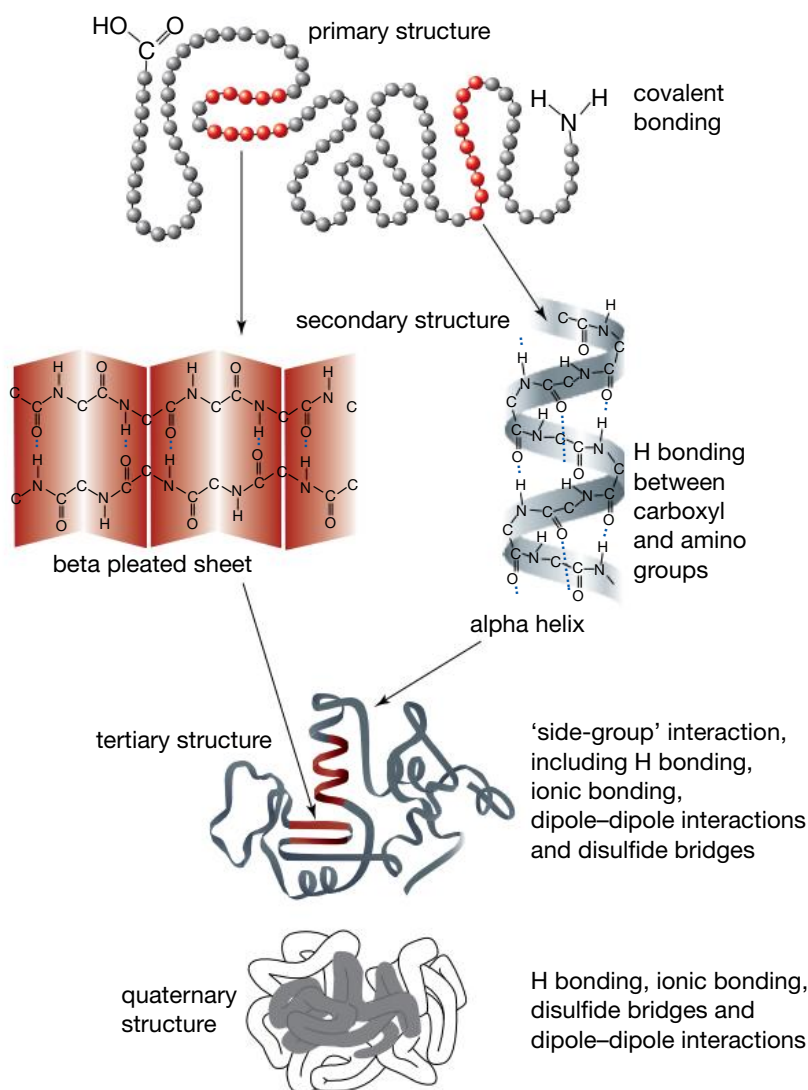


Amino acid residues

The formation and performance of proteins within the human body results from energy generated at the cellular level. The proteins formed may be fibrous (keratin, collagen) or globular (haemoglobin, most enzymes) in structure. Fibrous proteins are insoluble in water, but globular proteins are soluble.

Structure of proteins

The order of amino acids covalently bonded in a polypeptide chain is referred to as its **primary structure**. Different parts of the chain form into coils, pleats or folds due to hydrogen bonding between the C=O and N—H bonds in peptide links at different positions on the chain; this is known as the **secondary structure**. Bonding between side chains of the amino acids results in a complex three-dimensional shape, the **tertiary structure**; this may involve hydrogen bonding, ionic bonding or disulfide bridges. Cysteine is the only amino acid that can form disulfide bonds. A covalent bond between two cysteine molecules is known as a disulfide bridge. They stabilise protein structures and keep them in particular conformations. A **quaternary structure** is formed when individual protein molecules link together in a particular spatial arrangement. The shape of a protein determines its properties and function, and it loses its function if the shape is altered (which is called '**denaturing**') such as by changes in temperature or pH.



Revision questions

9. Draw the two possible dipeptides formed between alanine and aspartic acid, and circle the peptide link.
10. Calculate the molar mass of the dipeptide formed in question 9.
11. Which type of bonding is found in both the secondary and tertiary structures of proteins?
12. What is the strongest form of intermolecular bonding that could involve the residue of the amino acid glutamic acid?

Enzymes are biological catalysts. They lower the activation energy of reactions to enable the reaction to proceed.

Activation energy profile for enzyme-catalysed and non-enzyme-catalysed reactions

An enzyme speeds up a chemical reaction. Each enzyme has an active site.

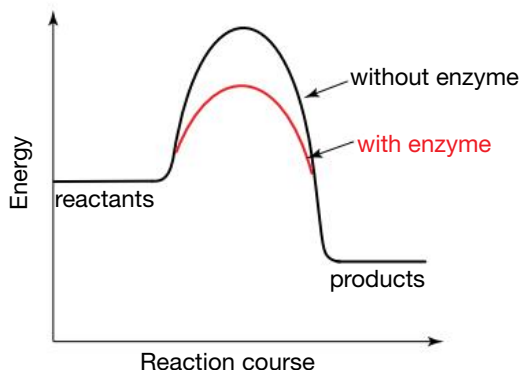
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Experiment 11.2 Action of enzymes
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Enzymes as protein catalysts

Most metabolic processes require **enzymes** to ensure that reactions occur fast enough to maintain life. Enzymes are biological catalysts. They lower the activation energy of reactions to enable the reaction to proceed. Enzyme names usually end in *-ase*, except for pepsin, rennin and trypsin. For example, lactase breaks down lactose, which is a milk sugar, sucrase breaks down complex sugars and starch, protease digests proteins, and lipase breaks down fats.

Enzymes cause reactions to occur up to millions of times faster than without enzymes. Like inorganic catalysts, enzymes speed up reactions by providing an alternative reaction pathway of lower activation energy. In chemical reactions, for two molecules to react, they must collide with one another with sufficient energy to overcome the energy barrier to the reaction. This is called the activation energy. As shown in the figure below, enzymes lower the activation energy of a reaction.



Most inorganic catalysts are not very selective and can speed up many different chemical reactions. Enzymes, however, are very specific. Each enzyme catalyses one specific reaction. The specificity lies in the shapes of the enzyme molecules. Like all catalysts, enzymes remain unchanged at the end of the reactions they catalyse. Enzymes alter the rates of reactions but not the position of the equilibrium.

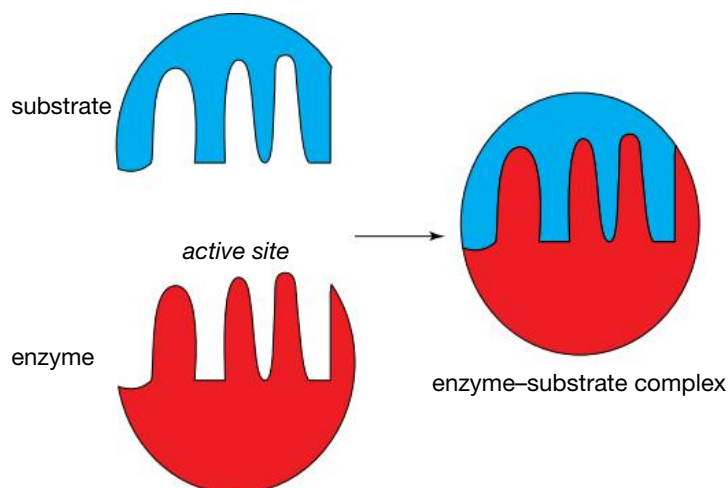
The structure and action of enzymes

Every enzyme has a unique three-dimensional shape, which is determined by the nature of the bonding and side chains of the amino acid residues in the protein. As a result of their structure, many enzymes have an **active site** into which the reactant molecule (called a **substrate**) is manoeuvred. The active site of each type of enzyme is unique; it is at the active site that the substrate is converted to a product molecule. There are two models proposed to explain the action of enzymes: the lock-and-key model and the induced fit model.

In the **lock-and-key model**, only molecules with complementary shapes can react with the enzyme. Enzyme action may be compared to a key fitting

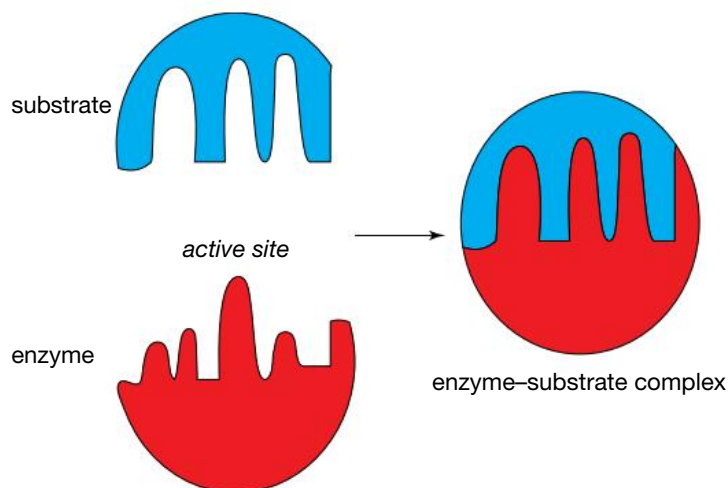
into a lock; only a key with a particular shape can open the lock. It is important to remember that enzymes are three-dimensional and chiral, so they are highly stereoselective. Only one enantiomer can fit into the active site of the enzyme and therefore react. It is just like having a gloved hand that binds to a substrate.

Lock-and-key model — the substrate and enzyme active site have complementary shapes.



The **induced fit model** suggests that, in the presence of the substrate, the active site may change in order to fit the substrate's shape. The shape of the active site is not an exact match but may change shape in the presence of a specific substrate to become complementary and then return to its original shape after the reaction.

Induced fit model — the enzyme active site forms a complementary shape to the substrate after binding.



Coenzymes — enzyme helpers

Coenzymes are organic non-protein molecules that assist the functioning of enzymes.

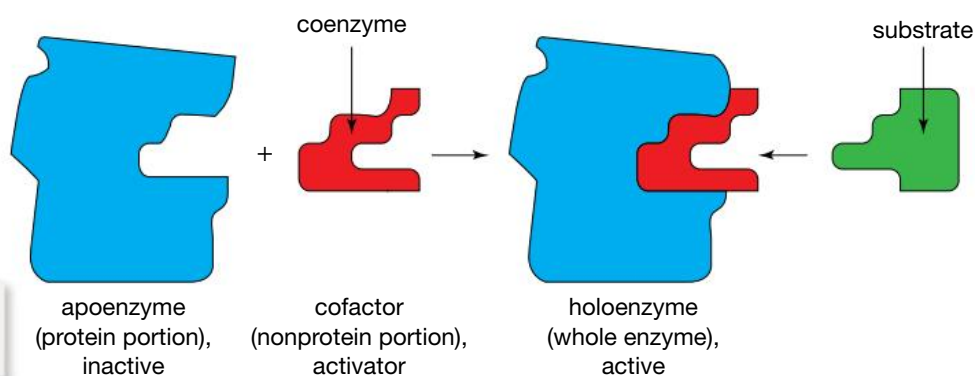
Some enzymes need a little help in order to act as catalysts. This assistance is provided by **coenzymes**. Coenzymes are organic non-protein molecules that are required to temporarily and loosely bind with the protein molecule (apoenzyme) to form the active enzyme (holoenzyme).

Their role is to act as intermediate transporters of electrons, particular atoms (such as H) or functional groups that are transferred in the final reaction. Once the reaction is completed, they then move away. The removal or addition of electrons, atoms or groups can change the shape of the coenzyme, allowing it to bind or be removed from an enzyme they are helping.

Whereas enzymes are specific to a substrate, coenzymes can assist a number of different enzymes. Coenzymes are altered as a consequence of the reaction and may then be reformed. Several important coenzymes are derived from vitamins such as vitamins B1, B2 and B6. An example of a coenzyme is NAD⁺, nicotinamide adenine dinucleotide. The nicotinamide part of the molecule comes from vitamin B3, niacin. NAD⁺ transfers hydrogen away from one molecule in a dehydrogenase reaction and takes it to another molecule.

TABLE 11.5 Examples of coenzymes

Vitamin	Coenzyme	Role
B1, thiamin	thiamine pyrophosphate (TPP)	transfers aldehydes
B2, riboflavin	flavin adenine dinucleotide (FAD)	oxidising agent (transfers electrons)
B3, niacin	nicotinamide adenine dinucleotide (NAD ⁺)	oxidising agent (transfers electrons)
B5, pantothenic acid	coenzyme A (CoA)	transfers acetyl group (CH ₃ CO—)
B12	coenzyme B-12	transfers alkyl groups
	adenosine triphosphate (ATP)	transfers phosphate

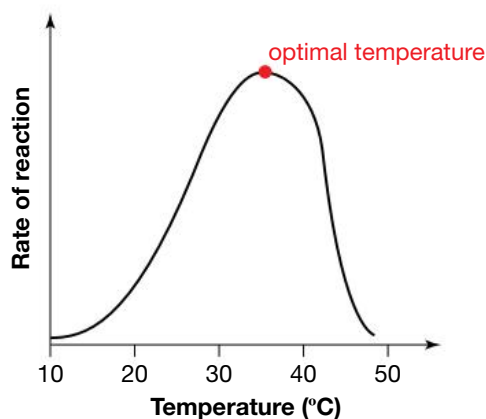


How a coenzyme assists an enzyme

Factors affecting the action of enzymes

Temperature

Enzymes can operate only at body temperatures. Each enzyme has an optimum temperature and pH range for maximum activity.



For every enzyme, the rate of reaction increases with an increase in temperature, up to an optimum temperature. As the temperature increases past the optimum range, the enzyme begins to denature and its catalytic properties are decreased.

As temperature increases, reacting molecules gain more energy and increase their chances of successful collisions, thereby increasing the rate of a reaction. For an enzyme, however, there is a temperature at which it performs its catalytic activities most quickly. This temperature is known as the optimum temperature; for most enzymes in the human body, this is around 37.5 °C. As

Enzyme activity is affected by pH and temperature changes. Enzymes operate to their maximum effect at a specific pH and temperature.



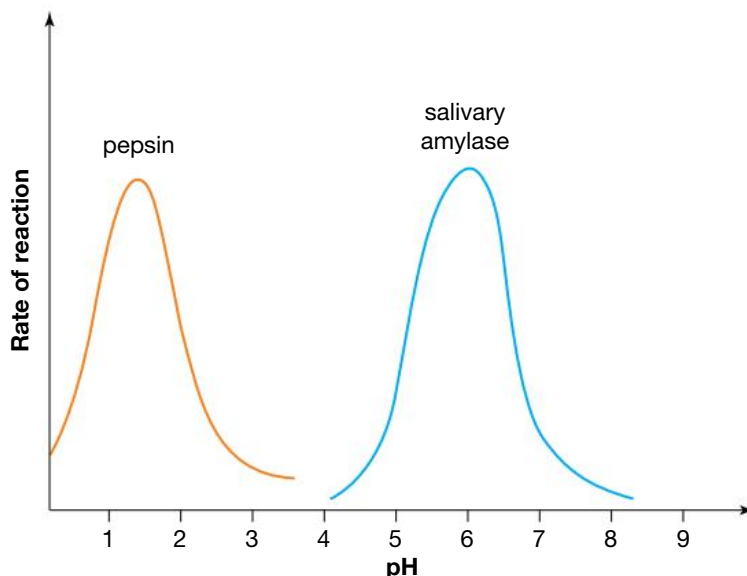
The protein in egg white is denatured when the egg is heated.

Effect of pH on enzyme activity

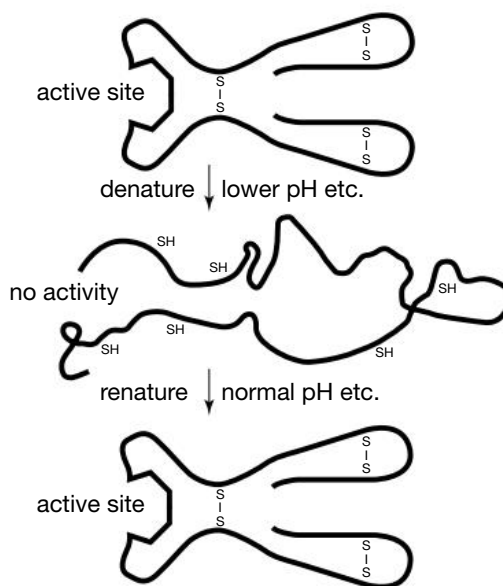
shown in the graph on the previous page, the rate of reaction starts to decline as the temperature rises above this temperature. Denaturing can be irreversible, as in the case of frying an egg. The albumen protein in the egg white denatures and becomes insoluble when heated.

pH level

Enzymes are also affected by pH due to uptake and release of protons, which affects the attractions between sections of the protein. Different enzymes have different optimum pH levels because of the carboxyl or amino functional groups on the side chains of the amino acids present. Enzymes begin to denature if the pH of their environment goes outside their optimum range. For example, pepsin works best in the acid conditions of the stomach.



Denaturation is due to the collapse of intra- and intermolecular bonds that maintain the shape in the quaternary, tertiary and secondary structures of the enzyme. The primary structure, with its strong covalent bonds, is not affected. Higher temperatures and extreme pH values disrupt the protein structure and alter the shape of an enzyme, hence altering the enzyme's active site and destroying its catalytic activity.

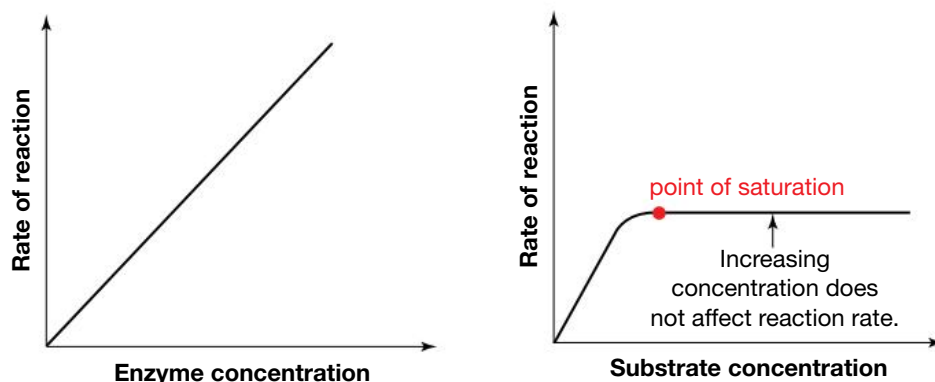


Denaturation of the protein structure by heating or extremes of pH reduces the activity of an enzyme by altering the active site. In a few cases, the protein can be renatured.

Concentration

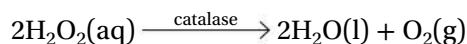
The rates of enzyme-catalysed reactions depend on the concentrations of the enzymes and the substrates. If temperature and pH are at optimum levels, an increase in the concentration of the enzymes increases the rate of reaction proportionally. For a given enzyme concentration, the rate of its catalytic reaction increases with increasing substrate concentration up to a point of saturation, above which any further increase in substrate concentration produces no significant change in reaction rate. This is because the active sites of the enzyme molecules at the given concentration are saturated with substrate. Once saturation is reached, dissociation of the enzyme-substrate complex is required to free up active sites for further reaction.

The rate of an enzyme-catalysed reaction can be increased in two ways: by increasing the enzyme concentration or by increasing the substrate concentration. However, increasing the substrate concentration increases the rate of reaction only up to the point at which the active sites of the enzyme are saturated with substrate molecules.



Measuring enzyme activity

Investigating the rate of an enzyme-catalysed reaction can provide an indication of the enzyme activity under different conditions. A possible experiment involves the use of catalase, which is present in plant and animal cells. Catalase breaks down hydrogen peroxide, H_2O_2 , which is produced during metabolism but is toxic if it builds up in a cell. The reaction that occurs is:



Yeast is one of a number of possible sources of catalase. The source of the enzyme or the conditions used can be varied and the rate of oxygen production measured.

Revision questions

13. What are the similarities and differences between the lock-and-key and induced fit models of enzyme function?
14. What are coenzymes?
15. Explain the effect of increasing the temperature of an enzyme beyond its optimum range.

Digestion of protein

During digestion, protein is hydrolysed by the enzyme pepsin to produce amino acids. These amino acids are reassembled in tissues to make new proteins.

In adults, proteins are hydrolysed by an enzyme called pepsin. In this reaction, water is added across the peptide link. The **hydrolysis** of protein using pepsin produces a mixture of polypeptides. However, these are still too large to be absorbed into the bloodstream and need further digestion in the intestine. Pepsin, unlike most protein-digesting enzymes, works efficiently in the acidic environment of the stomach, but becomes inactive in the alkaline environment of the intestine.

Protein-rich food



After partial digestion in the stomach, proteins are further hydrolysed when they reach the small intestine to form amino acids. When food enters the duodenum, the pancreas is stimulated to secrete a number of digestive enzymes, including trypsin and chymotrypsin.

The amino acids then pass into the bloodstream and are carried to tissues where they may be reassembled to form new protein. The enzyme-catalysed hydrolysis reactions for the digestion of protein are the reverse of the condensation reactions by which they were formed originally. The functional groups on the amino acid residues form covalent bonds with the atoms from the water, resulting in breakage of the peptide link.

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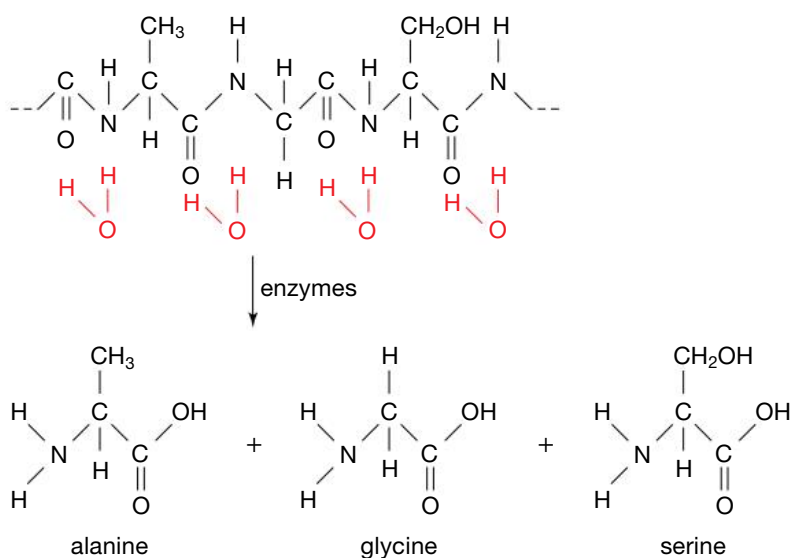
Unit 4

AOS 2

Topic 5

Concept 1

See more
Hydrolysis of
proteins

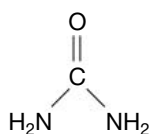


It is important to note that hydrolysis involves the breaking of strong covalent (peptide) bonds, whereas denaturation involves the breaking of weak bonds (dispersion forces, hydrogen bonds).

What happens to digested protein?

The end products of protein digestion, amino acids, are absorbed into the bloodstream so that they can be used by the cells in the body to build up new protein. However, we usually eat and digest more protein in a day than

Unused amino acids are broken down in the liver to form ammonia, and then further broken down to form urea, which is then eliminated in urine. The formula for urea is $(\text{NH}_2)_2\text{CO}$.



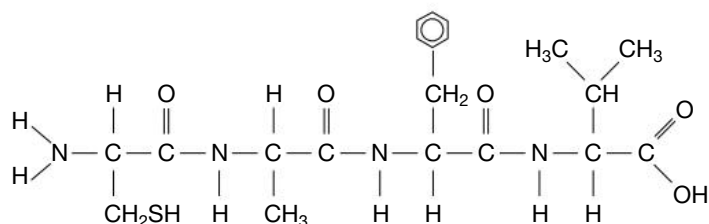
The structure of urea

is required by the body. The amino acids not used directly by the body are broken down in the liver in a process called deamination. In this process the amino, —NH_2 , group is converted to ammonia. The ammonia, in turn, is converted to urea and excreted, or used for the synthesis of other amino acids. Specific enzymes are required for this multi-step process to occur.

Ammonia is toxic if allowed to build up in the body, whereas urea is harmless, even in high concentrations. The remainder of the protein molecule, made up of carbon, hydrogen and oxygen, can be converted to glucose, fat (for storage) or other amino acids.

Revision questions

- 16.** Write a possible sequence of equations for the hydrolysis of the following polypeptide.



- 17.** What is the molecular formula of urea? What is its molar mass?

Chapter review

Summary

- Vitamins are a group of organic compounds that are essential for growth and nutrition and are required in small quantities in the diet because they cannot be synthesised by the body.
- Vitamins are categorised according to their solubility in water or fat; this is explained by the functional groups present.
- Water-soluble vitamins are the B-group vitamins and vitamin C. They cannot be stored in the body so need to be regularly ingested. They are unlikely to be toxic because they are excreted in urine. B-group vitamins can be converted to coenzymes.
- Fat-soluble vitamins, such as A, D, E and K, are stored in the liver. They could become toxic due to build up and are more stable to heat than water-soluble vitamins.
- Proteins are made up of carbon, hydrogen, oxygen and nitrogen. Some also contain sulfur. They are formed by the condensation polymerisation of amino acid units — the amino functional group of one amino acid reacts with the carboxyl functional group of another, and water is eliminated.
- There are 20 amino acids in biological systems in the body. Essential amino acids cannot be synthesised by animals from other materials in their diet; they must be supplied by the diet. Non-essential amino acids can be synthesised within the body from other materials in the diet.
- Amino acids form a dipolar ion called a zwitterion, due to the acid-base properties of the carboxylic acid and amino functional groups. Amino acids are amphoteric; that is, they may behave either as an acid or as a base, depending on the pH of the solution. In aqueous solutions with an approximately neutral pH, amino acids exist as zwitterions.
- Proteins have four structural levels:
 - primary structure — the number, sequence and type of the amino acids in the chains. Only strong covalent bonds are involved.
 - secondary structure — the helices, folds and pleats due to hydrogen bonding with non-*R*-group nitrogen and oxygen in small segments of the protein chain
 - tertiary structure — the three-dimensional shape of the protein, which is the result of interactions between different side-chain groups and involves dispersion forces, hydrogen bonding, ionic bonding and disulfide bridges
 - quaternary structure — the way the constituent protein branches are held together in space when separate polypeptide chains interact with each other. This involves hydrogen bonding, disulfide bridges, ionic bonding and dipole–dipole interactions.
- Proteins are sensitive to extremes in pH, heat and some chemicals. Proteins denature by unfolding when subjected to changes in pH or extreme conditions. They can become insoluble or lose biological activity.
- Enzymes are proteins that act as catalysts for the chemical reactions occurring in living things. They are highly specific, with each different type of enzyme catalysing only one chemical reaction. Each enzyme has an active site at which the reaction is facilitated. Enzymes operate in mild conditions; extremes of temperature and pH denature the enzyme, altering the active site and leading to a loss in activity.
- Amino acids that form proteins are the L-form, so alternate optical isomers do not fit in the active site of enzymes in the body.
- Coenzymes are organic non-protein molecules which assist the functioning of enzymes
- Digestion of proteins involves hydrolysis reactions where peptide bonds are broken. Nitrogen from proteins is excreted as urea.

Multiple choice questions

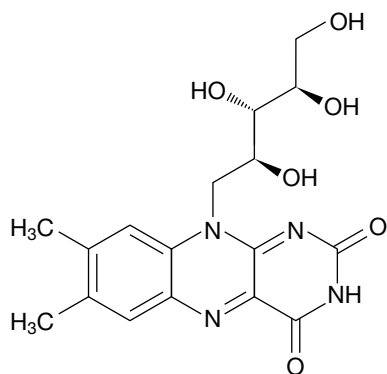
1. Vitamins may be categorised as:
 - A organic and inorganic
 - B fat-soluble and water-soluble
 - C essential and non-essential
 - D mixtures and compounds.
2. Which of the following statements is *incorrect* about fat-soluble vitamins?
 - A Excess amounts are readily excreted from the body.
 - B They can be consumed less frequently than the water-soluble vitamins.
 - C They are bound to proteins when travelling in the blood.
 - D They may accumulate to toxic amounts in the body.
3. Which of the following is not a good source of vitamin D?
 - A Fatty fish
 - B Sunshine
 - C Milk and margarine
 - D Fruit and vegetables
4. Vitamins are essential because the body:
 - A cannot synthesise these compounds at all
 - B can synthesise these compounds partially
 - C cannot synthesise these compounds in the adequate amounts required
 - D none of the above.

5. Vitamin C is considered a vitamin that is:
A water soluble **C** fat and water soluble
B fat-soluble **D** none of these.
6. Which vitamin is part of coenzymes NAD and NADP and is involved in hydrogen transfer?
A Vitamin C **C** Vitamin D
B Vitamin K **D** Vitamin B3
7. Excess intake of fat-soluble vitamins is stored in which part of the body?
A Stomach **C** Gall bladder
B Duodenum **D** Liver
8. The —NH_2 functional group is:
A an amino group
B a hydroxyl group
C a peptide group
D an amide group.
9. Which functional groups are involved in forming peptide bonds?
A The carboxyl group on two amino acids
B The carboxyl group on one amino acid and the amino side chain on another
C The amino group on both amino acids
D The amino group on one amino acid and the carboxyl group on another
10. What does the primary structure of a protein refer to?
A The covalent bonds that hold the protein in a particular shape
B The hydrogen bonds between sections of the amino acid side chains
C The amino acid sequence of the protein
D Whether it is globular or fibrous
11. The most common covalent cross-links are sulfur-sulfur bonds that form between two amino acids. Which amino acid has this side chain?
A Glycine **C** Cysteine
B Methionine **D** Proline
12. Which of the following terms refers to the overall three-dimensional shape of a protein?
A Primary structure
B Secondary structure
C Tertiary structure
D Quaternary structure
13. What is the strongest form of intermolecular bonding that could be formed involving the residue of the amino acid valine?
A Ionic bond
B Hydrogen bond
C Dispersion forces
D None of the above
14. Select the correct numbers to complete the following sentence.
 There are ___ essential amino acids in the total of ___ amino acids used in the body.
A 11, 20 **C** 9, 11
B 9, 20 **D** 20, 9
15. Which of the following terms refers to the sequence of different amino acids in a protein?
A Primary structure
B Secondary structure
C Tertiary structure
D Quaternary structure
16. The globular shape of a protein is called the:
A primary structure
B secondary structure
C tertiary structure
D quaternary structure.
17. The formation of carbohydrates, proteins and lipids in the human body requires numerous enzymes. Which of the following statements about enzymes is *incorrect*?
A Enzymes operate within narrow pH ranges.
B The catalytic action of enzymes increases with increasing temperatures up to 100°C .
C Enzymes specifically catalyse particular chemical reactions.
D Enzymes are proteins.
18. Select the best definition of an enzyme.
A An enzyme is an amino acid that speeds up chemical reactions.
B An enzyme is a protein that is consumed in the diet and aids in chemical reactions.
C Enzymes are proteins that speed up metabolic reaction and are consumed in the process.
D Enzymes are proteins that speed up metabolic reaction but are not consumed in the process.
19. Identify the *incorrect* statement about protein denaturation.
A It is a shape change.
B It is always irreversible.
C It may be caused by a pH change.
D It could result from a temperature change.
20. Which process causes the primary structure of a protein to be destroyed?
A Hydrolysis
B Denaturation
C Polymerisation
D Condensation
21. Hydrolysis of proteins involves:
A adding water to amino acids to form proteins
B adding water to proteins to form amino acids
C water forming hydrogen bonds in the secondary structure of proteins
D water forming hydrogen bonds in the tertiary structure of proteins.
22. Excess amino acids in the body are broken down to form urea in the:
A pancreas
B liver
C bladder
D kidneys.

Review questions

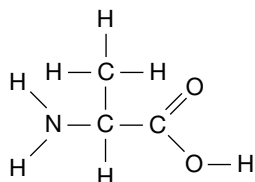
Vitamins

- (a) What is a vitamin?
(b) What role do vitamins play in the body?
- Explain why vitamin C is soluble in water and why vitamin D is insoluble. What implications does this have on the possibility of deficiency or excess vitamins in the body?
- (a) Name the functional groups present in the following vitamin.
(b) Determine whether this vitamin would be soluble in water or fat.



Proteins

- The amino acids cysteine and serine can react with each other to form a dipeptide.
 - State the type of reaction occurring when amino acids react together, and identify the other product of the reaction.
 - Draw the structures of the two possible dipeptides formed in the reaction between one molecule each of cysteine and serine.
- Explain why alanine (below) is described as an enantiomer.

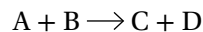


- Polypeptides and proteins are formed by the condensation reactions of amino acids.
 - Draw the structural formula of threonine, and label the carboxyl and amino groups.
 - Give the structural formula of a dipeptide formed by the reaction of glycine and threonine. State the other substance formed during this reaction.
 - Explain why threonine is considered to be optically active whereas glycine is not.
 - State two functions of proteins in the body.

- When many amino acid molecules react together, a protein is formed. These proteins have primary, secondary, tertiary and quaternary structures.
 - State the type of intermolecular force responsible for maintaining the secondary structure.
 - State two other ways in which the tertiary structure of the protein is maintained.
- Suppose you want to synthesise tripeptides using the amino acids alanine, glycine and aspartic acid.
 - How many different tripeptides can be prepared using each amino acid only once?
 - How many different tripeptides can be prepared using any of the three amino acids in any of the three positions if you can use each more than once?
 - Write a balanced equation for the formation of a tripeptide, indicating which functional groups react and which by-products are formed.
- Variations in pH affect amino acids and the proteins they form. Describe, using structural formulas, where appropriate, how amino acids and proteins are affected by changing pH.

Enzymes

- Enzymes are organic catalysts that operate in living things to facilitate chemical reactions essential to life. They are often referred to as 'biological catalysts'. List the differences between enzymes and inorganic catalysts. Include reference to mode of function, specificity and the conditions under which they are employed.
- Define the following terms.
 - Enzyme
 - Enzyme specificity
 - Active site
 - Coenzyme.
- Explain why the mechanism of action of an enzyme is sometimes referred to as a 'lock-and-key' mode of operation.
 - Imagine you want to use a catalyst to speed up the following reaction.



Draw a diagram that shows how an enzyme can facilitate this reaction. Label the substrate and active site.

- Describe the differences between enzymes and coenzymes.
- Define the term 'denaturation'.
 - List three ways in which an enzyme may be denatured.
- Milk that has gone past its 'use by' date curdles and develops a sour taste. This is caused by the production of lactic acid by the lactose-fermenting bacteria naturally present in milk. This increased

acid production leads to a decrease in pH that causes the milk protein caseinogen to first denature and then coagulate.

- (a) Explain, using a diagram, how caseinogen is denatured.
 - (b) Explain why the secondary structure of caseinogen is affected whereas the primary structure is unaffected.
- 16.** Digestive enzymes can be incorporated into washing powders. Instructions recommend that clothes are not boiled with the powder but, rather, that they are allowed to soak overnight.
- (a) Explain the reason for the recommendation regarding effective use of the powder.
 - (b) Explain why digestive enzymes would be used.
 - (c) Describe the action of an enzyme.
- 17.** Why can fresh bloodstains be easily removed in cold water but not in hot water?
- 18.** Meat and fish can be marinated (soaked) in fruit juices such as lime or pineapple juice to make them more tender.
- (a) Explain how some fruit juices may tenderise meat.
 - (b) Suggest why the juice from canned pineapples does not tenderise meat.
- 19.** Design an experiment to test the effect of different pH on enzyme activity.



Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Multiple choice questions

1. Why do water-soluble vitamins have to be taken in the diet more frequently than fat-soluble vitamins?
 - A They are metabolised faster than the fat-soluble vitamins.
 - B There are no general stores, as any excess taken in the diet is excreted.
 - C Only small amounts are present in foods.
 - D They are destroyed by bacteria in the digestive system.

1 mark
2. Two 2-amino acids that contain sulfur atoms are:
 - A cysteine and serine
 - B cysteine and threonine
 - C methionine and cysteine
 - D methionine and serine.

1 mark
3. The function of a protein depends on its three-dimensional structure. This structure can be disrupted, denaturing the protein. Which of the following changes could cause denaturing?

Change 1: the addition of a strong acid
Change 2: a significant increase in temperature
Change 3: a significant decrease in temperature

 - A Change I only
 - B Changes I and II only
 - C Change III only
 - D Changes I and III only

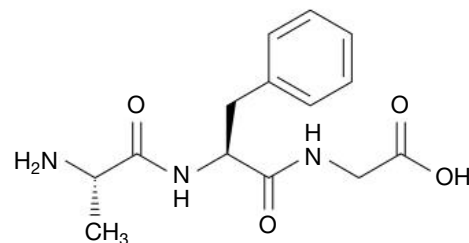
1 mark
4. Amino acids may be formed in humans by the digestion of proteins in the food that is eaten. Which of the following is true of most amino acids?
 - A The amino acids found in the human body may all be classified as essential, rather than non-essential, amino acids.
 - B Amino acids may act as both acids and bases.
 - C Amino acids can undergo addition polymerisation, forming polypeptides.
 - D Amino acids are highly soluble in non-polar solvents.

1 mark
5. The percentage of oxygen by mass in the amino acid glutamine is 32.9%. In a polypeptide formed from glutamine, the percentage of oxygen by mass is:
 - A 32.9%
 - B greater than 32.9%
 - C less than 32.9%
 - D unable to be determined from the information provided.

1 mark

Extended response questions

1. Circle and label the peptide links in the following structure, and name the amino acids used to produce the tripeptide.



3 marks

2. Serine is an α -amino acid that has a side chain group $\text{—CH}_2\text{OH}$.

(a) Draw the structure of serine.

1 mark

(b) Draw the structure of serine at low pH.

1 mark

(c) Draw the structure of serine at high pH.

1 mark

(d) Draw the structures of the two possible dipeptides that may form when a molecule of serine reacts with a molecule of glycine.

2 marks

3. Describe two differences between organic and inorganic catalysts.

2 marks

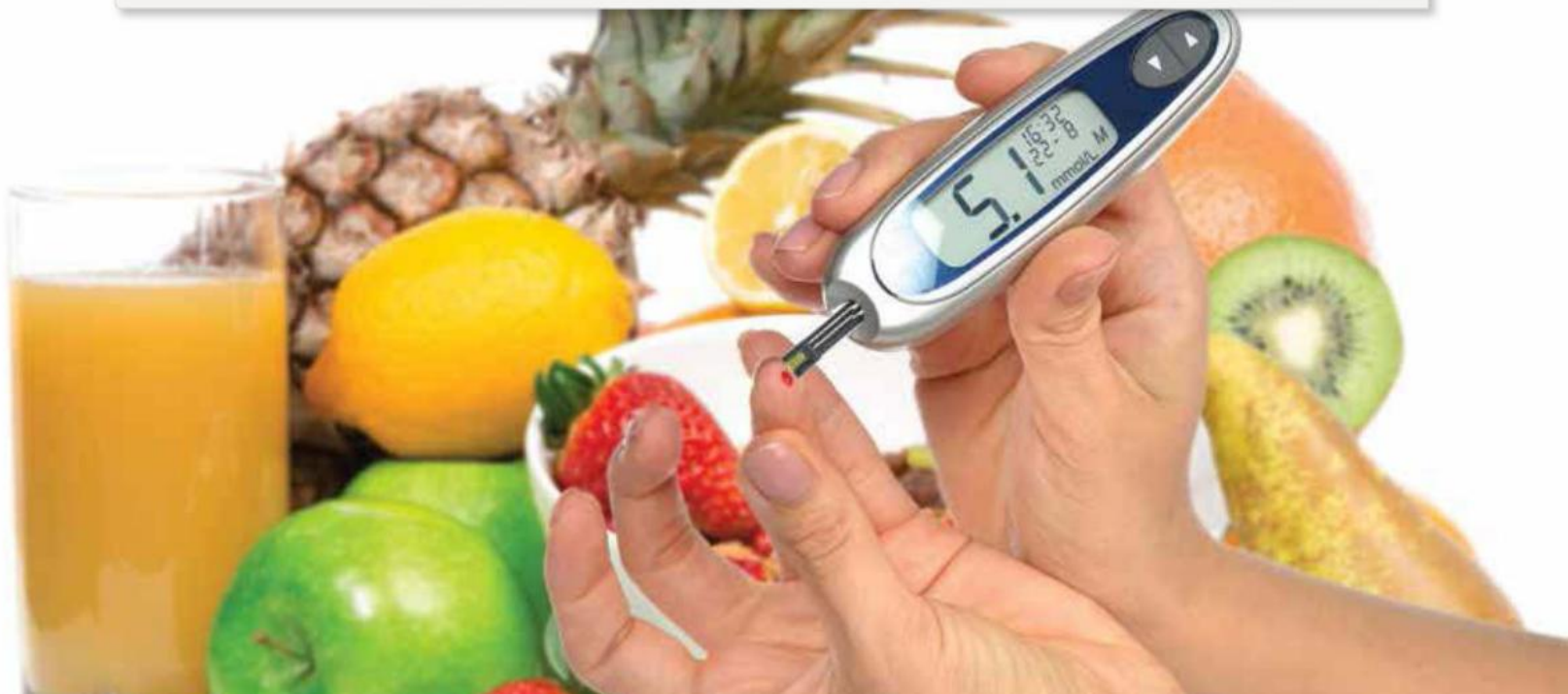
This chapter examines the structure and reactions of carbohydrates. It also discusses their significance in the human diet and how the type of carbohydrate is related to the glycaemic index. The artificial sweetener aspartame is compared with natural sweeteners. Furthermore, the structure and reactions of fats and oils in the body as well as different types of fatty acids are described. The energy content of foods is outlined and how it can be measured using calorimetry.

YOU WILL EXAMINE:

- carbohydrates
- the formation and structure of simple sugars
- the formation and structure of complex carbohydrates
- a comparison of structures and energy contents of glucose, fructose, sucrose and aspartame
- the digestion of carbohydrates
- lactose intolerance
- glucose and glycaemic index
- the properties and reactions of fats and oils
- essential fatty acids
- oxidative rancidity in foods
- the energy content of foods
- the principles of calorimetry.

Plants have an amazing ability. They can capture sunlight and use it to turn carbon dioxide and water into glucose, a molecule that is critical for life. Another name for glucose is blood sugar; it is an essential energy source not just for the muscles but also for the brain. Glucose levels vary during the day, but the body regulates the levels so that the change is not excessive.

After we eat, the glucose level in the blood rises and the pancreas releases a hormone, insulin, which is necessary to convert glucose to energy. Unhealthy levels of glucose in the blood can lead to health problems. For example, people with diabetes cannot produce enough insulin, or the body does not respond to the insulin properly. Diabetics can monitor and manage glucose levels, which are measured in mmol^{-1} (mM). Excessively high glucose in the bloodstream is a condition called hyperglycaemia, whereas too little glucose is known as hypoglycaemia. In this chapter, we look at the breakdown of food for energy and also how the energy in food can be measured.



Energy and food

Athletes sometimes take sports drinks to give them a boost of energy. Vigorous exercising can result in the rapid loss of fluids, particularly if the weather is hot; sports drinks can help replace the lost water, sugar and salt. Research tells us that ordinary water provides adequate hydration for everyone except elite

athletes, but sports drinks continue to be popular despite problems with excess sugar intake. What is in these sports drinks that is absorbed quickly and readily provides energy?



Sports drinks can help replace water, sugar and salt lost during exercise.

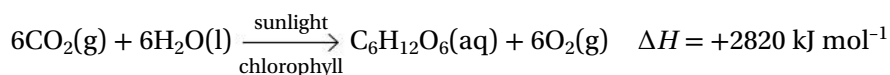
Glucose is formed from water and carbon dioxide during photosynthesis.

Monosaccharides (simple sugars) are the monomers of carbohydrates. They are not broken down during digestion.

Types of carbohydrates

The sugar in sports drinks helps replace the fuel that your body has used during exercise. The sugar is a simple carbohydrate, glucose, that is stored in the liver or muscles. It is readily available because it requires less oxygen to react than either protein or fat. **Carbohydrates** are molecules made up of carbon, hydrogen and oxygen. Their general formula can be represented as $C_x(H_2O)_y$.

Most carbohydrates in our food originate from plants, in the form of glucose, and are produced through the process of photosynthesis.



The glucose formed during photosynthesis may then be used by the plant to form complex carbohydrates through polymerisation reactions.

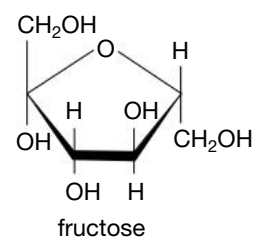
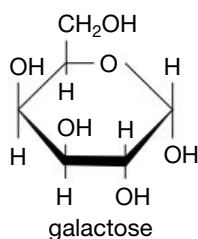
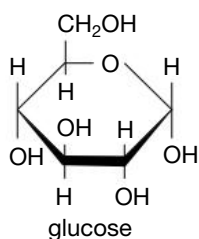
When an animal eats a plant, it can use the plant carbohydrates as an energy source. Carbohydrates provide the greatest proportion of energy in the diets of most humans. The energy is required for muscle movement and functioning of the central nervous system. They are also essential parts of other important molecules such as DNA. In addition, they have a number of beneficial effects on the taste and texture of foods.

Monosaccharides and disaccharides

Carbohydrates are classified into three groups according to their molecular structure: monosaccharides, disaccharides and polysaccharides.

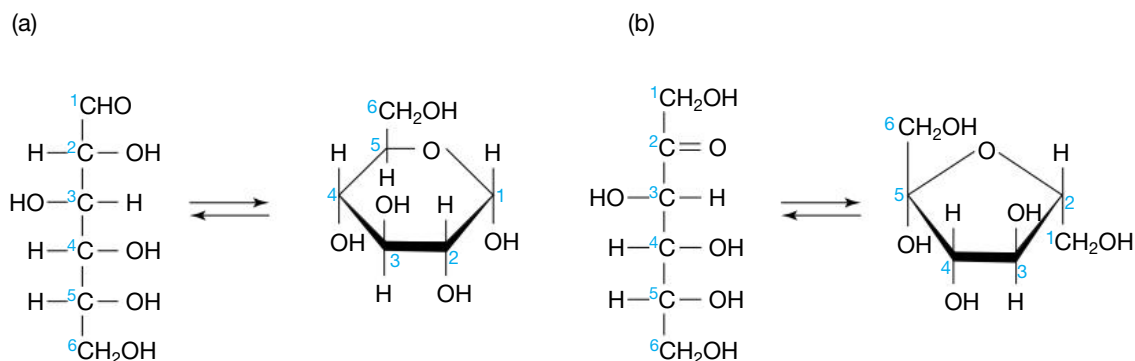
Monosaccharides (sometimes called simple sugars) are the basic building blocks of all carbohydrates. The most important monosaccharides are those containing five carbon atoms (pentoses) and those containing six carbon atoms (hexoses). They are not broken down during digestion.

Monosaccharides are white crystalline solids that are soluble in water. Their solubility is due to the presence of several polar —OH groups in the molecular structures. These can form hydrogen bonds with water molecules. They are also strong reducing agents.



Structures of some common monosaccharides. (Note: Carbon atoms in the ring have been omitted for clarity.)

Monosaccharides can be in straight-chain and cyclic forms. In aqueous solution, the cyclic form predominates.

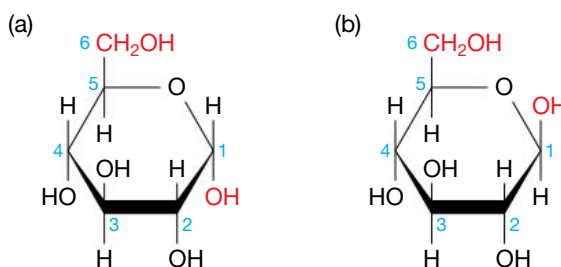


Straight-chain and cyclic forms of (a) D-glucose and (b) D-fructose

Glucose is found as a number of stereoisomers. The molecule of D-glucose illustrated above has four chiral centres. The isomer designated as the D-isomer occurs in nature, but the L-isomer, which is a mirror image, does not. Assigning an isomer as D- or L- is based on the arrangement of the groups in the molecule and not on the direction of rotation of polarised light. However, the two enantiomers rotate light in opposite directions by the same amount. The naturally occurring sugars discussed in this chapter are D-isomers.

In the structures above, note that, as the straight-chain form of glucose forms a ring, the CH₂OH group on C5 ends up *above* the plane of the ring. Also note that, as the ring closes, a new chiral centre is produced at C1, with —OH adopting one of two possible orientations:

- —OH *below* the plane of the ring (i.e. on the opposite side of the ring to CH₂OH) ⇒ α-D-glucose
- —OH *above* the plane of the ring (i.e. on the same side of the ring as CH₂OH) ⇒ β-D-glucose.



(a) Structure of α-D-glucose: the hydroxyl group on C1 and the —CH₂OH group lie on opposite sides of the ring's plane. (b) Structure of β-D-glucose: the hydroxyl group on C1 and the —CH₂OH group are on the same side of the ring's plane.

Thus, the orientation of the hydroxyl group on C1 differentiates the two molecules.

The carbohydrates in food are commonly made up of one or more of three simple monosaccharides — glucose, galactose and fructose.

Monosaccharides can be joined to form **disaccharides** (from two monosaccharides), **oligosaccharides** (from three to about ten monosaccharides) or **polysaccharides** (up to thousands of monosaccharides).

Carbohydrates in food are usually composed of glucose, galactose or fructose.

Simple carbohydrates, including disaccharides, contain fewer than five monosaccharides. Complex carbohydrates are polysaccharides that may contain up to 1000 monosaccharides.

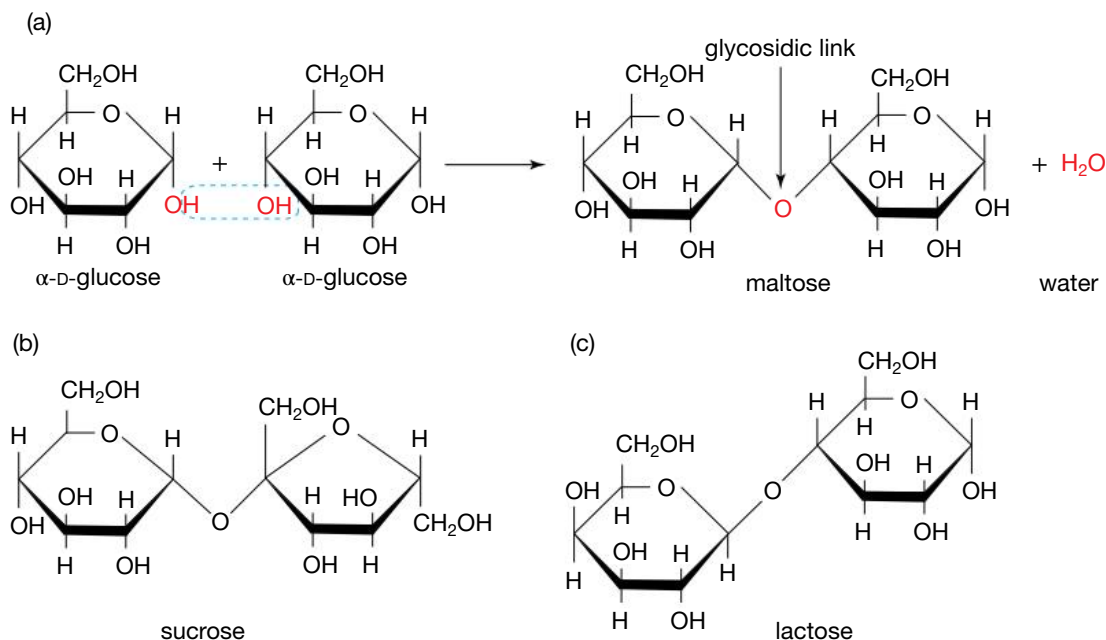
Carbohydrates containing fewer than five monosaccharides are sometimes called *simple carbohydrates*. Polysaccharides may also be called *complex carbohydrates*.

Disaccharides are made of two monosaccharides through a condensation reaction that occurs between the hydroxyl group on C1 of one glucose molecule and the hydroxyl on C4 of an adjacent glucose molecule. A molecule of water is eliminated as a **glycosidic link** (a special case of ether bond) is formed. The three disaccharides found most commonly in food are sucrose (found in fruits), maltose (end-product in the malting of barley during beer manufacture and also in starch digestion in the human gut) and lactose (found in milk). Table sugar is actually the disaccharide sucrose. However, all of these small carbohydrates are classified as sugars, and their names have the suffix *-ose*.



Refined white sugar is sucrose, a disaccharide. Digestion of sucrose produces glucose. In addition to being stored in the body as glycogen, or oxidised for energy, glucose may be converted to fat for storage.

A disaccharide is formed by a condensation reaction between two monosaccharides.



Food disaccharides: (a) Two monosaccharide units (glucose) may undergo a condensation reaction to form a disaccharide (maltose). A hydroxyl ($-\text{OH}$) functional group from each monosaccharide reacts to produce the disaccharide and water as a by-product. (b) Sucrose and (c) lactose, along with maltose, are the most common disaccharides found in foods. Sucrose is formed by a reaction between glucose and fructose, and lactose is formed by a reaction between glucose and galactose.

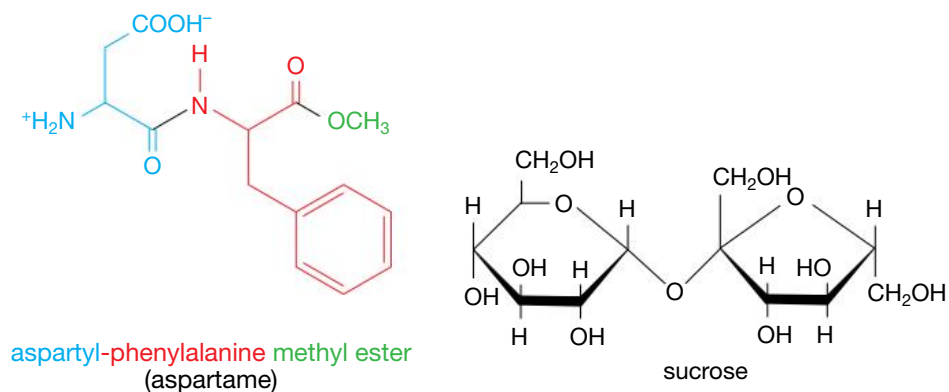
How sweet is it?

Aspartame is an artificial sweetener that is 200 times sweeter than sucrose.

The simple sugars discussed previously have various sweetness and effects on blood glucose levels, which will be discussed later in this chapter. Most people enjoy sweet food, but these foods contain mainly sugar and very few other nutrients. Eating excess sugar can lead to obesity and possibly diabetes, and so many people have turned to artificial sweeteners, particularly in soft drinks. One of the most commonly used is **aspartame**, which can be identified on labels as additive 951. A scientist who inadvertently licked his finger in the lab (a procedure that is definitely not recommended in a chemistry laboratory!) discovered it accidentally. Under conditions of high temperature or high pH, aspartame may break down, and so aspartame is not used for baking, and the shelf life of foods containing aspartame is limited for this reason.

TABLE 12.1 Sweetness, energy and GI of sugars and aspartame

Sugar/sweetener	Notes	Relative sweetness	Energy	Glycaemic Index
lactose	disaccharide composed of glucose and galactose; naturally occurring sugar found in milk	0.15	16.7 kJ/g	45
glucose	monosaccharide also known as dextrose; can cause glucose levels in blood to rise quickly	0.74	16.7 kJ/g	100
sucrose	disaccharide composed of glucose and fructose; also known as table sugar, castor sugar, cane sugar and beet sugar	1.0	16.7 kJ/g	65
fructose	monosaccharide usually found combined with glucose in sucrose in honey and fruit juice; bees hydrolyse sucrose into glucose and fructose	1.6–1.9	16.7 kJ/g	19
aspartame	an artificial, non-saccharide sweetener used as a substitute for sugar in some foods and drinks	150–250	16.7 kJ/g	0



Aspartame is 200 times sweeter than sucrose.

Aspartame is a white, odourless, soluble crystalline powder, a dipeptide methyl ester and chemically known as methyl L- α -aspartyl-L-phenylalaninate. In the body, aspartame is hydrolysed to aspartic acid, phenylalanine and methanol. Aspartame is about 200 times sweeter than sugar. Because it is so sweet, only a very small amount is required to achieve the same level of sweetness as sugar, so the effects of its breakdown products are minimal compared with the intake from other food sources.

- Aspartic acid is a non-essential amino acid and is important as a component of DNA and in the production of urea. It also acts as a neurotransmitter in the brain. Neurotransmitters are chemicals that transfer impulses from one nerve cell to the next.

- Phenylalanine is an essential amino acid needed for the synthesis of some neurotransmitters and is involved in energy metabolism, although people with the genetic disorder phenylketonuria (PKU) cannot metabolise phenylalanine. Phenylketonuriacs need a special diet to avoid brain damage caused by the build-up of phenylalanine.
- Very small amounts of methanol are found in many foods and are poisonous only if consumed in large quantities. Methanol is absorbed and oxidised into methanal and then to methanoic acid.

It is interesting to note that aspartame has two chiral carbon atoms resulting in one isomer that is sweet and the other that is bitter.

Revision questions

- Identify the monosaccharides from which sucrose, maltose and lactose are formed, and write balanced equations (showing structural formulas) for the formation of each disaccharide.
- What functional groups are present in:
 - glucose
 - sucrose
 - aspartame?
- Aspartame has the same number of kilojoules per gram as sucrose, so why is it used in diet foods?
- Aspartame is not a carbohydrate. What type of compound is it?

Polysaccharides

Polysaccharides are carbohydrates of high molar mass. Unlike monosaccharides and disaccharides, they are non-crystalline, generally insoluble and tasteless. Polysaccharides are polymers that consist of large numbers of monosaccharide monomers that have combined in a **condensation polymerisation** reaction and are sometimes called complex carbohydrates. Starch, glycogen and cellulose are important polysaccharides in plant and animal systems.

Starch

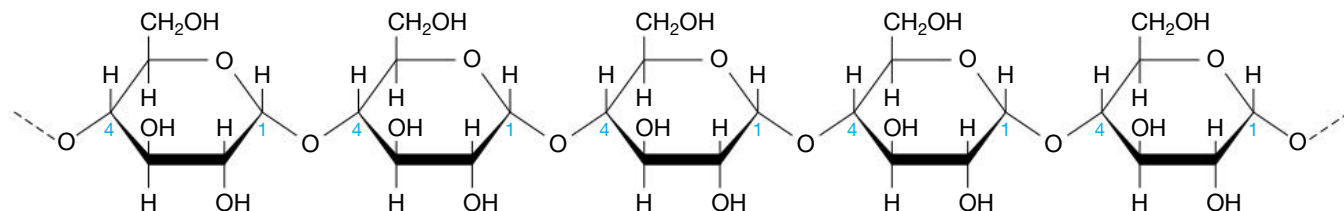
Starch is the major storage form of glucose and is found in seeds and the fleshy part of vegetables and fruit. It is the second most common organic compound. The human body can readily digest starch to form glucose, which is used to produce energy through respiration. Starch is only slightly soluble in water.

Starch is a condensation polymer of α -D-glucose and is made up of two polymers: amylose and amylopectin.

Amylose, which comprises about 20% of starch, is a soluble molecule and smaller than amylopectin. Amylose consists of 50–300 α -D-glucose units in a continuous chain formed from C1–C4 linkages only. As the hydroxyl groups on C1 and C4 are both *below* the plane of the ring, polymerisation is straightforward with all the molecules aligned the same way. This results in a long-chain molecule that forms spirals due to hydrogen bonding along its length.

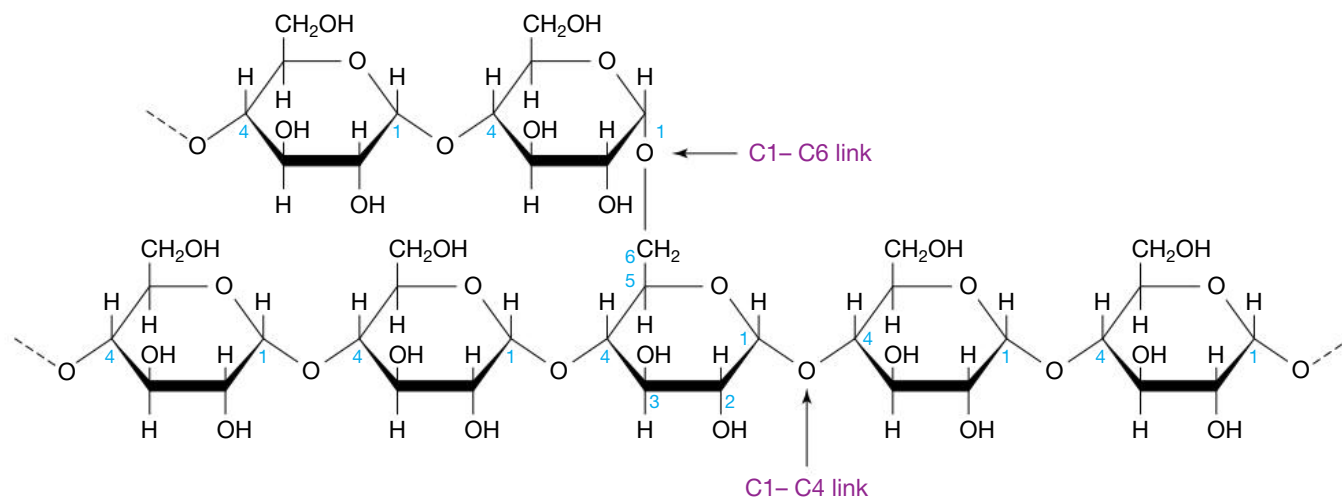
Starch, the storage form of glucose in plants, and glycogen, the animal form of starch, are made of α -D-glucose monomers. Cellulose is made from β -D-glucose; it is not digestible by humans.

Starch is made up of amylose and amylopectin.



Section of amylose

Amylopectin is insoluble and is a longer more loosely branched molecule consisting of 300–5000 α -D-glucose units. The branching occurs as a result of C1–C6 linking between smaller segments of the C1–C4-linked straight chain.



Section of amylopectin

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Experiment 12.1 Studying starch

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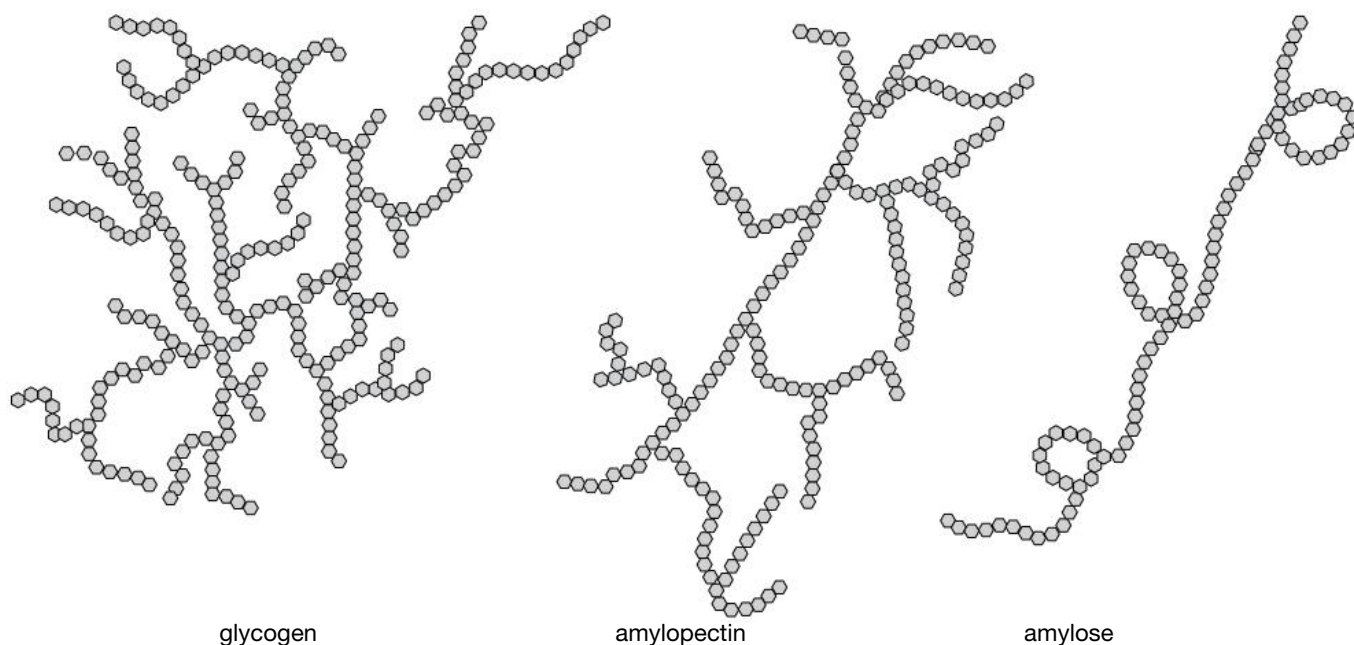
These three test tubes show a positive test for three different concentrations of starch solutions. Moving from left to right, the starch concentrations decrease by a factor of 10; they are 1%, 0.1% and 0.01%. The amylose portion of the starch molecule is a long, coiled carbohydrate polymer that can trap a brown iodide atom in its structure. The iodine atom then appears to take on a purple colour, and even appears black at high iodine concentrations.

Glycogen

Glycogen is the storage form of glucose in animals, and it is stored in the liver and muscles. It has a similar structure to amylopectin but is even more highly branched. In glycogen, as in amylopectin, the branching is due to C1–C6 linkages. However, in glycogen, these linkages occur about every 8–12 glucose units compared with about every 25–30 glucose units in amylopectin. The

Glycogen is the storage form of glucose in animals.

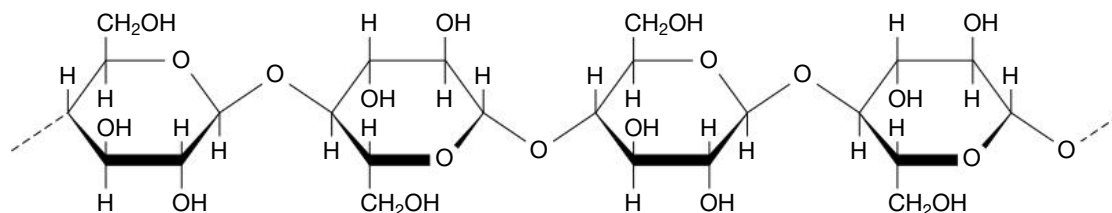
many ends of the molecule are readily available to react and release energy during respiration.



Arrangement of α -D-glucose units in glycogen, amylopectin and amylose

Cellulose

Cellulose is the most common carbohydrate and the most common organic molecule. Like starch, cellulose is a condensation polymer of D-glucose, but in cellulose the monomer is β -D-glucose. This differs from α -D-glucose in that the C1 and C4 hydroxyl groups are on opposite sides of the ring plane. For the glycosidic bond to form between C1 and C4 in β -D-glucose, alternate glucose molecules must be inverted. This is the case for cellulose, the structural component in plants. As with starch, this reaction occurs in plants using the glucose they form during photosynthesis.



Structure of part of a cellulose molecule. Cellulose results from the condensation polymerisation of β -D-glucose.

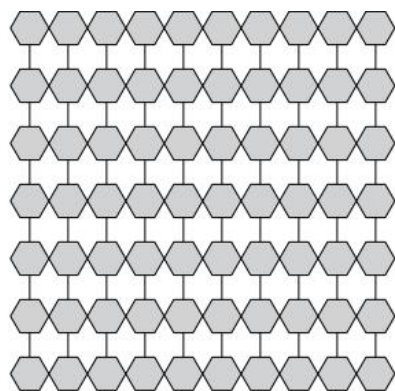
Humans do not have the enzymes necessary to digest cellulose.

Cellulose is the main structural component of the cell wall in plants. The arrangement of β -D-glucose units and the extensive hydrogen bonding between the unbranched chains provides strength to cell walls. Humans cannot hydrolyse cellulose as we do not have the enzyme to hydrolyse the β -C1-C4 glycosidic link; hence, cellulose is not a source of energy. Cellulose

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Experiment 12.2 Constructing models of carbohydrates
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Arrangement of β -D-glucose units in cellulose

is known as fibre or roughage, and it assists the passage of food through the digestive system. A few animals, such as cows, horses and koalas, have particular bacteria in their digestive systems to digest cellulose.

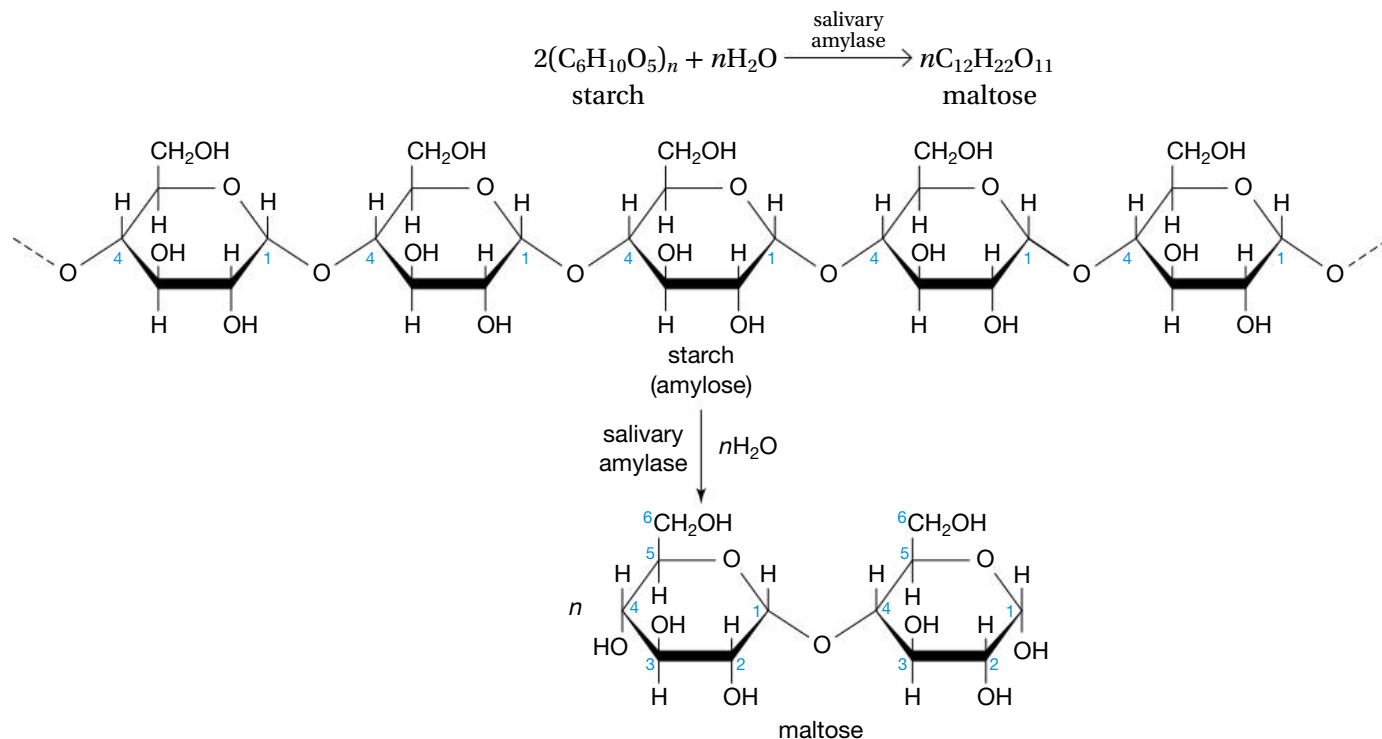
Revision questions

5. Describe the similarities and differences between starch and cellulose.
6. Name the polysaccharide that matches each of the descriptions below.
 - (a) It is hydrolysed to the monosaccharide glucose, and it is found in vegetables, fruits, and grains.
 - (b) It is made from β -glucose monomer units.
 - (c) If excess glucose is present in the body, it is first stored in muscle and the liver in this form.
 - (d) It is made up of two polymers: one branched and the other unbranched.
 - (e) It has no nutritional value to humans.

Digestion of carbohydrates

The process in which complex carbohydrates, lipids and proteins are broken down in our digestive system by enzymes is hydrolysis. The only complex carbohydrate digested to any degree by humans is starch (cellulose cannot be hydrolysed by digestive enzymes).

Starches are initially hydrolysed in the mouth by an enzyme present in the saliva called salivary amylase. Salivary amylase does not completely hydrolyse starch to glucose. However, it can split the bonds between every second pair of glucose units, producing the disaccharide maltose. Hydroxyl functional groups form from the glycosidic (ether) linkages that are broken:



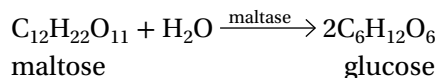
Since food stays in the mouth for only a short time, the salivary amylase has little chance to work there. Digestion by saliva continues in the stomach for about 20 minutes until the action of the enzyme is stopped by the acidic gastric juices. The optimal pH for salivary amylase is about 6, whereas the pH in the

Complex carbohydrates and proteins are broken down in the digestive system by hydrolysis.

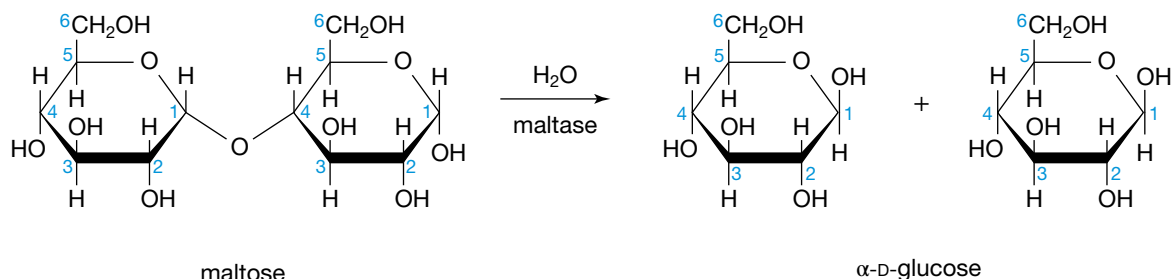
stomach is about 1.5. Only a small percentage of the starch in food is digested by salivary amylase. This is a case of pH causing denaturation of the enzyme. The major enzyme for breaking down starches is pancreatic amylase. This enzyme can convert any unchanged starch (cooked or raw) to maltose.

Carbohydrate digestion is completed in the ileum (the last part of the small intestine) where the disaccharides maltose, lactose (milk sugar) and sucrose (cane sugar) are changed by the enzymes maltase, lactase and sucrase, respectively, into their constituent glucose, fructose and galactose monosaccharides. These monosaccharides can then pass through the intestinal villi into the bloodstream.

The equation for the digestion, or hydrolysis, of maltose by maltase to glucose is:



The formation of glucose eliminates the glycosidic linkages and creates two hydroxyl functional groups.



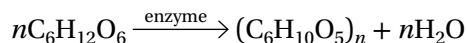
Revision question

7. Write equations for the hydrolysis of maltose, lactose and sucrose. For each reaction, include:
- (a) structural formulas
 - (b) the enzymes required.

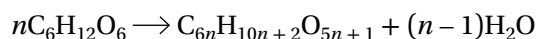
Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is stored in the liver as glycogen, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, a polysaccharide of glucose. When needed, glycogen is converted back to glucose in a hydrolysis reaction. Excess glucose may also be stored as fat.

What happens to digested carbohydrates?

Glucose may be obtained from the digestion of carbohydrates. Glucose is the primary source of energy for all cells. Three monosaccharides — glucose, fructose and galactose — are derived from the hydrolysis of carbohydrates and are absorbed from the digestive tract. They pass to the liver, which converts fructose and galactose to glucose, using specific enzymes. If glucose is not immediately required by the body as an energy source, it is stored in the liver (and, to a lesser extent, in the body tissues) as glycogen, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. Glycogen is a highly branched polysaccharide of glucose, with a high molar mass. It is formed by the condensation polymerisation reaction between α -D-glucose units:



Another way of writing this equation is:



The liver reconverts glycogen to glucose by hydrolysis for use by the body when energy is required. In this way, the liver keeps the glucose concentration of the blood relatively constant in the body.

In addition to being stored as glycogen, or oxidised for energy, glucose may be converted to fat for storage. This fat may be used for energy at some later time.

When exercising, muscles convert glucose into energy using oxygen from within haemoglobin in the blood.



Sample problem 12.1

Calculate the molar mass of a starch molecule made from 500 glucose monomers.

Solution: Mass of 500 glucose monomers = 500×180
 $= 90\,000 \text{ g mol}^{-1}$

In this condensation reaction, 499 water molecules are released.

Mass of 499 water molecules = 499×18.0
 $= 8982 \text{ g mol}^{-1}$

Molar mass of starch = $90\,000 - 8982$
 $= 81\,018$
 $= 8.10 \times 10^4 \text{ g mol}^{-1}$

Lactose intolerance

Lactose intolerance is caused by having insufficient amounts of the enzyme lactase to hydrolyse the disaccharide lactose.

Milk is a source of many nutrients including proteins, lipids and carbohydrates; it also provides minerals and vitamins. These nutrients are important for strong bones and teeth and also play a part in nerve and muscle function, digestive enzymes and the immune system. For some people, milk can be a source of discomfort due to their inability to digest lactose, sometimes called milk sugar. Lactose, which is a disaccharide, is found in milk produced by mammals to feed their young. The lactose molecule consists of a molecule of galactose and a molecule of glucose. People who are lactose intolerant lack the enzyme lactase, which is required in the hydrolysis of lactose, so it cannot be absorbed into the bloodstream in the small intestine. This intolerance can be permanent or temporary as a result of certain digestive diseases. Undigested lactose passes into the large intestine, and then anaerobic bacteria break down the lactose into small carboxylic acids and then to hydrogen, carbon dioxide and methane. The symptoms may include cramps, diarrhoea, flatulence and nausea. This is not an allergic reaction, as the immune system is not involved.

The ability to produce lactase declines from childhood. People of Asian, African, South American, southern European and Australian Aboriginal heritage are more likely to become lactose intolerant than people of northern European descent. To test for lactose intolerance, glucose levels are measured

2 hours after having a lactose drink. Alternative methods include measuring the amount of hydrogen in the breath or acidity in stools.

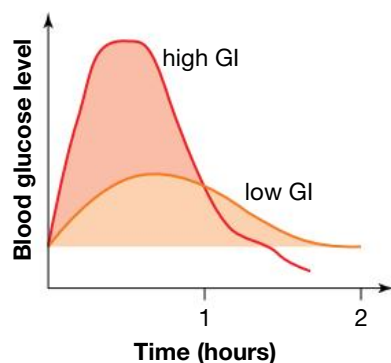


Processed dairy products contain less lactose than milk.

Revision question

8. Lactose is a small and polar molecule. Explain why it is more likely to be soluble in milk than in butter or cheese.

The glycaemic index (GI) is a scale used to describe how quickly the carbohydrate in a food is broken down and absorbed into the bloodstream.



Changes in blood sugar levels brought about by high GI (glycaemic index) and low GI foods

Are all carbohydrates equally beneficial?

Carbohydrates supply us with glucose (also known as blood sugar) to provide energy for our bodies to function and for physical activity; but some carbohydrates are more useful than others. The most beneficial carbohydrates are fruits, vegetables and whole grains. Glucose levels rise and fall as we eat, exercise, rest and sleep. Optimal health requires a slow increase in glucose, rather than fluctuations to extreme levels.

The **glycaemic index** (GI) is used to indicate how quickly various carbohydrates influence glucose levels. Diets rich in high GI foods have been linked to an increased risk of diabetes, heart disease and obesity. Extremes in glucose levels can affect people differently but, for diabetics, if the glucose level becomes too low (hypoglycaemia), a person may have increased heartbeat, feel dizzy and hungry, or even lapse into a coma! If it becomes too high (hyperglycaemia) more of the hormone insulin is released to lower the level, and the person may be thirsty or hungry, and have headaches and vision problems. If treatment is not sought, then more severe health issues will arise. The GI is determined by giving a group of people a particular mass of carbohydrate and measuring their glucose levels over 3 hours. These readings are then compared with eating pure glucose. Glucose is assigned a GI value of 100. The greater the GI, the greater is the increase in glucose. Eating lower GI foods helps you to feel fuller for longer.

How quickly and easily food is digested depends on a number of factors. Starch is the most important source of carbohydrates in our diet. As discussed earlier in this chapter, starch consists of amylose and amylopectin. Amylose is digested more slowly because it consists of closely packed linear chains of α -D-glucose monomers arranged in a helical structure. Amylopectin is a longer more loosely branched molecule that has many free ends that can be easily hydrolysed. Therefore, foods with a greater amount of amylose have a lower GI. Other factors are listed in table 12.2.

TABLE 12.2 Other factors affecting the rate of digestion of carbohydrates

Factor	Explanation
ripeness of fruit	changes in the structure of starch as fruit ripens
bran (the outer coating of wheat grains)	limits the ability of enzymes to reach the starch
fibre (cellulose)	takes up space in the stomach and slows rate of digestion
sugars	have different ability to be hydrolysed; fructose has a lower GI than other sugars
proteins, fats and oils	slow down time for stomach to empty
food processing	smaller particles have greater surface area for reaction; bran is removed
cooking method	food swells and softens
acidity of food	acidic fruit slows down stomach emptying

Planning meals

The glycaemic index does not take into account the following factors:

- other nutrients are present in the food
- the portion size
- the effect of eating different combinations of food
- foods with the same glycaemic index that produce different amounts of the hormone insulin, making the effects on health different.

Another measurement, glycaemic load (GL) takes into account how much carbohydrate a food contains. For example, carrots, bananas, watermelon and wholemeal bread have a high GI but a low glycaemic load because their carbohydrate content is small. These foods have minimal effect on glucose levels. The glycaemic load is calculated by multiplying the number of grams of carbohydrate in a serving by the GI, and dividing by 100. For example, a 120-gram serving of watermelon (GI = 72) has 6.0 grams of available carbohydrate, so its glycaemic load is $6.0 \times \frac{72}{100} = 4.3$, and this is quite low.

In summary, in a healthy diet it is recommended that you eat moderate amounts of food and that the food is high in fibre, low in kilojoules, naturally occurring and minimally processed. A healthy and varied diet includes the following nutrient groups in the approximate proportions:

- 30% grain foods
- 30% vegetables and legumes/beans
- 17% lean meats, poultry, fish, eggs, tofu, nuts and seeds and legumes/beans
- 13% dairy products
- 10% fruit.

Use only small amounts of oils, drink lots of water, and enjoy the occasional treat (alcohol, sweet or savoury).

Revision question

9. The recommended glucose (blood sugar) level is about 5.0 mM. Another unit used is mg dL^{-1} (1 decilitre (dL) = 100 mL). Calculate the recommended glucose level in mg dL^{-1} .

Fats and oils

Fats and oils contain more than twice the amount of energy as carbohydrates. They belong to a group of compounds called **lipids**, which also include a small number of other compounds such as waxes, fat-soluble vitamins, monoglycerides and diglycerides. Fats and oils are found in fish, dairy products, oils, fried foods, seeds and nuts. Fats are solids whereas oils are liquids at room temperature. Our bodies need lipids because, as well as their function as an

Fats and oils are triglycerides formed by condensation reactions between glycerol and three fatty acids.

energy store, they form components in cell membranes and are important for hormone production, insulation, protection of vital organs and transport of fat-soluble vitamins. Lipids contain the elements carbon, hydrogen and oxygen. In this respect, they are similar to carbohydrates, but lipids have a smaller percentage of oxygen and are not polymers. A triglyceride is a fat or oil formed by a condensation reaction between glycerol and three **fatty acids**.

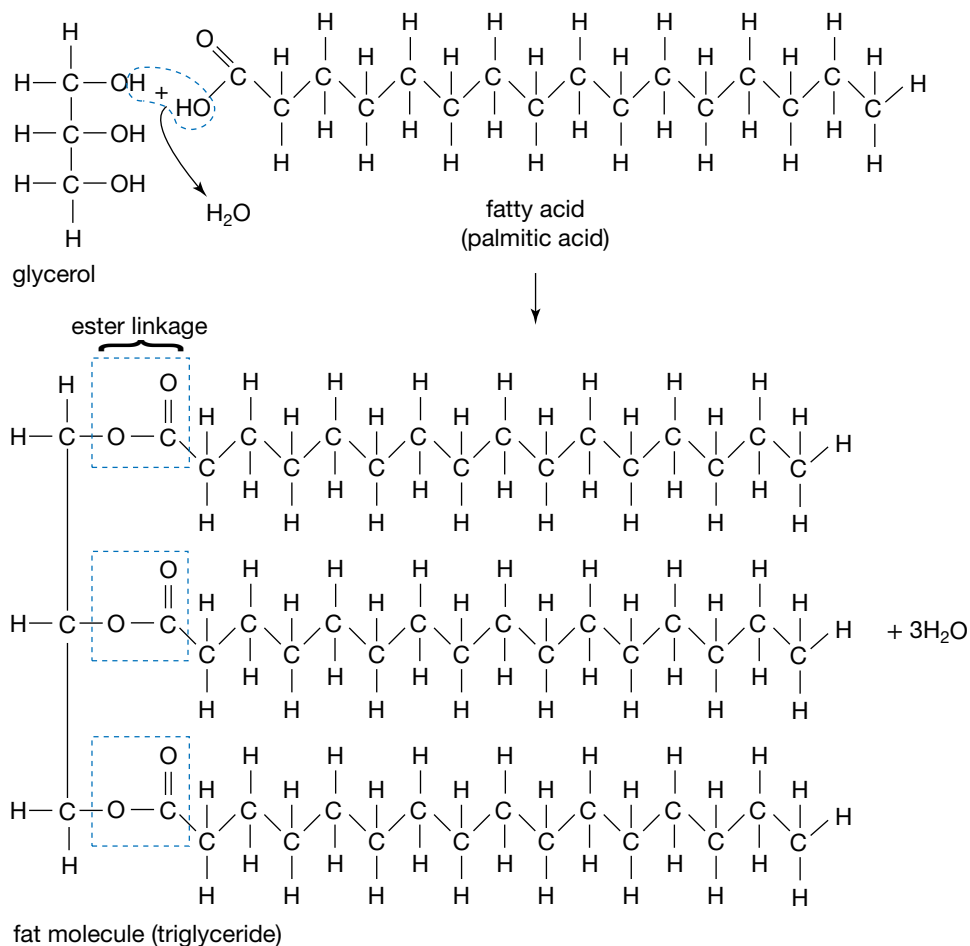
Glycerol has the semi-structural formula $\text{CH}_2\text{OHCH}(\text{OH})\text{CH}_2\text{OH}$. Fatty acids are long-chain carboxylic acids with 12–18 carbon atoms and may be classified as saturated or unsaturated.

- **Saturated fatty acids** have all single C—C bonds.
- **Mono-unsaturated fatty acids** contain one C=C double bond.
- **Polyunsaturated fatty acids** contain more than one C=C double bond.

TABLE 12.3 Some common carboxylic acids found in fats and oils

Common name	Number of carbon atoms	Semi-structural formula	Example of source	Degree of unsaturation
palmitic acid	16	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	palm oil	saturated
stearic acid	18	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	animal fats	saturated
oleic acid	18	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	peanut oil	monounsaturated
linoleic acid	18	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	vegetable oils	polyunsaturated

Fatty acids are long-chain carboxylic acids containing an even number of carbon atoms. The carboxyl groups in the fatty acids react with the hydroxyl groups in the glycerol to form an ester link, $-\text{COO}-$.





higher the iodine number
reduce cholesterol

Revision question

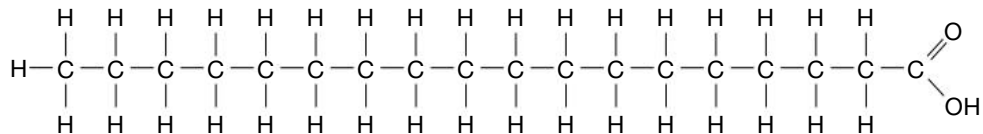
Properties and reactions of fats and oils

In polyunsaturated triglycerides, double bonds create bending in the fatty acid chains (see revision question 10); this disrupts the dispersion forces between the molecules because they cannot get so close together. They are usually oils at room temperature. Hydrogen can be added to unsaturated fatty acids to convert them to saturated fatty acids in the process called **hydrogenation**. The amount of hydrogen added determines the melting point of the triglyceride. The **iodine number** is used to measure the degree of unsaturation. The iodine number is the mass of iodine that reacts with 100 grams of a fat or oil. Iodine reacts with the carbon-carbon double bonds. The more double bonds there are, the

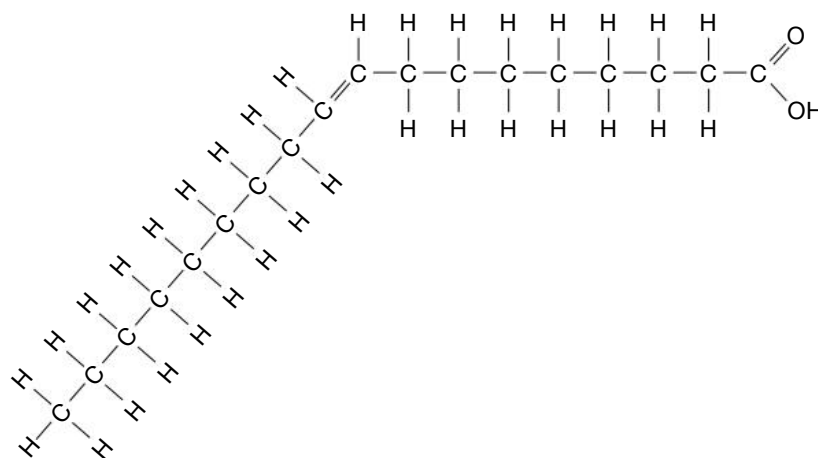
higher the iodine number. Unsaturated triglycerides, whether mono- or poly-, reduce cholesterol and so are preferable in the diet.

Revision questions

10. Examine the structures of these saturated and mono-unsaturated fatty acids.



stearic acid (a saturated fatty acid)



oleic acid (a mono-unsaturated fatty acid)

- (a) Which substance would be able to bond between molecules with the greatest number of dispersion forces?
- (b) Which substance would be an oil at room temperature?

11. Explain in terms of bonding why lipids are insoluble in water.
12. Which would have the higher iodine number: fats or oils? Why?
13. Sketch the structural formula of a triglyceride formed from the reaction between glycerol, two molecules of stearic acid and one molecule of oleic acid.

Oxidation of food

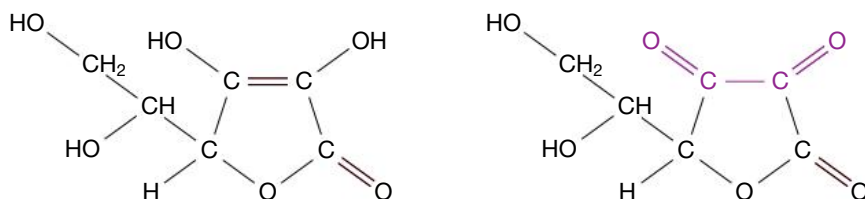
You may have had the unfortunate experience of finding out that something that you were about to eat was 'off', the horrible smell emanating from the food confirming your realisation. This is what happens when some foods react with oxygen in the air. The presence of light can speed up the process. Unsaturated fats are less stable and are more susceptible to oxidation than saturated fats, as the oxygen reacts across the double bonds in unsaturated fats. This results in the food going rancid and becoming unpalatable. When certain molecules interact with oxygen, they can form free radicals. These are atoms or groups of atoms with unpaired electrons, which make them very reactive. These free radicals can then start a chain of destructive chemical reactions. The smaller volatile molecules, such as aldehydes, ketones and carboxylic acids, produced when food deteriorates can give it unpleasant smells and flavours. For example, the flavour of rancid butter is due to the presence of butanoic acid.

Preventing rancidity

Antioxidants can be natural or synthetic, and they play an important part in slowing down oxidation and preventing food from spoiling. They are reducing agents and are therefore preferentially oxidised. An example of a natural antioxidant is vitamin C (ascorbic acid), which reacts to form dehydroascorbic acid by losing two hydrogen atoms from the ring section of the molecule.

Polyunsaturated fats are less stable and are more susceptible to oxidation.

Vitamin C (ascorbic acid) and dehydroascorbic acid



Antioxidants slow down the oxidation of food.

Citric acid is also used; it helps flavour food and increases the effectiveness of other antioxidants. Another natural antioxidant that may be present in foods is vitamin E, which is a fat-soluble antioxidant found in seeds, nuts, whole grains, green leafy vegetables, soya beans and vegetable oils. Synthetic antioxidants may be added to food to prevent deterioration, such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and propyl gallate. Bread, vegetable oils and cheese all have antioxidants added.

Other methods of preventing rancidity include: vacuum packaging or using nitrogen; filling containers up to the lid; storing food in the dark and cold; restricting access to copper, iron and nickel; and using dark containers or, in the case of the similar process of photooxidation, opaque containers.



Potato chip packaging prevents light and moisture from entering. Nitrogen is pumped into the bags to eliminate oxygen.

Revision questions

14. Explain why unsaturated fats are more susceptible to becoming rancid than saturated fats.
15. (a) Write the half-equation for the formation of dehydroascorbic acid, $C_6H_6O_6$, from ascorbic acid, $C_6H_8O_6$.
(b) Explain whether this is an oxidation or reduction reaction.
(c) Which functional groups are affected in ascorbic acid, and what type of functional group is formed?

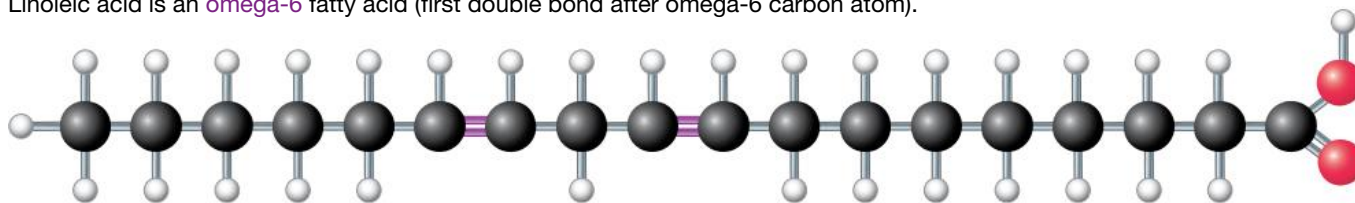
Essential fatty acids

Normal functioning of the body requires some essential fatty acids. Deficiency can affect the liver, kidneys, blood, immune system and condition of the skin. Essential fatty acids (EFAs) are fatty acids that must come from our diet because the body cannot produce them. They are often called omega fatty acids. Examples are alpha-linolenic acid (ALA) and linoleic acid (LA). Alpha-linolenic acid is found in flaxseed oil, canola oil, linseed, tuna, trout and salmon, whereas linoleic acid is present in oils such as soybean, sunflower, corn and safflower, as well as nuts and seeds.

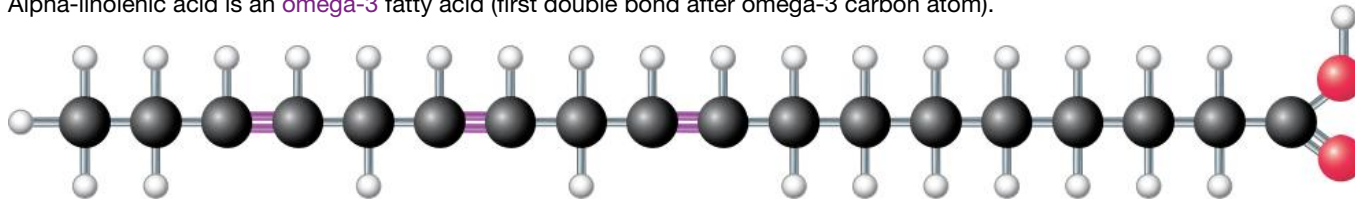
Alpha-linolenic acid is an omega-3 fatty acid, and linoleic acid is an omega-6 fatty acid. The position of the double bond is critical to the function of the fatty acid as the body's enzymes cannot react with double bonds near the methyl end; the names arise from the number of the carbon atom in the double bond that is closest to the methyl end, rather than the carboxyl end. (Omega (symbol ω) is the last letter of the Greek alphabet.)

Humans require essential fatty acids, including alpha-linolenic acid and linoleic acid, for the body to function effectively. These acids are called omega fatty acids.

Linoleic acid is an **omega-6** fatty acid (first double bond after omega-6 carbon atom).



Alpha-linolenic acid is an **omega-3** fatty acid (first double bond after omega-3 carbon atom).



omega-1 carbon

● = carbon ● = oxygen ● = hydrogen

Omega-6 and omega-3 amino acids

Humans can synthesise longer omega-6 and omega-3 fatty acids from LA and ALA. The human body can transform linoleic acid into arachidonic acid (AA), which has 20 carbon atoms, and alpha-linolenic acid into eicosapentaenoic acid (EPA), which also contains 20 carbon atoms. These are important fatty acids that are needed to make chemicals for the process of inflammation and the nervous system.

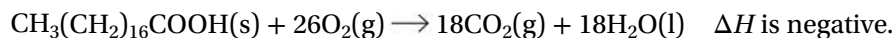
During digestion, fats and oils are hydrolysed to glycerol and fatty acids, which can be assembled into triglycerides.

Digestion of fats and oils

Digestion of lipids takes place in the alkaline conditions of the small intestine, where the lipid is mixed with bile. Bile is an emulsifier; it increases the surface

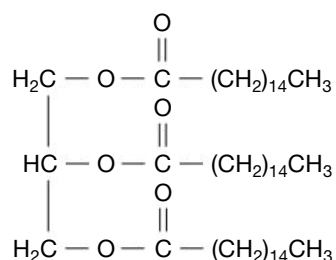
area of the fat by breaking it into smaller droplets. This means that it can react faster. The fat undergoes hydrolysis, catalysed by enzymes from the pancreas; glycerol and free fatty acids are produced. These are absorbed by cells lining the small intestine and converted back into triglycerides. These enter the body's lymphatic system and eventually the bloodstream for transport around the body. Excess fats not needed for energy production are stored as triglycerides in adipose tissues until needed as a source of energy.

The fatty acid stearic acid can be oxidised and energy produced according to the following equation.



Revision questions

- 16. (a)** Provide a chemical equation for the hydrolysis of the fat with the following formula.



- (b)** Identify the functional groups involved in this reaction.
- 17.** Write equations for the oxidation of:
- (a)** palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
- (b)** oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$.



In this X-ray of a finger, the subcutaneous fat layer is visible as the yellow layer under the skin and around the bone. This fat stores triglycerides. During digestion, lipids are hydrolysed to glycerol and fatty acids, which can be assembled into triglycerides.

Energy in foods

TABLE 12.4 Energy content of the major food groups

Nutrient	Energy (kJ g ⁻¹)
carbohydrates	17
protein	17
fat	37

People have become more conscious of the energy content of the food that they eat and regularly check the labels on food packaging. The amount of energy a person needs depends on how active the individual is and whether the person is still growing. This energy is used during processes such as digestion, heart-beat, breathing, nervous system and movement. The energy is obtained from carbohydrates, fats and protein in the food we eat. These nutrients provide different amounts of energy; fat has the most energy per gram, followed by protein and carbohydrate, as shown in table 12.4. These energy values have been adjusted to take into account the fact that not all of the energy in the food ingested is available to the body because it is not completely digested and absorbed. Even though water, minerals, vitamins and fibre are necessary for good health, they are not sources of energy.

Nutrition information labels

Care should be taken when reading nutrition information on food labels. The ingredients are listed in descending order according to weight. The overall value of food energy stated on packaging is obtained by multiplying the energy values by the mass of protein, fat and carbohydrate as listed in table 12.4. The serving size is determined by the manufacturer and may not be the amount that you use. It is better to compare the quantity per 100 g when making food choices. As a general guide, and depending on the food, in 100 g you should aim for less than 10 g of total fat, less than 10 g of sugar, less than 400 mg salt and 3–6 g of fibre in breads and cereals. The fat total includes all of the different types of fats; it is healthier to choose less saturated fat where possible. The total carbohydrate figure includes starches and sugars, but be aware that sugars may be listed under other names, often ending in *-ose*. Foods with no added sugar could contain a large amount of natural sugar, and low-fat foods can also contain large quantities of sugar. Learning how to read and understand food labels can help you make healthier choices.

Simple carbohydrates are metabolised very quickly which is why people get hungry again soon after eating them, whereas complex carbohydrates allow the energy to be released less rapidly. Once carbohydrates, including the stored form glycogen, are consumed, the body starts to break down fat. Fat is not as efficient at providing energy as carbohydrates. Protein is rarely used as an energy source except in situations of starvation. The body can break down amino acids to produce glucose if required.

So how can the amount of energy in food be determined? A simple method of measuring the heat content in food is just to ignite a weighed sample of food, use it to heat a particular volume of water, and measure its increase in temperature. The specific heat capacity of water can then be used to determine the heat energy provided by the food sample. This method has been described in detail in chapter 2. A more accurate method of measuring the energy content of food is to use a bomb calorimeter.

Measuring energy changes in chemical reactions — calorimetry

Calorimetry is the measurement of the amount of heat released or absorbed in a chemical reaction, change of state or formation of a solution. Chapter 2 explained that enthalpy or heat content (H) is the total energy in a substance. The change in enthalpy in a chemical reaction is known as the heat of reaction, and it is denoted by the symbol ΔH . A **calorimeter** is an instrument that can

Proteins and carbohydrates provide 17 kJ g⁻¹ and fats provide 37 kJ g⁻¹.

A calorimeter is used to measure energy changes in chemical reactions.

be used to determine the energy changes that occur when a chemical reaction, such as burning food, takes place. There are different types of calorimeters, including solution calorimeters and bomb calorimeters.

In all calorimeters, a reaction takes place inside an insulated container with a fixed amount of liquid (usually water), and the temperature rise or fall is recorded using an accurate thermometer. This temperature change (in °C) must be converted to an energy change (in J or kJ) before a value of ΔH can be determined. Such a conversion is achieved by calibrating the calorimeter using an electrically heated coil. Since the temperature rise for a reaction depends on the substance itself, the amount of substance used and the nature of the immediate surroundings, the value of the conversion factor or calibration factor must be established for each calorimeter before determining an enthalpy change for a reaction.

A calorimeter may be calibrated by using an electric heater to pass a known quantity of heat energy through a known mass of substance, usually water, and then measuring the temperature rise. The energy released to the calorimeter is given by:

$$E = V \times I \times t$$

The calibration factor is given by:

$$\frac{\text{energy released}}{\text{temperature rise}}$$

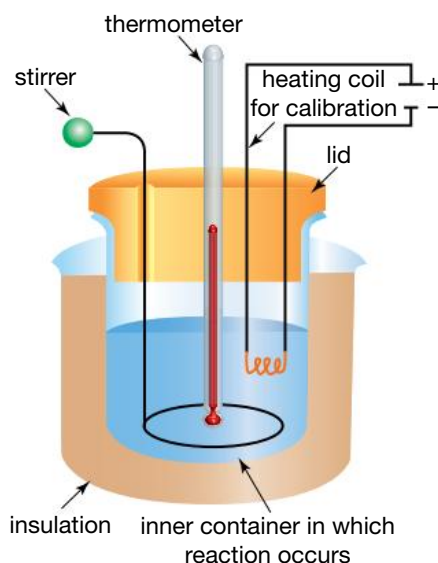
So, if a current of I amps flows for t seconds at a potential difference of V volts, the calibration factor may be calculated as follows.

$$\text{calibration factor (J } ^\circ\text{C}^{-1}) = \frac{V (\text{volts}) \times I (\text{amps}) \times t (\text{s})}{\text{temperature rise}}$$

Solution calorimeters and bomb calorimeters are commonly used to determine the enthalpy change in chemical reactions.

Solution calorimeter

A solution calorimeter is the simplest type of calorimeter and is used to find the energy change occurring in aqueous solutions. The heat of solution (when 1 mole of any substance dissolves in water) and the heat of neutralisation (when an acid reacts with a base) for a reaction may be determined using a solution calorimeter.



$$\text{Calibration factor (J } ^\circ\text{C}^{-1}) = \frac{V (\text{volts}) \times I (\text{amps}) \times t (\text{s})}{\text{temperature rise}}$$

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Unit 4

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Calibrating a
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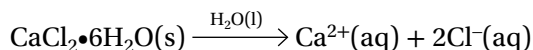
Experiment 12.3 Solution calorimetry
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In a solution calorimeter, experiments are usually carried out in aqueous solution. The change in temperature is measured and then multiplied by the calibration factor to determine the heat change for the reaction.

Sample problem 12.2

A calorimeter containing 100 mL of water was calibrated by passing a 4.00 A current through the instrument for 35.0 s at a potential difference of 3.00 V. The temperature rose by 0.700 °C.

When 6.60 g of calcium chloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, was added to the calorimeter and dissolved by rapid stirring, the temperature dropped by 0.895 °C. Determine ΔH for the reaction:



Solution: The calibration factor for the calorimeter may be calculated from the relationship:

$$\begin{aligned} \text{calibration factor (J } ^\circ\text{C}^{-1}) &= \frac{\text{voltage (volts)} \times \text{current (amps)} \times \text{time (s)}}{\text{temperature rise (} ^\circ\text{C)}} \\ &= \frac{3.00 \times 4.00 \times 35.0}{0.700} \\ &= 600 \text{ J } ^\circ\text{C}^{-1} \end{aligned}$$

The energy change during the reaction may be calculated as follows.

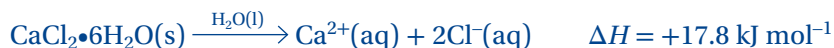
$$\begin{aligned} \text{energy change in calorimeter (J)} &= \text{calibration factor (J } ^\circ\text{C}^{-1}) \\ &\quad \times \text{temperature change (} ^\circ\text{C)} \\ &= 600 \times 0.895 \\ &= 537 \text{ J} \end{aligned}$$

$$\begin{aligned} n(\text{CaCl}_2 \cdot 6\text{H}_2\text{O}) &= \frac{m}{M} \\ &= \frac{6.60}{219.1} \\ &= 0.0301 \text{ mol} \end{aligned}$$

So, since 537 J of energy is absorbed by 0.0301 mol of the sample, by proportion, 1 mole of the sample absorbs:

$$\frac{537}{0.0301} = 17\,819 \text{ J}$$

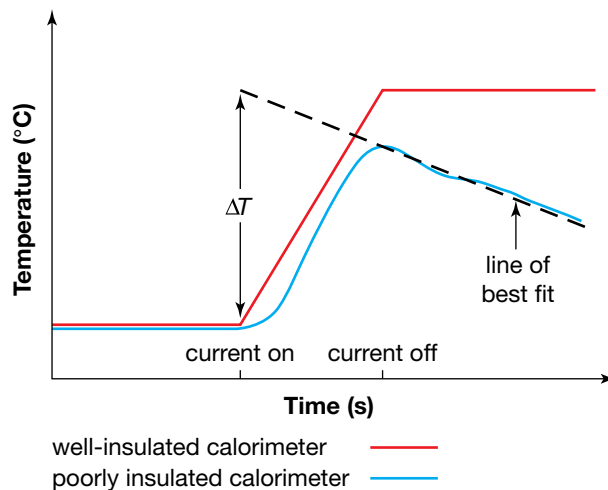
So, the ΔH for the equation is +17.8 kJ. Since energy was absorbed during the reaction, the reaction is endothermic and the sign of the ΔH value is positive.



Heat loss in calorimeters

If a calorimeter is well insulated, there is little heat loss, and the temperature of the contents decreases slowly. This is shown by the graph at right, which is a plot of temperature against time as the reaction proceeds.

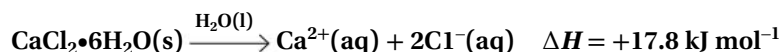
In a poorly insulated calorimeter, the temperature rise would be



less than that in a well-insulated calorimeter. However, the theoretical ΔH for the reaction can be calculated by extrapolating the graph to when the reaction commenced. This compensates for the error caused by loss of heat from the water to the surroundings.

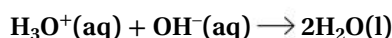
Revision questions

18. Determine the temperature change in a calorimeter when 5.00 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ dissolves in 200 mL of water according to the equation:



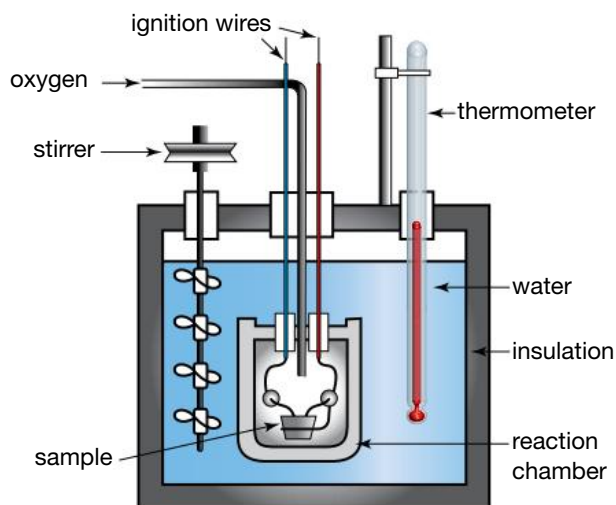
The calibration factor for the calorimeter under these conditions was found to be $825 \text{ J } ^\circ\text{C}^{-1}$.

19. A student used a simple calorimeter to determine the heat of neutralisation of a strong acid with a strong base according to the reaction:



After calibrating the calorimeter, the student calculated the calibration factor to be $343 \text{ J } ^\circ\text{C}^{-1}$. The student then carefully added 50.0 mL of 0.100 M HCl to 50.0 mL of 0.110 M NaOH in the calorimeter. The temperature in the calorimeter rose from 20.4°C to a maximum of 21.2°C .

- Explain how the student determined the calibration factor.
- Calculate the heat of neutralisation for the reaction.
- Suggest why a higher concentration of base than acid was used.
- How would the heat of neutralisation have been affected had the student added 50.0 mL of 0.100 M NaOH to 50.0 mL of 0.110 M HCl in the calorimeter?
- Identify the sources of error in the experiment and suggest how these could be minimised.
- Write an experimental report for the experiment.



Features of a bomb calorimeter. To start combustion in a bomb calorimeter, oxygen is pumped into the reaction chamber containing a combustible sample, and an electrical discharge is sent through the ignition wires. A thermometer measures the change in temperature of the water in the insulated water bath. This temperature is then used to calculate the heat of combustion of the sample.

Bomb calorimeter

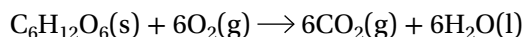
A **bomb calorimeter** can be used to determine the energy change for reactions involving gases. The heat of combustion (when a substance burns in oxygen, according to a particular equation) for a reaction may be determined using a bomb calorimeter. The 'bomb' is a container that is designed to withstand high pressure; its volume does not change, and it has valves for adding gases and an ignition source for combustion reactions. It is used to measure enthalpy of combustion of other chemicals as well as food samples. When burning food, a bomb calorimeter is used, as burning is chemically similar to breaking down food in cellular respiration, and this combustion reaction involves oxygen. However, the reaction occurs more quickly than in a solution calorimeter, and the energy content of a food, as determined by bomb calorimetry, usually differs from its energy content from a nutritional point of view. This is because fruits and vegetables contain indigestible carbohydrates in the form of cellulose, and some energy is converted to heat in the body.

A sample of the compound with a measured mass is placed in the inner chamber of the calorimeter. This

A bomb calorimeter can be used to measure the energy content of food.

chamber is filled with oxygen at high pressure. A wire leads into the sample from outside the calorimeter. When a current is passed through this wire, it glows and ignites the sample, which reacts with the oxygen. The heat from this reaction passes through the walls of the chamber into the water in the reservoir, which is stirred constantly. The temperature increase of the calorimeter is measured and used to calculate the heat given off by the compound. Each bomb calorimeter must be calibrated before use.

Bomb calorimeters may be used to measure the energy content of foods. In the human body, energy is obtained from the combustion of glucose.



When this reaction is carried out in a bomb calorimeter, it is found that 1 mole of glucose evolves 2083 kJ of heat in a rapid reaction. In the body, however, glucose reacts in a sequence of steps to produce a slow release of energy. This gives the cells in the body a continual supply of energy for their needs.

Sample problem 12.3

A bomb calorimeter was calibrated by passing a current of 3.55 A at a potential difference of 6.40 V through a heating coil for 123.7 seconds. The temperature of the calorimeter rose from 21.82 °C to 26.13 °C. A dried biscuit weighing 2.34 g was then burned in the calorimeter in the presence of excess oxygen. The temperature of the calorimeter rose from 22.75 °C to 24.98 °C. Calculate the energy content of the biscuit in J g⁻¹.

Solution: Calibration factor = $\frac{VIt}{\Delta T} = \frac{6.40 \times 3.55 \times 123.7}{26.13 - 21.82}$
= 652 J °C⁻¹

Change in temperature on combustion of biscuit = 24.98 – 22.75
= 2.23 °C

So, the energy released by the biscuit = 652 × 2.23
= 1453.96 J

Therefore, the energy content of the biscuit = $\frac{1453.96}{2.34}$
= 621 J g⁻¹

Revision question

20. A VCE student calibrated a bomb calorimeter by passing a current of 3.20 A at a potential difference of 5.40 V through a heating coil for 1 minute 15 seconds. The temperature of the calorimeter rose from 19.4 °C to 20.5 °C. A sample of breakfast cereal weighing 1.37 g was then burned in the calorimeter in the presence of excess oxygen. The temperature of the contents of the calorimeter rose from 19.2 °C to 22.7 °C.
- (a) Calculate the calibration factor.
 - (b) Calculate the heat content of the breakfast cereal in J g⁻¹.
 - (c) Explain why this experiment was performed in a bomb calorimeter rather than a solution calorimeter.
 - (d) Why is the energy content calculated per gram instead of per mole?
 - (e) Write an experimental report for the experiment.

Chemical calibration

Bomb calorimeters can also be calibrated by chemical means by using a combustion reaction with a known ΔH . For example, the heat of combustion of benzoic acid at constant pressure is known to be 3227 kJ mol^{-1} (that is, $\Delta H = -3227 \text{ kJ mol}^{-1}$) and $M(\text{C}_6\text{H}_5\text{COOH}) = 122 \text{ g mol}^{-1}$. When a sample of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, with a mass of 1.18 g was ignited in a bomb calorimeter, it produced a temperature rise of 2.43 K . The calibration factor can be calculated using this information.

$$n(\text{C}_6\text{H}_5\text{COOH}) = \frac{1.18}{122} = 0.00967 \text{ mol}$$

$$\text{Energy produced by benzoic acid} = 0.00967 \text{ mol} \times 3227 \text{ kJ mol}^{-1} = 31.2 \text{ kJ}$$

$$\text{Calibration factor} = \frac{31.2 \text{ kJ}}{2.4 \text{ K}} = 12.8 \text{ kJ K}^{-1}$$

Chapter review

Summary

- Carbohydrates are made up of carbon, hydrogen and oxygen and have the general formula $C_x(H_2O)_y$.
- Carbohydrates can be classified into three groups according to their molecular structures: monosaccharides, disaccharides and polysaccharides.
- Glucose is a monosaccharide that has a number of isomers including α -D-glucose and β -D-glucose. In aqueous solution, monosaccharides may exist in equilibrium in both straight-chain and cyclic forms. It is the major energy source for the body.
- Glucose is formed from water and carbon dioxide during photosynthesis.
- Two monosaccharide units may undergo a condensation reaction to form a disaccharide. The hydroxyl ($-OH$) functional group from each monomer unit reacts to form water as a by-product.
- Aspartame is an artificial sweetener that is 200 times sweeter than sucrose.
- Starch is a polysaccharide formed from the condensation polymerisation of α -D-glucose from photosynthesis. Starch is the major storage form of glucose in plants. It is made up of amylose and amylopectin. Amylose is smaller than amylopectin and consists of compacted linear chains arranged in a helical structure. Amylopectin is a longer more loosely branched molecule that is insoluble.
- Glycogen is the major storage form of glucose in animals. It is more highly branched than amylopectin. Excess glucose is stored in the liver as glycogen. It may also be stored as fat.
- Cellulose is a polysaccharide formed from the condensation polymerisation of β -D-glucose from photosynthesis. The arrangement of glucose monomers in cellulose is different from that in starch. Cellulose is the major structural component of cell walls in plants. Humans do not have the enzyme to digest cellulose.
- Complex carbohydrates and proteins are broken down in the digestive system by hydrolysis.
- Lactose intolerance is caused by having insufficient enzyme lactase to hydrolyse the disaccharide lactose.
- The glycaemic index (GI) is a scale used to describe how quickly the carbohydrate in a food is broken down and absorbed into the bloodstream.
- Fats and oils are a part of a group of nutrients called lipids; they are made up of carbon, hydrogen and oxygen.
- Fats and oils are large esters called triglycerides made from the condensation reaction of one molecule of glycerol and three long-chain carboxylic acids called fatty acids.

- Saturated fatty acids are long-chain carboxylic acids that do not contain a $C=C$ double bond.
- Mono-unsaturated fatty acids contain one $C=C$ double bond, and polyunsaturated fatty acids contain more than one $C=C$ double bond.
- Unsaturated fats can be converted to saturated fats by the addition of hydrogen.
- Unsaturated fats are less stable and are more susceptible to oxidation.
- Antioxidants slow down the oxidation of food.
- Humans require the essential fatty acids α -linolenic and linoleic acids for the body to function effectively. These acids are known as omega fatty acids.
- During digestion, fats and oils are hydrolysed to glycerol and fatty acids, which can be assembled into triglycerides.
- On average, proteins and carbohydrates provide 17 kJ g^{-1} , and fats provide 37 kJ g^{-1} of energy.
- A calorimeter is an instrument that can be used to determine the energy changes that occur when a chemical reaction takes place.
- A calibration constant or calibration factor for a calorimeter may be calculated according to:

$$\text{calibration factor (J } ^\circ\text{C}^{-1}) = \frac{V(\text{volts}) \times I(\text{amps}) \times t(\text{s})}{\text{temperature rise (} ^\circ\text{C)}}$$

- A calibration constant or calibration factor for a calorimeter may also be calculated by chemical means using a reaction with a known ΔH .
- Solution calorimeters can be used to determine the energy changes occurring in aqueous solutions.
- Bomb calorimeters can be used to determine energy changes for combustion reactions.

Multiple choice questions

1. What is the main function of carbohydrates?
 - A For repair of body tissues
 - B To fight infection
 - C Source of energy
 - D To speed up chemical reaction
2. Which of the following is *not* a monosaccharide?
 - A Glucose
 - B Fructose
 - C Lactose
 - D Galactose
3. Two monosaccharides are joined by a:
 - A peptide bond
 - B glycosidic bond
 - C hydrogen bond
 - D ester bond.

4. Which of the following lists compounds in order of increasing sweetness?
 - A Fructose, glucose, sucrose
 - B Glucose, fructose, sucrose
 - C Glucose, sucrose, fructose
 - D Fructose, glucose, sucrose
5. Starch consists of:
 - A unbranched amylopectin and branched amylose
 - B unbranched amylose and branched amylopectin
 - C branched amylopectin and branched amylose
 - D unbranched amylose and unbranched amylopectin.
6. In which molecule is glucose stored in plants?
 - A Glycogen
 - B Cellulose
 - C Fructose
 - D Starch
7. A functional group that is *not* present in aspartame is:
 - A amine
 - B carboxyl
 - C aldehyde
 - D amide.
8. Which enzyme is missing in the small intestine of a person who is lactose intolerant?
 - A Dipeptidase
 - B Lipase
 - C Lactase
 - D Maltase
9. Symptoms of lactose intolerance include:
 - A coughing
 - B intestinal gas
 - C runny nose
 - D rashes.
10. Lactose intolerance:
 - A is common in most people of all ages, from newborn to adulthood
 - B is most common in people of northern European descent
 - C causes difficulty breathing
 - D is not a problem if drinking soy milk.
11. The glycaemic index indicates the:
 - A amount of nutrients in food
 - B amount of fats in food
 - C effect of food on blood glucose levels
 - D glycogen stores in the body.
12. Which of the following would have the lowest glycaemic index?
 - A Greek yoghurt
 - B Banana
 - C Kidney beans
 - D Chocolate
13. Fatty acids without double carbon-carbon bonds are said to be:
 - A saturated
 - B mono-saturated
 - C polyunsaturated
 - D unsaturated.
14. Which of the following is *not* true for the formation of a molecule of fat?
 - A Water molecules are produced as by-products.
 - B The process is a condensation reaction.
 - C The alcohol and carboxylic acid functional groups are involved.
 - D The reactants combine in a 1 : 1 ratio.
15. Lipids are formed by a condensation reaction between fatty acids and:
 - A an alcohol
 - B an amino acid
 - C an ester
 - D a monosaccharide.
16. Which of the following is an unsaturated fatty acid?
 - A Lauric acid
 - B Stearic acid
 - C Linolenic acid
 - D Myristic acid
17. The number of double bonds in arachidonic acid is:
 - A 1
 - B 2
 - C 3
 - D 4.
18. An example of a polyunsaturated acid is:
 - A arachidic acid
 - B linolenic acid
 - C oleic acid
 - D palmitic acid.
19. All of the following have 18 carbon atoms except:
 - A stearic acid
 - B palmitic acid
 - C oleic acid
 - D linolenic acid.
20. Which of the following fatty acids would have the highest melting point?
 - A Stearic acid
 - B Linoleic acid
 - C Oleic acid
 - D Linolenic acid
21. Which statement about fats and oils is *incorrect*?
 - A They are non-polar molecules.
 - B They are less dense than water.
 - C They are the result of condensation polymerisation reactions.
 - D They contain ester links.
22. Which of the following would *not* be a molecule used for energy storage in humans?
 - A Starch
 - B Cellulose
 - C Glycogen
 - D Fat
23. Which group of compounds do triglycerides belong to?
 - A Carboxylic acids
 - B Alcohols
 - C Ketones
 - D Esters

24. Which reaction is used to convert an oil into a fat?

- A Esterification
- B Dehydration
- C Hydrogenation
- D Hydrolysis

25. A water-soluble vitamin that is also an antioxidant is:

- A vitamin B
- B vitamin C
- C vitamin D
- D vitamin E.

26. In the process of oxidative rancidity:

- A saturated compounds are more likely to be involved than unsaturated compounds
- B oxygen attacks the double bond in a compound
- C less volatile compounds are produced
- D light is never involved.

27. Bomb calorimeters can be used to measure the energy released by burning a small piece of food. Before the bomb calorimeter can be used to determine heat of combustion of any compound, it must be calibrated. The following steps in random order are taken to perform the calibration.

Step 1: Supply a measured amount of electricity to the calorimeter for a particular time interval.

Step 2: Record the highest temperature obtained.

Step 3: Fill the calorimeter with a measured volume of water.

Step 4: Connect the calorimeter to a power source.

Step 5: Measure the initial temperature.

Which of the following presents an appropriate sequence of steps?

- A Steps 5, 1, 3, 2, 4
- B Steps 3, 1, 5, 4, 2
- C Steps 3, 4, 5, 1, 2
- D Steps 4, 3, 1, 5, 2

28. 2.31×10^{-2} mol of a compound is burned in a bomb calorimeter. The calorimeter factor is $4700 \text{ J } ^\circ\text{C}^{-1}$, and the temperature of the calorimeter increases by 5.75°C when the compound is burned. Calculate the molar heat of combustion of the compound in J mol^{-1} .

- A +18.9
- B -18.9
- C 1.17×10^6
- D -1.17×10^6

29. A bomb calorimeter measures the energy:

- A released in a reaction in solution
- B absorbed in a reaction in solution
- C released by a combustion reaction
- D absorbed by a combustion reaction.

30. The temperature rises from 25.00°C to 27.90°C when 2.55 g of sucrose undergoes combustion in

a bomb calorimeter. Calculate the molar enthalpy of combustion of sucrose. The calibration factor of the calorimeter is $4.90 \text{ kJ } ^\circ\text{C}^{-1}$. The molar mass of sugar is 342.0 g mol^{-1} .

- A $1.91 \times 10^3 \text{ kJ mol}^{-1}$
- B $-1.91 \times 10^3 \text{ kJ mol}^{-1}$
- C $-1.51 \times 10^0 \text{ kJ mol}^{-1}$
- D $1.45 \times 10^1 \text{ kJ mol}^{-1}$

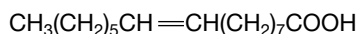
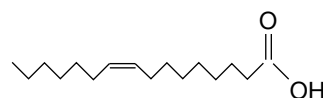
Review questions

Carbohydrates

1. The molecular formula of glucose, a monosaccharide, is $\text{C}_6\text{H}_{12}\text{O}_6$. What is the molecular formula of maltose, a disaccharide formed from glucose?
2. Starch is an important nutrient in the human diet. Describe the similarities and differences in the structures and properties of the two components that make up starch.
3. A cellulose molecule contains 640 glucose units. If the molar mass of glucose is 180 g mol^{-1} , what is the molar mass of the cellulose molecule?
4. A student comments that, after ingestion of dairy products, he experiences bloating, cramps and sometimes diarrhoea. With this information, it is reasonable to think that the student is intolerant to lactose. What is lactose intolerance and which age group or population are more likely to be lactose intolerant?
5. Describe the chemical structure of cellulose, and explain why humans cannot digest it. Why is it still necessary in the human diet?
6. (a) Which nutrient is important for the glycaemic index?
(b) Why are low glycaemic index foods better to eat before playing a game of basketball?
(c) Would it be preferable to eat high or low glycaemic foods after activity? Explain your answer.
(d) How does the proportion of amylose and amylopectin affect the GI value of food?

Fats and oils

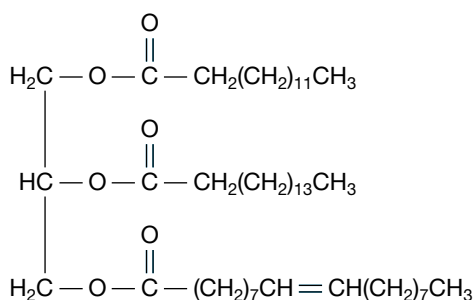
7. The structure of palmitoleic acid, a fatty acid found in olive oil, is shown below.



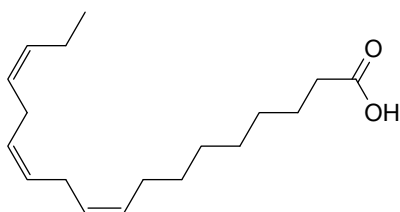
- (a) Palmitoleic acid is described as a *mono-unsaturated fatty acid*. Explain how each of the three italicised words relates to the structure of palmitoleic acid.

- (b) Use structural formulas to show how three molecules of palmitoleic acid may form a triglyceride when reacted with one molecule of glycerol.
- (c) Why is the formation of a triglyceride often described as an esterification reaction?

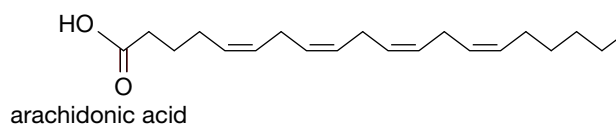
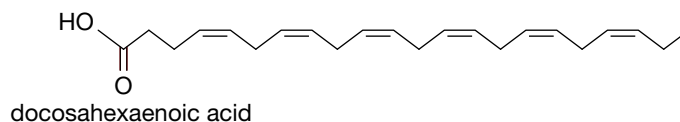
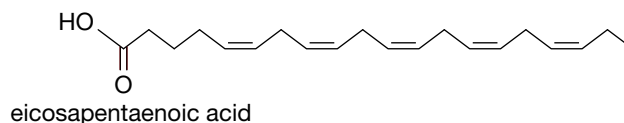
8. Write an equation showing the hydrolysis of this triglyceride.



9. Discuss the differences in 'spreadability' between butter and margarine in terms of their chemical structure and bonding.
10. Explain, in terms of their chemical structures, the differences in solubility in water of carbohydrates and fats.
11. List the similarities and differences between the structures, properties and susceptibility to oxidation of saturated and unsaturated fatty acids.
12. An unsaturated fat can be converted into a saturated fat by reacting it with hydrogen gas using a metal catalyst. If 16.8 g of hydrogen gas reacts with 1.40 moles of the unsaturated fat, determine the number of carbon-carbon double bonds present in each molecule of the unsaturated fat.
13. (a) What is rancidity?
 (b) What name is given to compounds that limit rancidity in foods?
 (c) Canola oil contains vitamin E as a natural component. Explain how this prevents the oil becoming rancid.
 (d) Explain three other methods of limiting oxidation of foods.
14. The molecule below is alpha-linolenic acid. It is described as an essential fatty acid and also an omega-3 fatty acid. Explain the reasons for this description.

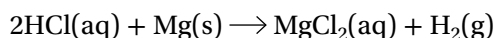


15. Indicate which of the following are omega-3 and which are omega-6 fatty acids. Explain your choices.



Energy in food

16. Nutrient labels can have a wide variety of names to describe the presence of sugar in the ingredient list. Construct your own list of names of substances that could be used to sweeten food.
17. 'Mates' savoury biscuits contain 14.7 g carbohydrate in 11 biscuits (25 g), which is described as a recommended serve. What is the energy available from 100 g of biscuits?
18. The heat of combustion of oleic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, can be determined by burning it in a bomb calorimeter. Write an equation for the complete combustion of oleic acid in excess oxygen.
19. A calorimeter was calibrated by passing an electrical current through a heater and measuring the rise in temperature that resulted. When a current of 133 mA from a 23.1 V source was passed through the heater for 264 s, the temperature of the calorimeter rose by 2.65°C . Determine the calibration factor of the calorimeter.
20. A simple calorimeter was used in a school laboratory to determine the heat of reaction when magnesium filings were added to hydrochloric acid according to the equation:



The calorimeter was calibrated by filling it with 100 mL of deionised water and then passing a current of 1.85 A at a voltage of 4.70 V through a heating coil for 1 minute 17 seconds. The temperature rose by 3.8°C . The calorimeter was then emptied, and 0.766 g of magnesium filings was added to it. Subsequently, 100 mL of 2.0 M HCl was added to reach the 100 mL calibration mark in the calorimeter. The temperature in the

calorimeter rose from 19.8 °C to a maximum of 21.1 °C.

- (a) Calculate the calibration factor for the calorimeter.
- (b) Calculate the heat of reaction.
- (c) The experimentally determined heat of reaction in (b) is much lower than the actual heat of reaction. Suggest reasons for this discrepancy.
- (d) What assumptions are made in this experiment?

21. A bomb calorimeter is used to measure the energy content of a 'Crispy' biscuit. The calibration factor of the calorimeter is 2.03 kJ °C⁻¹. When 2.50 g of the biscuit was burned in the calorimeter, the

temperature of the water rose from 24.2 °C to 45.5 °C.

- (a) Calculate the heat energy in kJ g⁻¹ of the biscuit.
- (b) Why is the energy measured in kJ g⁻¹ and not kJ mol⁻¹?
- (c) The energy obtained by the body is actually less than this calculated value. Excluding experimental error, what might be the reason for this?

22. The molar heat of combustion of glucose is 2816 kJ mol⁻¹. Estimate the approximate heat of combustion of sucrose, and explain how you arrived at the answer.



Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Multiple choice questions

1. Sucrose is a disaccharide consisting of glucose and:
A fructose
B glucose
C maltose
D galactose. 1 mark
2. Humans cannot digest cellulose because:
A cellulose is insoluble in water
B humans lack the necessary enzymes
C cellulose is too branched
D no organisms can digest cellulose. 1 mark
3. Triglycerides exhibit which organic chemistry functional group?
A Ester
B Hydroxyl
C Carboxyl
D Glycosidic 1 mark
4. Foods with a high glycaemic index would have a high proportion of:
A sugars
B fats
C polysaccharides
D cellulose. 1 mark

Extended response questions

1. The calibration factor of a bomb calorimeter was determined to be $26.3 \text{ kJ } ^\circ\text{C}^{-1}$. When a marshmallow weighing 0.870 g was placed in the calorimeter with excess oxygen and ignited, the temperature of the water bath increased by $1.32 \text{ }^\circ\text{C}$. Calculate the heat of combustion of the marshmallow in kJ g^{-1} . 2 marks
2. A bomb calorimeter was calibrated by passing a current of 4.15 A at a potential difference of 3.680 V through a heating coil for 2 minutes 15 seconds. The temperature of the calorimeter rose from $21.5 \text{ }^\circ\text{C}$ to $23.7 \text{ }^\circ\text{C}$. A sample of a high-energy bar weighing 2.50 g was then burned in the calorimeter in the presence of excess oxygen. The temperature of the contents of the calorimeter rose from $20.9 \text{ }^\circ\text{C}$ to $35.2 \text{ }^\circ\text{C}$.
 - (a) Calculate the heat content of the bar in J g^{-1} . 3 marks
 - (b) Identify the sources of error in the experiment, explaining how they may have affected the results. 2 marks

PRACTICAL INVESTIGATIONS

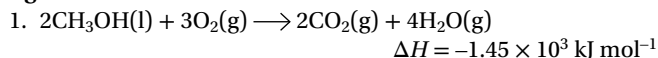
- EXPERIMENT 1.1** Fractional distillation of an ethanol/water mixture
- EXPERIMENT 2.1** Investigating heat changes in reactions
- EXPERIMENT 2.2** The relationship between pressure and volume
- EXPERIMENT 3.1** Investigating the Daniell cell
- EXPERIMENT 3.2** Predicting redox reactions
- EXPERIMENT 3.3** Galvanic cells and redox potentials
- EXPERIMENT 3.4** Looking at a dry cell
- EXPERIMENT 3.5** Investigating the hydrogen–oxygen fuel cell
- EXPERIMENT 4.1** Electrolysis of aqueous solutions of electrolytes
- EXPERIMENT 4.2** Factors affecting electrolysis
- EXPERIMENT 4.3** Electroplating
- EXPERIMENT 4.4** Anodising aluminium
- EXPERIMENT 5.1** Reaction rates
- EXPERIMENT 5.2** Catalytic oxidation of ammonia
- EXPERIMENT 5.3** Rate of hydrogen production – a problem-solving exercise
- EXPERIMENT 6.1** Investigating changes to the position of an equilibrium
- EXPERIMENT 6.2** Temperature and the equilibrium constant
- EXPERIMENT 6.3** Modelling an equilibrium
- EXPERIMENT 8.1** Constructing models of hydrocarbons
- EXPERIMENT 8.2** Constructing models of organic compounds
- EXPERIMENT 9.1** Constructing models of structural isomers
- EXPERIMENT 9.2** Investigating optical isomers
- EXPERIMENT 9.3** Esterification
- EXPERIMENT 10.1** Separation of food dyes using chromatography
- EXPERIMENT 10.2** Separating mixtures using column chromatography
- EXPERIMENT 10.3** Spectroscopy
- EXPERIMENT 10.4** Standardisation of hydrochloric acid
- EXPERIMENT 10.5** Analysis of vitamin C
- EXPERIMENT 11.1** Investigating proteins
- EXPERIMENT 11.2** Action of enzymes
- EXPERIMENT 12.1** Studying starch
- EXPERIMENT 12.2** Constructing models of carbohydrates
- EXPERIMENT 12.3** Solution calorimetry
- EXPERIMENT 12.4** Energy in a corn chip



Answers

Chapter 1

Page 5



Page 7

2. 34.3%
3. 85 MJ
4. $1.7 \times 10^5 \text{ kJ}$

Page 15

5. Brown coal is readily obtained from three open-cut mines in the Latrobe Valley: Hazelwood, Loy Yang and Yallourn. The economics of using the lower quality fuel for on-site power generation outweighs the cost of transporting higher grade coal from interstate.
6. (a) The rate is increased due to the increased demand from a larger population.
 (b) The rate is decreased due to a conscious need to conserve energy.
 (c) The rate is decreased when alternative energies and fuel sources replace fossil fuels as preferred sources of energy.
 (d) Fuel pricing policies are notoriously difficult to predict given their political nature. Put simply, the rate of fossil fuel use may drop if fuel prices increase, or increase if fuel prices drop.
 (e) Fossil fuel trade embargoes between nations could reduce fossil fuel use. This is a complex issue.

Page 17

8. Criterion	Petrol	Ethanol
Molecular structure	a complex mixture of hydrocarbon molecules	$\text{CH}_3\text{CH}_2\text{OH}$
Combustion products	produce CO, CO_2 , unburnt hydrocarbons and nitrogen oxides	produce lower CO and CO_2 emissions and similar or lower levels of unburnt hydrocarbon and nitrogen oxides
Renewability	non-renewable	renewable
Energy content (kJ g^{-1})	48	30

Criterion	Petrol	Ethanol
Environmental issues	CO_2 contributes to global warming by releasing carbon from non-renewable energy sources. - Extraction of petroleum (the source of petrol) can cause degradation of the immediate environment. - Transportation of petroleum by sea (and its extraction from sea based oil rigs) has resulted in environmentally damaging spills.	- There is a smaller contribution to global warming due to the essentially carbon-neutral process of recycling atmospheric CO_2. - Growing crops for ethanol involves the use of large amounts of synthetic fertilisers and herbicides.

Page 21

9. linolenic acid, $\text{C}_{17}\text{H}_{29}\text{COOH}$
10. $\text{C}_{15}\text{H}_{31}\text{COOCH}_3$
11. (a) $2\text{C}_{15}\text{H}_{31}\text{COOCH}_3(\text{l}) + 49\text{O}_2(\text{g}) \longrightarrow 34\text{CO}_2(\text{g}) + 34\text{H}_2\text{O}(\text{g})$
 (b) $\text{C}_{15}\text{H}_{31}\text{COOCH}_3(\text{l}) + 16\text{O}_2(\text{g}) \longrightarrow 17\text{CO}(\text{g}) + 17\text{H}_2\text{O}(\text{g})$

Multiple choice questions

1. B 2. D 3. B 4. B 5. C 6. A 7. A 8. B
 9. D 10. A 11. D 12. B 13. D 14. B 15. A

Review questions

1. (a) A fuel is a material used to produce energy or power.
 (b) Examples could include all foods, petrol (if you have driven or have been driven anywhere), natural gas (if you have cooked on a gas stove), wood, oil and diesel.
2. (a) inexpensive; available; burns cleanly; ignites easily; gives out a lot of energy
 (b) inexpensive; readily available; burns efficiently; high energy density
3. (a) Renewable fuels can be replaced by natural processes within a relatively short period of time. Non-renewable fuels are used more quickly than they can be produced.
 (b) Yes, because they are made from naturally formed biological materials.
 (c) No, because renewable energy sources also include energy obtained from solar, geothermal, hydro-electric, wave and tidal sources.

4. (a) $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
 $\Delta H = -2.20 \times 10^3 \text{ kJ mol}^{-1}$
 (b) $2\text{C}_3\text{H}_8(\text{g}) + 7\text{O}_2(\text{g}) \longrightarrow 6\text{CO}(\text{g}) + 8\text{H}_2\text{O}(\text{g})$
 (c) The reaction to CO is essentially 'incomplete', and more energy can be released if the reaction proceeds to completion (CO_2) as this allows more bonds to form.
 (d) Carbon monoxide is toxic. Carbon monoxide bonds much more strongly to haemoglobin in the blood than oxygen. As a consequence, carbon monoxide replaces the oxygen being carried to cells, and loss of consciousness and death can result.
5. chemical energy in the paper and dry twigs $\longrightarrow$ thermal (or heat) energy and light energy in the flame
6. Heat is progressively lost at each energy transformation stage.
7. (a) kinetic to sound
 (b) chemical to electrical to light
 (c) chemical to thermal and light
 (d) potential to kinetic
 (e) kinetic to thermal
 (f) potential to kinetic to potential
 (g) kinetic to thermal, sound and light
 (h) kinetic to potential
8. (a) chemical energy in the organic waste $\longrightarrow$ chemical energy in the biogas $\longrightarrow$ thermal energy (e.g. in furnaces) or electrical energy (e.g. for lighting)
9. When energy is converted from one form to another, varying yields of usable energy are produced. In highly efficient systems, more of the energy is converted to usable forms, while only small amounts of usable energy are available in inefficient systems. In both situations, however, the total amount of usable plus non-usable energy is equal to the initial quantity of energy being converted.
10. (a) chemical energy in coal $\longrightarrow$ thermal energy when combusted $\longrightarrow$ thermal energy in steam $\longrightarrow$ mechanical energy of the turbine $\longrightarrow$ electrical energy from the generator
 (b) coal and natural gas
 (c) methane
11. 37%
12. (a) A fossil fuel is a fuel formed from the remains of living organisms such as animals, trees and smaller plants that lived many years ago.
 (b) Examples include coal, petroleum and natural gas.
14. (a) A biofuel is a fuel that is produced from renewable, organic resources, especially biomass (organic material).
 (b) Examples include bioethanol, biodiesel and biogas.
17. (a) non-renewable
 (b) It is extracted by digging wells into underground coal deposits.
 (c) methane
 (d) possible pollution of underground water aquifers, and pollution from chemicals used in the fracking process
18. (a) Electricity production by coal-fired power stations is an inefficient process (only 30–40% of the chemical energy in coal is converted into electrical energy) as heat is lost when coal is burned and heat is also lost when steam is condensed back into water.
 (b) overuse of electrical appliances (e.g. clothes driers, air conditioners), not turning appliances off at the wall

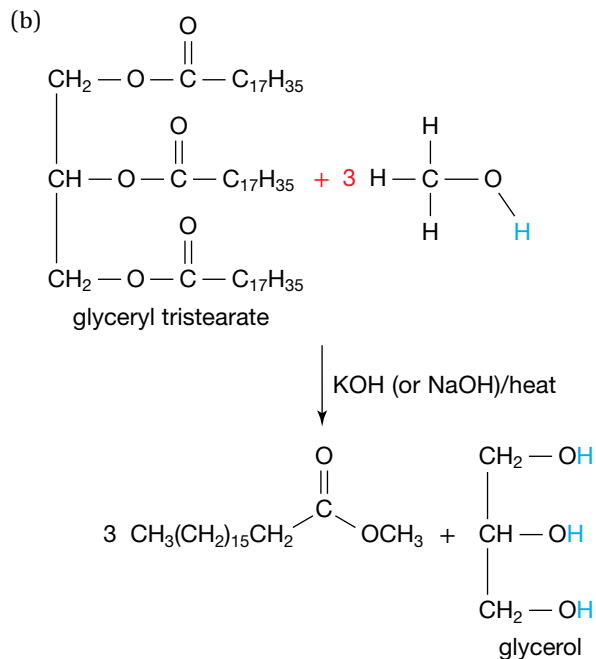
20. \$5.33

23. The combustion of fossil fuels puts carbon back into the environment (as carbon dioxide) that has been locked underground for millions of years. By comparison, biofuels are considered to be carbon neutral because the carbon released into the atmosphere was obtained relatively recently from the atmosphere via photosynthesis.
24. (a) Biodiesel comprises alkyl esters manufactured from vegetable oils or animals fats. Petrodiesel comprises long-chain alkanes obtained from the fractional distillation of petroleum.
 (b) At low temperatures, biodiesel can gel and increase its viscosity, which can compromise engine life.
 (c) Biodiesel is biodegradable and it is a renewable resource that can replace the use of fossil fuels, which contributes to global warming.
 (d) Food crops for human consumption may be diverted into biodiesel manufacture.

Exam practice questions (page 30)

Extended response questions

1. (a) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
 (b) Methane is non-renewable when obtained from a fossil fuel (natural gas) but is renewable when obtained from a biofuel (biogas).
 (c) when methane undergoes combustion in an insufficient supply of oxygen
 (d) $2\text{CH}_4(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
 (e) Carbon monoxide is toxic.
2. (a) Transesterification involves a chemical reaction where one type of ester is turned into another.



- (c) $2\text{C}_{17}\text{H}_{35}\text{COOCH}_3(\text{l}) + 55\text{O}_2(\text{g}) \longrightarrow 38\text{CO}_2(\text{g}) + 38\text{H}_2\text{O}(\text{g})$
 (d) glycerol
 (e) ester
 (f) advantages: renewable, carbon neutral; disadvantages: using crops for fuel rather than food production, deforestation to grow crops

Chapter 2

Page 34

- (a) endothermic (d) exothermic
(b) endothermic (e) exothermic
(c) exothermic (f) endothermic

Pages 36–7

- 117 kJ of heat energy
- (a) 1.14×10^3 kJ (b) 286 kJ
- 1.23×10^6 kJ of heat energy
- 607 kJ of heat energy
- 44.1 g
- (a) 4.94×10^3 kJ (b) 103 g
- The total energy stored in a substance (its enthalpy or heat content) depends upon the state of that substance. For example, in the reaction $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$, $\Delta H = +44 \text{ kJ mol}^{-1}$, it can be seen that $\text{H}_2\text{O}(\text{g})$ stores 44 kJ mol^{-1} more energy than $\text{H}_2\text{O}(\text{l})$. Hence, it is crucial to correctly show the state of water (and all other substances) in a thermochemical equation.

Page 38

- $-4238 \text{ kJ mol}^{-1}$
- $-1.23 \times 10^3 \text{ kJ mol}^{-1}$

Page 41

- (a) 1.03 atm (g) $3.0 \times 10^3 \text{ L}$
(b) $4.1 \times 10^5 \text{ Pa}$ (h) $2.5 \times 10^5 \text{ mL}$
(c) $1.33 \times 10^5 \text{ Pa}$ (i) 1.6 L
(d) 167 kPa (j) $3 \times 10^3 \text{ L}$
(e) 473 K (k) $5 \times 10^{-3} \text{ m}^3$
(f) 227°C (l) $6.00 \times 10^{-4} \text{ m}^3$

Page 46

- (a) 0.60 mole (b) 1.0 mole
- (a) 32 L (c) 0.22 L
(b) 5.6 L
- (a) 13.4 g (b) 2.71 g
- 0.960 kg
- $M = 83.3 \text{ g mol}^{-1}$; gas is Kr

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- For all parts of this question, $PV = nRT$ and, therefore,

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

- 94 L
 - 35 L
 - 10.1 L
 - $6.1 \times 10^{-3} \text{ L}$
 - 0.010 L
 - 0.24 L
- 21.8 L
 - 361 K
 - $1.3 \times 10^4 \text{ kPa}$

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- 3.47 L
- 0.96 L

Page 49

- 101 g
- 0.059 g

Page 50

- (a) 50 mL (b) 25 mL (c) 50 mL
- (a) 40 mL (c) 40 mL
(b) 60 mL (d) 20 mL

Page 51

- 47.3 kJ
- 17.6 kJ

Page 53

- (a) 224 g
(b) 175% increase
(c) If P and T are kept constant, $V(\text{CH}_4)$ consumed = $V(\text{CO}_2)$ produced; that is, there is no percentage change in volume. This contrasts significantly with the 175% increase when comparing masses.

Page 54

- 64.7 g
- (a) 60.7 g
(b) Similar masses of CO_2 will be produced per MJ of heat energy by both methanol and ethanol.
- (a) 180 g MJ^{-1} (b) 101 L MJ^{-1}

Pages 55–6

Property	Ethanol	Candle wax	Butane
mass of fuel used (g)	1.23	0.22	0.23
temperature rise ($^\circ\text{C}$)	15.0	10.0	9.0
molar mass (g mol^{-1})	46.0	282	58

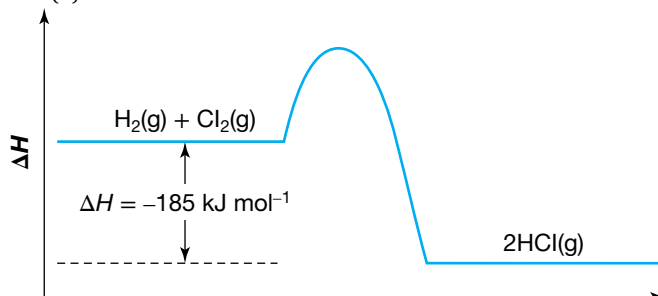
- ethanol: energy per g = 10.2 kJ g^{-1}
candle wax: energy per g = 38 kJ g^{-1}
butane: energy per g = 33 kJ g^{-1}
- ethanol: $\Delta H = -469 \text{ kJ mol}^{-1}$
candle wax: $\Delta H = -1.1 \times 10^4 \text{ kJ mol}^{-1}$
butane: $\Delta H = -1.9 \times 10^3 \text{ kJ mol}^{-1}$
- (a) exothermic
(b) 34.4%
(c) sources of error: heat loss from the candle flame to the surrounding air; heat loss from the copper can; heat loss from the water in the can; incomplete combustion of the fuel
minimising errors: totally surround the flame with a heat-reflecting barrier; cover the side of the can with insulating material; place a lid on the can

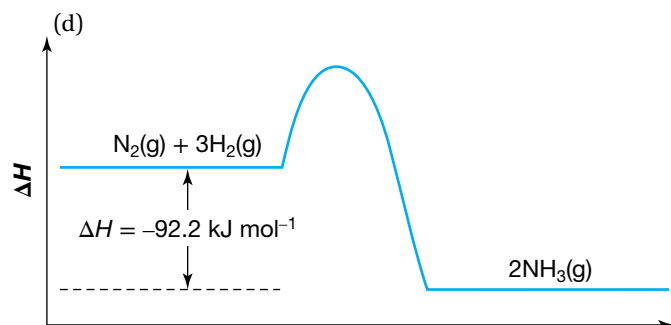
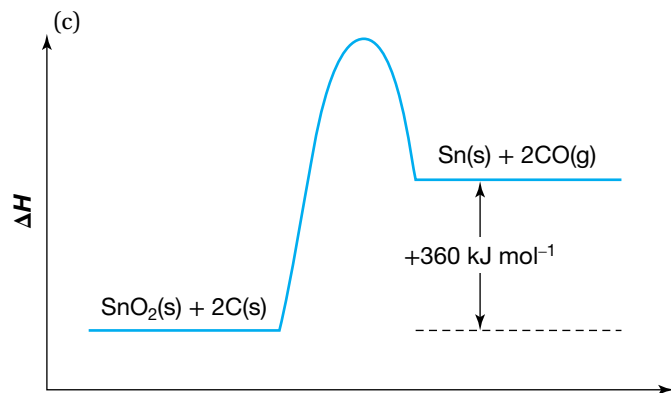
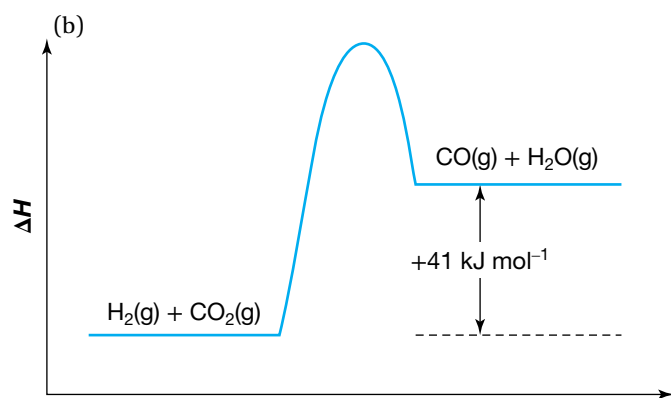
Multiple choice questions

- C 2. C 3. B 4. C 5. A 6. A 7. B 8. D
9. B 10. D 11. D 12. B 13. A 14. B 15. B 16. A
17. D 18. C 19. C 20. C

Review questions

- The enthalpy change of a chemical reaction is the change in heat content (stored chemical energy) as reactants are converted to products in that chemical reaction.
- (a) exothermic (c) endothermic
(b) endothermic (d) exothermic
- (a)





4.

	Exothermic	Endothermic
(a)	negative	positive
(b)	energy evolved into the surroundings	energy absorbed from the surroundings
(c)	energy level of reactants greater than that of products	energy level of reactants less than that of products

5. In an exothermic reaction, the total energy is conserved as stored chemical energy is transformed into thermal energy.

6. (a) $\text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$
 $\Delta H = -1364 \text{ kJ mol}^{-1}$
 (b) $\text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 2\text{O}_2(\text{g}) \longrightarrow 2\text{CO}(\text{g}) + 3\text{H}_2\text{O}(\text{l})$
 $\Delta H = -1192 \text{ kJ mol}^{-1}$
 (c) Carbon dioxide forms in plentiful air (3O_2) while carbon monoxide forms in limited air (2O_2).
 (d) -172 kJ mol^{-1}
 7. $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
 $\Delta H = -3.12 \times 10^3 \text{ kJ mol}^{-1}$
 $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 $\Delta H = -1.41 \times 10^3 \text{ kJ mol}^{-1}$

8. $\text{C}_{12}\text{H}_{26}(\text{l}) + 37\text{O}_2(\text{g}) \longrightarrow 24\text{CO}_2(\text{g}) + 26\text{H}_2\text{O}(\text{l})$
 $\Delta H = -1.50 \times 10^4 \text{ kJ mol}^{-1}$
9. (a) alkane
 (b) $\text{C}_{25}\text{H}_{52}$
 (c) $\text{C}_{25}\text{H}_{52}(\text{s}) + 38\text{O}_2(\text{g}) \longrightarrow 25\text{CO}_2(\text{g}) + 26\text{H}_2\text{O}(\text{g})$
 (d) $\text{C}_{25}\text{H}_{52}(\text{s}) + 38\text{O}_2(\text{g}) \longrightarrow 25\text{CO}_2(\text{g}) + 26\text{H}_2\text{O}(\text{l})$
 $\Delta H = -1.47 \times 10^4 \text{ kJ}$
 (e) The molar mass of $\text{C}_{24}\text{H}_{50}$ would be less; therefore, the calculated moles of the wax would be greater, and the heat energy released per mole would be less, as would the value of the heat of combustion.
10. (a) Gas particles move with continual random motion and, when doing so, collide with the walls of any container, producing the effect we know as pressure.
 (b) As temperature increases, gas particles move more rapidly. This results in an increase in the frequency of collisions of the gas particles with the walls of any container.
11. (a) $1.02 \times 10^3 \text{ mm Hg}$, 136 kPa
 (b) $4.87 \times 10^4 \text{ Pa}$, 0.480 atm
 (c) 1.026 atm, 770 mm Hg
12. (a) 373 K (b) 253 K (c) 73 K (d) 618 K
13. (a) 27 °C (d) 119 °C
 (b) 154 °C (e) -200 °C
 (c) -100 °C
14. (a) 0.125 m³ (d) 0.0026 L
 (b) $1.25 \times 10^5 \text{ mL}$ (e) $2 \times 10^3 \text{ L}$
 (c) 0.300 L (f) 3 L
15. (a) 0.061 mol (b) 0.103 mol (c) 0.0101 mol
16. (a) 37.9 L (b) 21.1 L (c) $1.0 \times 10^8 \text{ L}$
17. (a) 0.194 g (b) 7.9 g
18. (a) 1.05 mol (b) 6.32×10^{23} molecules
19. Absolute zero is the lowest temperature that is theoretically possible. At this temperature, the motion of all particles would stop. While this motion can be minimised, it cannot be stopped and hence absolute zero can be approached but not reached.
20. 3.25 L
21. $3.3 \times 10^2 \text{ L}$
22. (a) -267 °C (b) -93 °C
23. (a) 1.38 mol (c) 0.566 mol
 (b) 12.7 mol (d) 1.00 mol
24. (a) 13.3 L (b) 35.9 L (c) 597 L (d) 3.50 L
25. (a) 0.0433 mol (b) 2.65×10^{22} (c) 60 °C
26. 27 °C
27. 5.00 g
28. $3.7 \times 10^2 \text{ kPa}$
29. 28 g mol⁻¹; N₂
30. 6.0 L
31. 1.9×10^{20} molecules
32. 11.4 g
33. (a) 9.9 g (c) 15 L
 (b) 11 L (d) 0.092 mL
34. (a) $4.41 \times 10^5 \text{ L}$ (b) 1.78 tonne
35. (a) 25.0 L (b) 125 L
36. 12.8 L
37. 4.0 L of H₂(g) will react exactly with 2.0 L of O₂(g). O₂(g) is in excess by 8 L.
38. (a) N₂(g) + 3H₂(g) → 2HN₃(g)
 (b) 15 m³
 (c) 30 m³

39. (a) The equation can be described as a thermochemical equation because the equation includes the amount of heat absorbed by the reaction.
 (b) 0.5 kJ
 (c) 0.0707 J
 (d) 4.24 kg
 (e) 2.83×10^3 L
40. (a) 592 kJ (b) 1.84×10^3 kJ (c) 5.36 kJ (d) 20.5 kJ
41. -66 kJ mol^{-1}
42. (a) $\text{C}_4\text{H}_{10}(\text{g}) + \frac{13}{2}\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$
 $\Delta H = -2874 \text{ kJ mol}^{-1}$
 (b) 1.4×10^3 kJ
43. (a) 1.57×10^3 kJ (b) 1.4×10^7 L
44. (a) 1.5×10^2 L (b) 64 g (c) 37.2 L MJ^{-1}
45. (a) 19.8 g (e) 5.0 g MJ^{-1}
 (b) 59.4 g MJ^{-1} (f) 3.2 g MJ^{-1}
 (c) 20.9 g (g) 1.31 L
 (d) 64.4 g MJ^{-1}
- (h) According to the calculations, LPG has a net reduction of CO_2 emission of 5.0 g MJ^{-1} , whereas petrol has a reduction of only 3.0 g MJ^{-1} ; therefore, LPG is the better fuel on this basis.
46. 6.48 kJ
47. $0.129 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$
48. 50 kJ g^{-1}
49. (a) 18.4 kJ
 (b) -846 kJ mol^{-1}
 (c) 62.0%
- (d) Sources of error include heat loss from the flame, heat absorbed by the can, heat loss from the water in the can, and incomplete combustion of the ethanol. An improved design could include a barrier surrounding the apparatus to minimise radiated heat loss from the flame, using insulating material surrounding the can and placing a top on the can.
50. (a) $-2.87 \times 10^3 \text{ kJ mol}^{-1}$
 (b) The value obtained experimentally is lower than the expected value primarily because of the heat losses that accompanied the experiment. The % accuracy = $(2.87 \times 10^3 / 3509) \times 100 = 81.9\%$. That is, 18.1% of the heat energy generated by the pentane when it was combusted was lost to the atmosphere.

Exam practice questions (page 65)

Extended response questions

- 464 L
- (a) Kerosene comprises a complex mixture of different hydrocarbon molecules and hence it does not have a known molar mass.
 (b) 5.52 cups
- (a) 44.2 g (c) 4.9 g MJ^{-1}
 (b) 29.8 g (d) 2.62 L

Chapter 3

Page 70

- (a) H +1; Br -1 (d) Na +1; Cl +5; O -2
 (b) Na +1; O -2 (e) Al +3; O -2
 (c) C -4; H +1 (f) H +1; P +5; O -2
- (a) +6 (c) +6
 (b) +4 (d) -2
- left to right: +6, +3, +2
- (a) N -3; H +1 (d) V +4; O -2
 (b) Mn +7; O -2 (e) I +5; O -2
 (c) H +1; S -2 (f) P +5; O -2

Pages 71–2

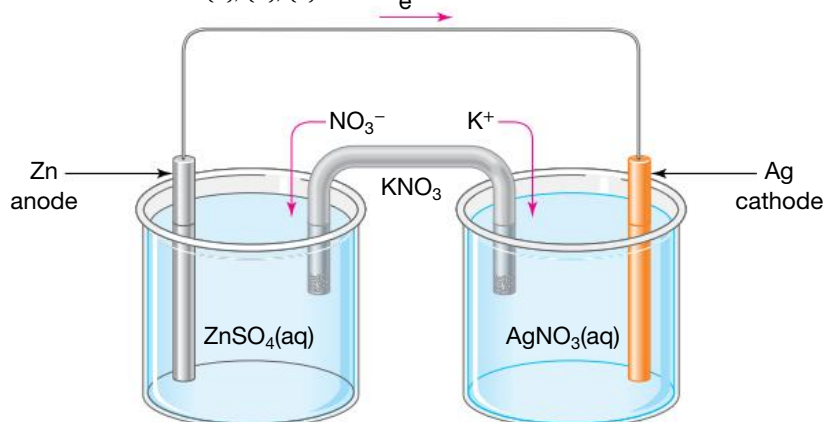
- (a), (c), (g), (h)
- (a) Fe is oxidised and Cl_2 is reduced.
 (c) N (in NO) is oxidised and O_2 is reduced.
 (g) C (in CO) is oxidised and O_2 is reduced.
 (h) H_2 is oxidised and C (in C_2H_4) is reduced.

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- (a) $\text{CH}_3\text{CH}_2\text{OH}(\text{l}) \longrightarrow \text{CH}_3\text{CHO}(\text{l}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$
 (b) $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
 (c) $5\text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 2\text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow$
 $5\text{CH}_3\text{CHO}(\text{l}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$
 (d) $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$ is the reducing agent and $\text{MnO}_4^-(\text{aq})$ is the oxidising agent.
- (a) $\text{CH}_3\text{CHO}(\text{l}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{CH}_3\text{COOH}(\text{l}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$
 (b) $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
 (c) $5\text{CH}_3\text{CHO}(\text{l}) + 2\text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow$
 $5\text{CH}_3\text{COOH}(\text{l}) + 2\text{Mn}^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
- $\text{Cu}(\text{s}) + 2\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) \longrightarrow$
 $\text{Cu}^{2+}(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

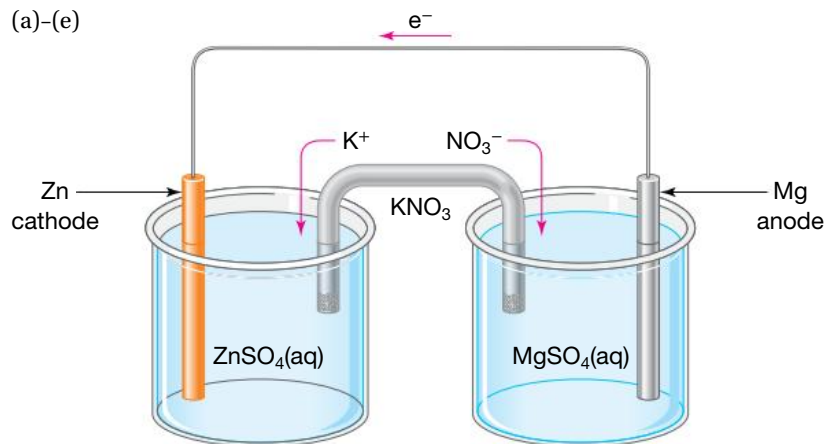
Page 76

11. (a), (d), (e)



- (b) oxidation: $\text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
 reduction: $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$
 (c) $\text{Zn}(\text{s}) + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$

12. (a)-(e)



(f)-(i)

oxidation (at anode): $\text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$

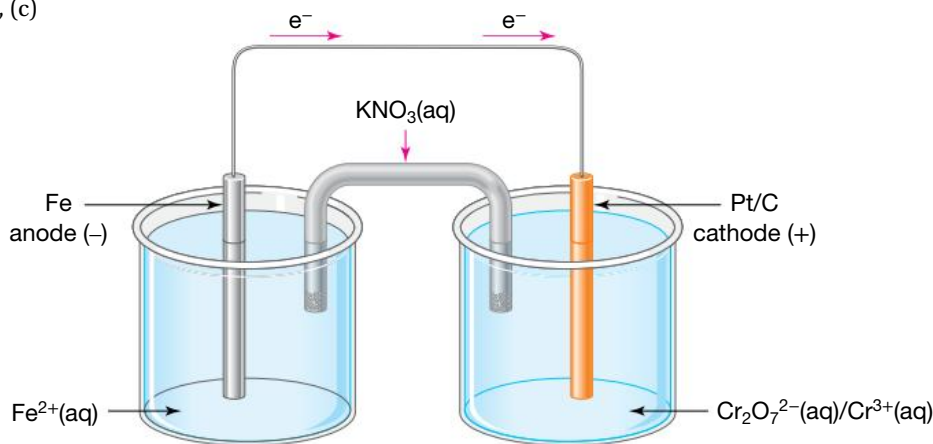
reduction (at cathode): $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}$

overall reaction: $\text{Mg(s)} + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Zn(s)}$

Zn^{2+} is the oxidising agent; Mg is the reducing agent.

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13. (a), (c)



(b) $\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$ $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O(l)}$

(d) This reaction will not occur without $\text{H}^+(\text{aq})$.

Page 82

14. (a) (i) MnO_4^- (ii) Al (iii) Al^{3+} (iv) Mn^{2+}

(b) $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$

$\text{I}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$

$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al(s)}$

$\text{MnO}_4^- + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O(l)}$

$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb(s)}$

15. It will be a non-spontaneous reaction because $\text{Ag}^+(\text{aq})$ is the weaker of the two oxidising agents and $\text{Br}^-(\text{aq})$ is the weaker of the two reducing agents.

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16. (a) $\text{Cl}_2(\text{g}) + \text{Ni(s)} \rightarrow 2\text{Cl}^-(\text{aq}) + \text{Ni}^{2+}(\text{aq})$

(b) $2\text{Al}^{3+}(\text{aq}) + 3\text{Mg(s)} \rightarrow 2\text{Al(s)} + 3\text{Mg}^{2+}(\text{aq})$

(c) $2\text{MnO}_4^- + 6\text{H}^+(\text{aq}) + 5\text{ClO}_3^-(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 3\text{H}_2\text{O(l)} + 5\text{ClO}_4^-(\text{aq})$

(d) $2\text{MnO}_4^- + 16\text{H}^+(\text{aq}) + 5\text{Fe(s)} \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O(l)} + 5\text{Fe}^{2+}(\text{aq})$

17. The rate of reaction may be too slow to be observed initially or non-standard conditions may have been used, making the reaction less favourable/observable.

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18. (a) anode: zinc; cathode: lead; standard cell potential = 0.63 V

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

$\uparrow$
 2e^-

(b) anode: platinum/carbon; cathode: silver; standard cell potential = 0.03 V

$\text{Fe}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{Ag(s)} + \text{Fe}^{3+}(\text{aq})$

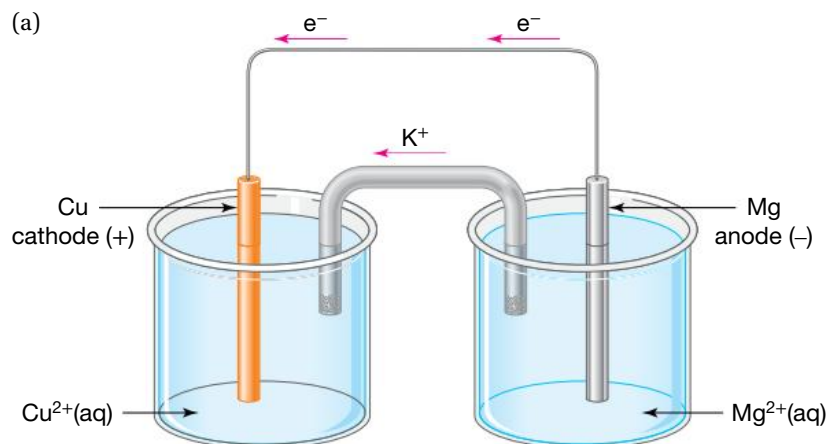
$\uparrow$
 e^-

(c) anode: iron; cathode: platinum/carbon; standard cell potential = 1.64 V

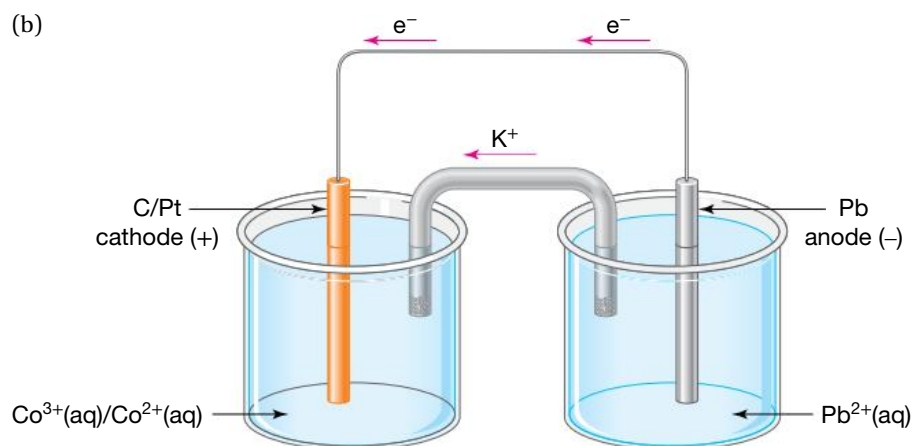
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 2\text{Fe(s)} \rightarrow 2\text{H}_2\text{O(l)} + 2\text{Fe}^{2+}(\text{aq})$

$\uparrow$
 4e^-

19. (a)



(b)



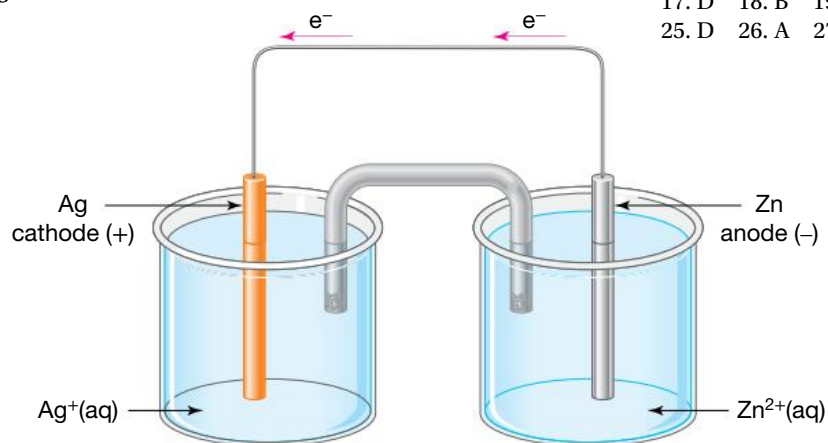
20. cell contents used up; salt bridge dried out; electrical circuit not complete if ions from salt bridge precipitate with ions in the half-cell (the wrong electrolyte used in the salt bridge)

Page 88

21. Primary cells are not rechargeable while secondary cells are rechargeable.
22. zinc (Zn)
23. +4 in MnO_2 to +3 in Mn_2O_3

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24.



25. decreased
26. Lithium cells produce a high cell voltage. They also last for a long time and have a high energy density.

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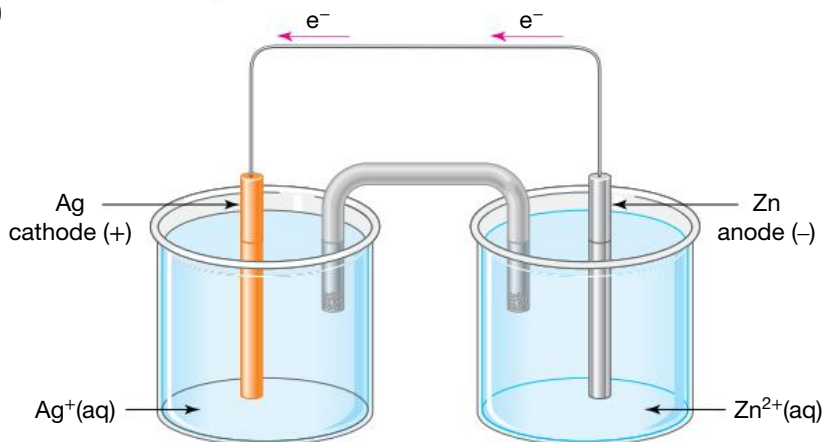
28. Fuel cells can be used as portable power sources for small appliances and devices, back-up power for hospitals and industry, power sources for forklifts and boats and power sources for high-usage transport vehicles such as cars and buses.

Multiple choice questions

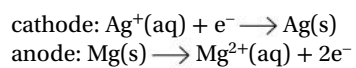
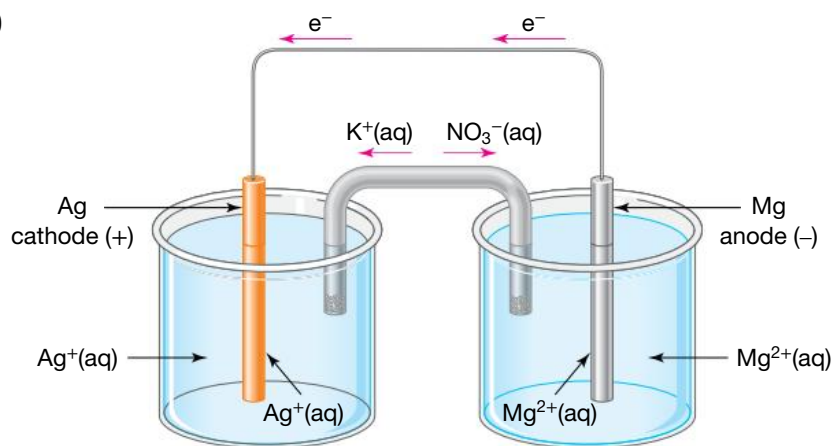
1. B 2. B 3. D 4. B 5. B 6. D 7. A 8. C
9. B 10. C 11. C 12. D 13. A 14. B 15. C 16. B
17. D 18. B 19. A 20. B 21. A 22. A 23. C 24. D
25. D 26. A 27. D

Review questions

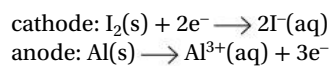
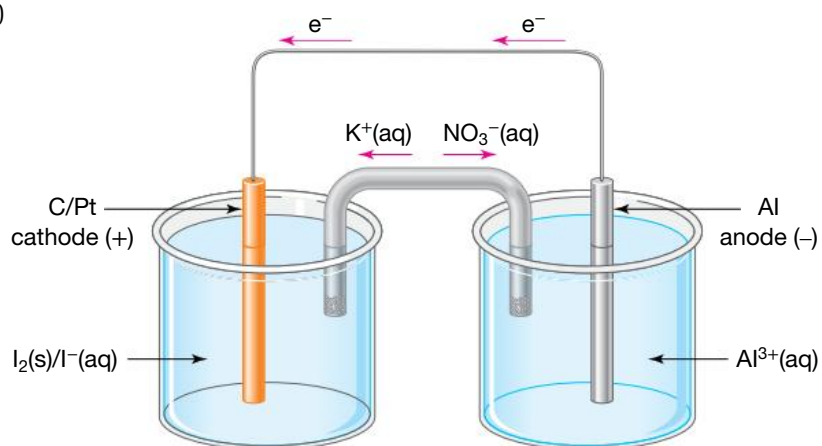
- Answers will vary.
- An oxidising agent is an electron acceptor. It causes another substance (the reducing agent) to be oxidised.
 - A reducing agent is an electron donor. It causes another substance (the oxidising agent) to be reduced.
 - An oxidation number is a number assigned to an element. Any change in this number represents a loss of electrons (oxidation) or gain of electrons (reduction).
For example: $\begin{matrix} -4 & +1 & 0 & +4 & -2 & +1 & -2 \\ \text{CH}_4(\text{g}) & + & 2\text{O}_2(\text{g}) & \longrightarrow & \text{CO}_2(\text{g}) & + & 2\text{H}_2\text{O}(\text{l}) \end{matrix}$
C in CH_4 (ON = -4) is oxidised to C in CO_2 (ON = +4), while O in O_2 (ON = 0) is reduced to O in H_2O (ON = -2).
- Zn is oxidised; HCl is reduced.
 - NO is oxidised; O_2 is reduced.
 - Mg is oxidised; H_2SO_4 is reduced.
 - Al is oxidised; Cl_2 is reduced.
- Na is the reducing agent; S is the oxidising agent.
 - K is the reducing agent; Cl_2 is the oxidising agent.
 - Al is the reducing agent; O_2 is the oxidising agent.
 - HBr is the reducing agent; Cl_2 is the oxidising agent.
 - C is the reducing agent; O_2 is the oxidising agent.
 - Zn is the reducing agent; MnO_2 is the oxidising agent.
- oxidising agent: Cl_2 ; reducing agent: I^-
 - oxidising agent: Br_2 ; reducing agent: Cl^-
 - oxidising agent: I_2 ; reducing agent: Br^-
 - oxidising agent: Co^{3+} ; reducing agent: Pb
 - oxidising agent: Pb^{2+} ; reducing agent: Fe
 - oxidising agent: H^+ ; reducing agent: Hg
 - oxidising agent: Cl_2 ; reducing agent: F^-
- $2\text{Br}^-(\text{aq}) + \text{SO}_4^{2-} + 4\text{H}^+(\text{aq}) \longrightarrow \text{Br}_2(\text{l}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 - $2\text{Al}(\text{s}) + 3\text{Cl}_2(\text{g}) \longrightarrow 2\text{AlCl}_3(\text{s})$
 - $\text{I}_2(\text{s}) + \text{H}_2\text{S}(\text{g}) \longrightarrow 2\text{I}^-(\text{aq}) + \text{S}(\text{s}) + 2\text{H}^+(\text{aq})$
 - $3\text{Cu}(\text{s}) + 2\text{NO}_3^-(\text{aq}) + 8\text{H}^+(\text{aq}) \longrightarrow 3\text{Cu}^{2+}(\text{aq}) + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
 - $\text{Cu}(\text{s}) + 2\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 - $3\text{CuO}(\text{s}) + 2\text{NH}_3(\text{g}) \longrightarrow 3\text{Cu}(\text{s}) + 3\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$
 - $\text{PbS}(\text{s}) + 4\text{H}_2\text{O}_2(\text{l}) \longrightarrow \text{PbSO}_4(\text{s}) + 4\text{H}_2\text{O}(\text{l})$
 - $2\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 16\text{H}^+(\text{aq}) + 3\text{CH}_3\text{CH}_2\text{OH}(\text{aq}) \longrightarrow 4\text{Cr}^{3+}(\text{aq}) + 11\text{H}_2\text{O}(\text{l}) + 3\text{CH}_3\text{COOH}(\text{aq})$
- $\text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
 - $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$
 - $\text{Zn}(\text{s}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Fe}(\text{s})$
- $\text{Zn}(\text{s}) + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$
 - cathode: $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$
 - anode: $\text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
- Not all of the chemical energy is transformed into electrical energy. Some of the chemical energy stored in the reactants is released as heat energy.
- An electrochemical cell that creates electrical energy from spontaneous redox reactions occurring within the cell
 - The electrolyte in the two half-cells and the salt bridge
 - The external wiring that connects the anode and cathode
 - A solid conductive surface where reduction occurs
 - A solid conductive surface where oxidation occurs
 - The electrolyte connecting the anode and cathode compartments
 - An unreactive electrode, such as carbon or platinum, used as a conductive surface on which the redox half-reaction can occur
- Electrons cannot flow in the external circuit unless ions can move in the internal circuit to balance the charge.
- spontaneous
 - non-spontaneous
 - non-spontaneous
 - spontaneous
 - spontaneous
 - non-spontaneous
 - non-spontaneous
 - non-spontaneous
 - spontaneous
 - non-spontaneous
- yes
 - no
 - yes
 - no



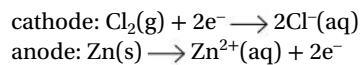
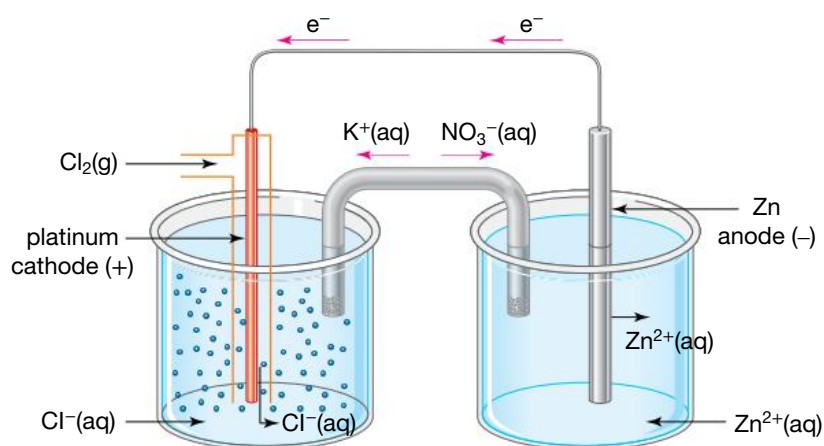
13. (a)



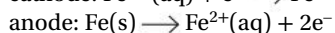
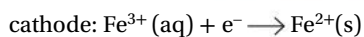
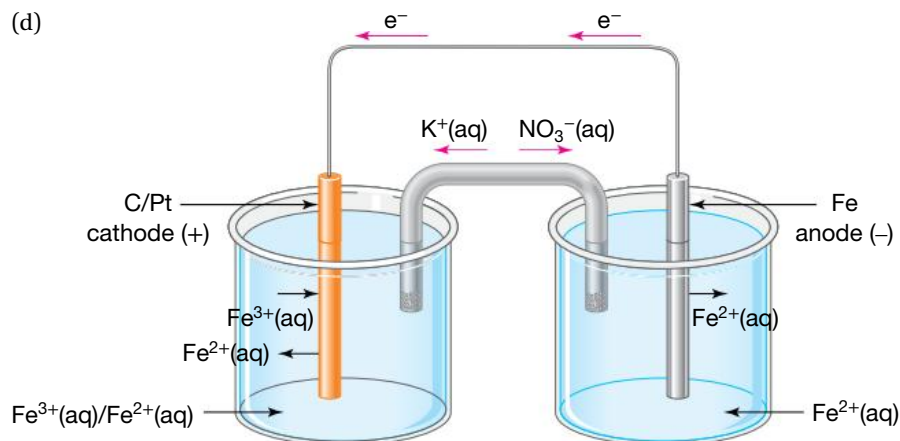
(b)



(c)



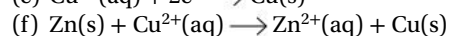
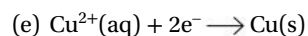
(d)



15. (a) Electrons flow from zinc to copper.

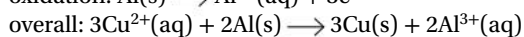
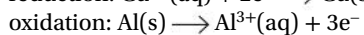
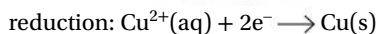
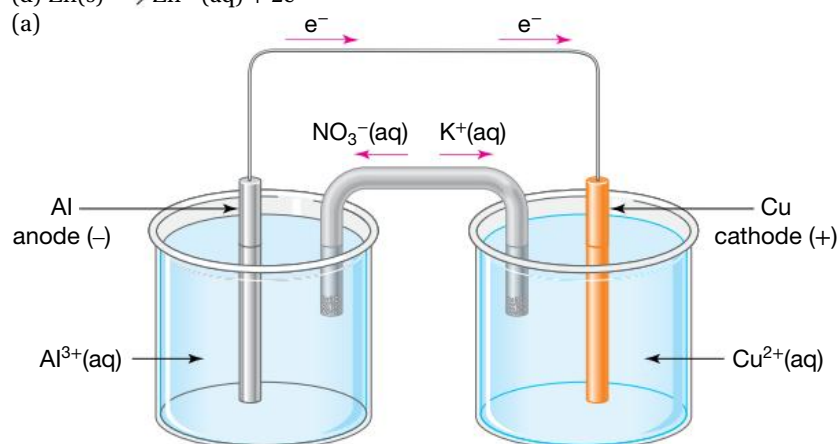
(b) Zinc is the anode.

(c) The copper container is the cathode.

(d) $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$ 

(g) porous pot

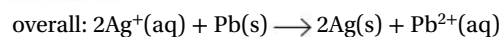
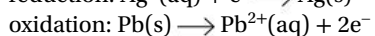
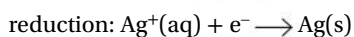
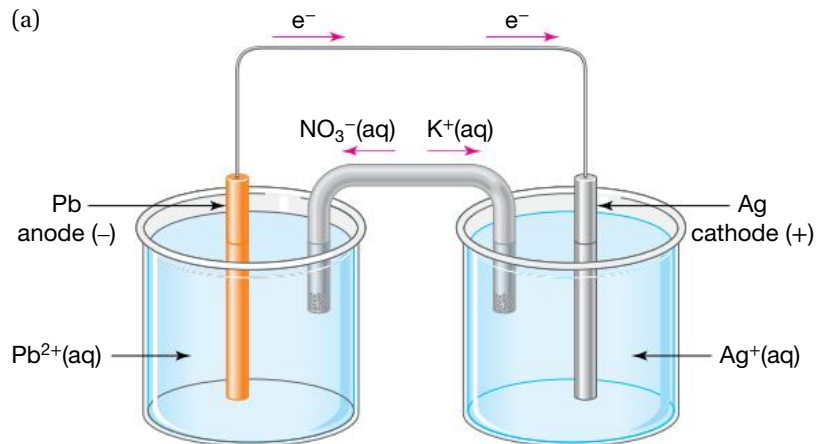
16. (a)



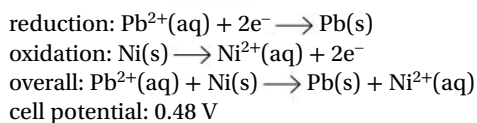
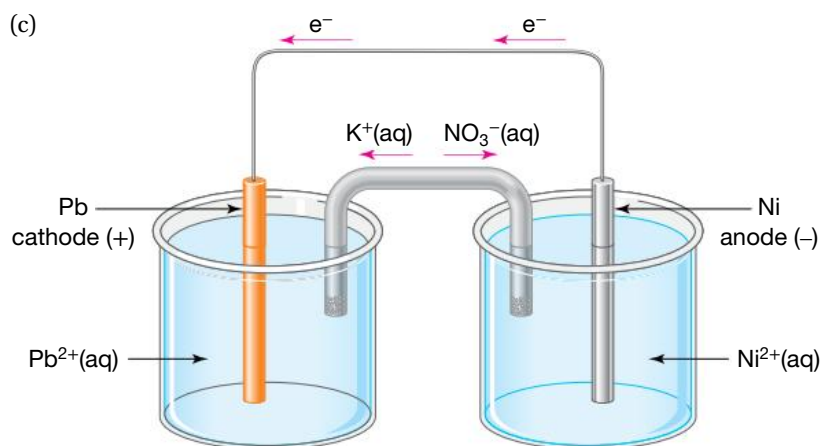
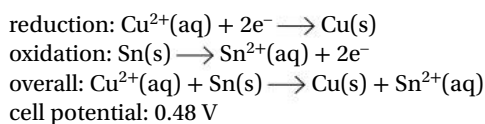
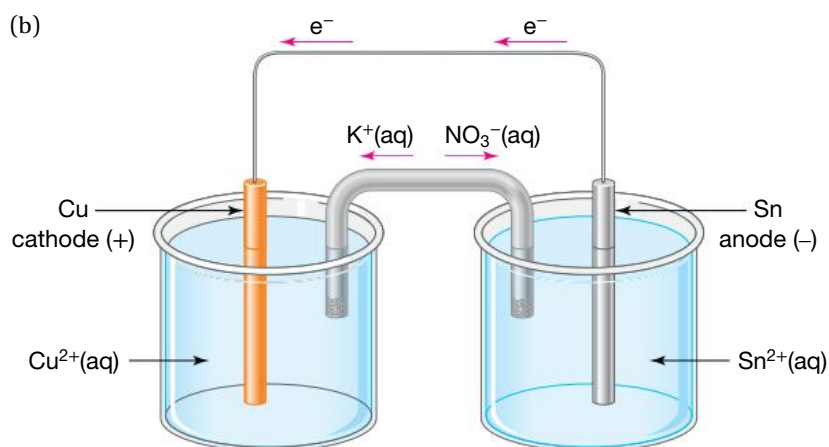
(b) There would be no electron flow — the transformation from chemical energy to electrical energy would stop.

(c) The intensity of the blue colour would slowly fade as the Cu^{2+} ions react at the cathode.

17. (a)

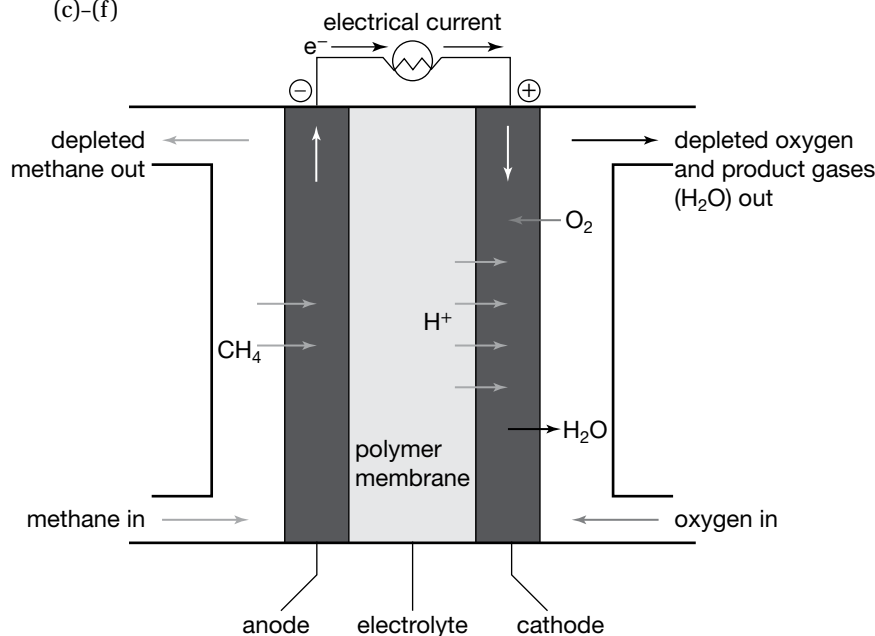


cell potential: 0.93 V



18. (a) The paint would form a barrier surrounding the iron. Also, the aluminium in the paint would preferentially undergo oxidation; it is a stronger reducing agent than iron and so it would protect the iron.
- (b) Aluminium is a stronger reducing agent than both copper and iron and so, when the windows are exposed to a corrosive environment (oxygen in the air/water from rain), the aluminium will corrode.
19. Both Mg and Zn are stronger reducing agents than iron so, when iron is exposed to a corrosive environment (oxygen in the air/water from rain), the Mg or Zn will preferentially corrode, thus protecting the iron from corrosion.
20. B is a stronger reducing agent than C, and C is a stronger reducing agent than A.
21. Typically, a battery is a series connection of two or more cells, although it is common (but incorrect) to refer to single cells as batteries.
22. (a) Commercial cells use an electrolyte paste to prevent the contents of the cell from mixing. They also use separators to prevent mixing of the anode and cathode compartments.
23. (a)–(c) A longer life is usually linked to an increased quantity of reacting materials, as this increases the quantity of chemical energy that is available to be converted into electrical energy.
25. (a) Materials that are at 'opposite ends' of the electrochemical series provide the largest cell voltages; that is, it is desirable to combine a strong oxidising agent with a strong reducing agent.
- (b) anode: $\text{Ag}^+(\text{l}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$
 cathode: $\text{Li}(\text{s}) \rightarrow \text{Li}^+(\text{l}) + \text{e}^-$
 overall: $\text{Ag}^+(\text{l}) + \text{Li}(\text{s}) \rightarrow \text{Ag}(\text{s}) + \text{Li}^+(\text{l})$
- (c) Lithium reacts violently with water.

- (d) advantage: easier to fit inside the body; less invasive to insert
disadvantage: reduced life span; inconvenient to replace
26. (a) anode: $\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$
cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$
overall: $4\text{Al(s)} + 3\text{O}_2(\text{g}) + 6\text{H}_2\text{O(l)} \rightarrow 4\text{Al(OH)}_3(\text{s})$
- (b) anode: $\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$
cathode: $2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
overall: $2\text{Al(s)} + 6\text{H}_2\text{O(l)} \rightarrow 2\text{Al(OH)}_3(\text{s})$
27. (a) A fuel cell is an electrochemical device that converts chemical energy into electricity without combustion as an intermediary step; that is, a fuel cell converts chemical energy directly into electrical energy rather than into heat energy. There is also a continual supply of reactants.
- (b) Operating and maintenance costs are low because they can be used continually rather than being discarded when depleted. Fuel cells often need the supply of only one reagent, as oxygen can be sourced from the atmosphere.
28. (a) high energy conversion efficiency; easy to maintain; low temperature operation
- (b) expensive; not fully technologically developed; difficulties with the distribution, storage and transportation of fuels (particularly hydrogen gas)
29. (a) $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O(l)} \rightarrow \text{CO}_2(\text{g}) + 8\text{H}^+(\text{aq}) + 8\text{e}^-$
(b) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$
(c)-(f)



30. (a) $2\text{C}_8\text{H}_{18}(\text{l}) + 25\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O(l)}$
(b) Fuel cells are more efficient at transforming the chemical energy in the fuel. Also, they are environmentally better because less carbon dioxide is released per unit of transformed energy.
(c) anode: $\text{C}_8\text{H}_{18}(\text{l}) + 16\text{H}_2\text{O(l)} \rightarrow 8\text{CO}_2(\text{g}) + 50\text{H}^+(\text{aq}) + 50\text{e}^-$
cathode: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$
(d) $2\text{C}_8\text{H}_{18}(\text{l}) + 25\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O(l)}$
The answers to (a) and (d) are the same.
31. Fossil fuels are non-renewable and their use as fuels is a major contributor to global warming. Electrochemical cells, and fuel cells in particular, can use renewable fuels (e.g. hydrogen gas obtained from water using solar energy for

electrolysis) and hence are a sustainable alternative to fossil fuels.

32. Electricity produced from an electrochemical cell involves just one energy transformation (chemical energy to electrical energy) and hence has a relatively high level of efficiency. Both hydro-electricity schemes and coal-fired power stations produce electricity less efficiently as they involve multiple energy transformations.

- (a) potential $\rightarrow$ kinetic $\rightarrow$ mechanical $\rightarrow$ electrical
(b) chemical $\rightarrow$ thermal (when combusted) $\rightarrow$ thermal (in steam) $\rightarrow$ mechanical $\rightarrow$ electrical

Exam practice questions (pages 105–6)

Extended response questions

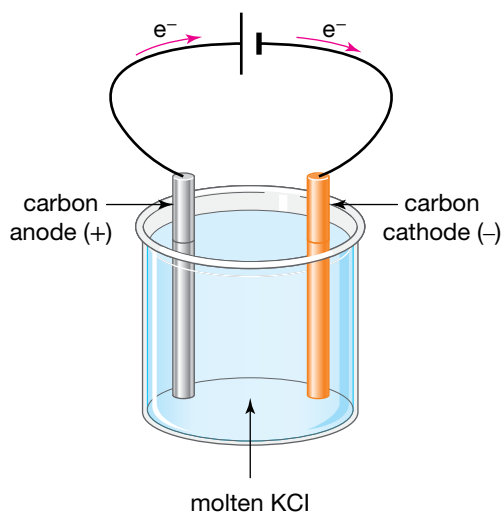
- (a) By noting the direction of electron flow. Electrons flow from the site of oxidation (the anode) to the site of reduction (the cathode).
(b) Electrons can flow from a reducing agent to an oxidising agent only if there is a difference in the half-cell reduction potential.
(c) The order of increasing reducing agent strength is $\text{Ag(s)} < \text{Cu(s)} < \text{Ni(s)} < \text{Pb(s)} < \text{Fe(s)} < \text{Al(s)} < \text{Mg(s)}$.

- (a) $E^\circ_{\text{cell}} = 2.01 \text{ V}$
(b) The copper electrode would increase in mass (would become larger) because it would have an increasing layer of copper deposited on it. The colour intensity of the blue copper sulfate solution would fade over time.
(c) positive
(d) a
(e) $\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$
- (a) $\text{C}_3\text{H}_8(\text{g}) + 6\text{H}_2\text{O(l)} \rightarrow 3\text{CO}_2(\text{g}) + 20\text{H}^+(\text{aq}) + 20\text{e}^-$
(b) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$
(c) more efficient energy transformation; less CO_2 evolved per unit of transformed energy
(d) The electrodes must be porous, and they must catalyse the half-cell reactions.

Chapter 4

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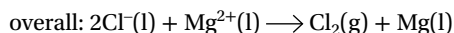
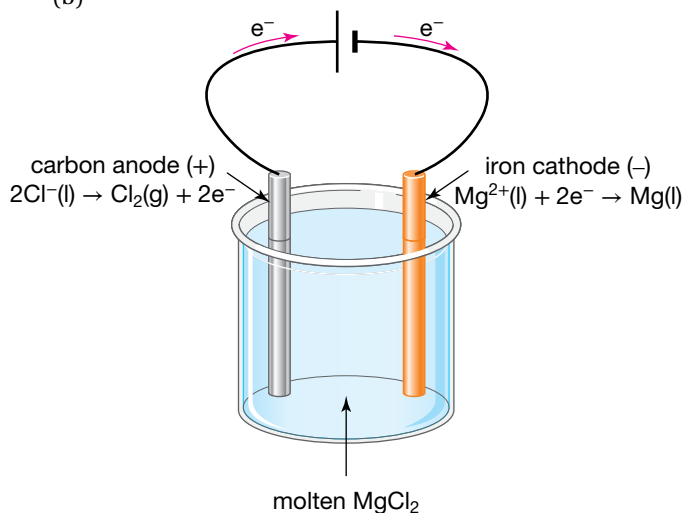
1.



2. Reactants in a galvanic cell would react spontaneously if they were placed in the same compartment. Reactants in an electrolytic cell do not react until a critical amount of energy is supplied, so a single compartment cell can be used.

Pages 117–18

3. (a) Iron would be preferentially oxidised at the anode as it is a stronger reducing agent than Cl^- .
(b)



4. (a) copper
(b) lead
(c) hydrogen gas and hydroxide ions
5. (a) cathode: $\text{Pb}(\text{s})$; anode: $\text{Cl}_2(\text{g})$
(b) cathode: $\text{Pb}(\text{s})$; anode: $\text{O}_2(\text{g})$ and $\text{H}^+(\text{aq})$

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6. The density of the cryolite is less than the density of the alumina, so the alumina can be separated easily.
7. Alumina's structure is a giant structure and contains metal ions and oxide ions. There are very strong intermolecular bonds between the ions; therefore, a large amount of energy is required to break them.

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8. 1.0 g
9. 0.32 L
10. (a) 26.4 g
(b) 126.9 g
(c) 7.76 g
11. (a) 11.4 hours
(b) 5.58 minutes
(c) 1 hour 46 minutes

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12. 3+
13. 2+

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14. (a) 60.4 kg
(b) 9.93 minutes
(c) $9.99 \times 10^5 \text{ L}$

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15. The products of discharge, PbSO_4 , remain attached to the electrodes.
16. During recharge, H_2SO_4 is regenerated and hence the pH will decrease.
17. to increase the surface area of the electrode
19. $\text{Ni}(\text{OH})_2(\text{s}) + \text{M}(\text{s}) \longrightarrow \text{NiO}(\text{OH})(\text{s}) + \text{MH}(\text{s})$
20. $2\text{NiO}(\text{OH})(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{Cd}(\text{s}) \longrightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s})$

Multiple choice questions

1. B 2. B 3. D 4. D 5. C 6. D 7. B 8. D
9. D 10. C 11. A 12. D 13. C 14. B 15. D 16. C
17. C 18. D 19. B 20. B 21. D 22. C 23. A 24. D
25. D 26. C 27. D 28. C 29. D 30. B

Review questions

1. Similarities:
• Oxidation occurs at the anode and reduction occurs at the cathode.
• Anions migrate to the anode and cations migrate to the cathode.
• Circuit requires an electrolyte between the electrodes.
• Electrons move through the 'external circuit' and ions move through the 'internal circuit'.
Differences:
Galvanic cell
• Cell polarity is determined by the reactions occurring within the cell.
• Chemical energy is transformed into electrical energy.
• anode (-) and cathode (+)
Electrolytic cell
• Cell polarity is determined by the external power source.
• Electrical energy is transformed into chemical energy.
• anode (+) and cathode (-)
2. With a direct current, the electrodes maintain a fixed polarity: anode (+) and cathode (-).
3. (a) In the solid state, $\text{Na}^+(\text{s})$ and $\text{Cl}^-(\text{s})$ ions are held firmly in the ionic lattice ($\text{Na}^+(\text{s})$ and $\text{Cl}^-(\text{s})$ ions are not free to move), whereas, in the molten (or liquid) state, $\text{Na}^+(\text{l})$ and $\text{Cl}^-(\text{l})$ ions are free to move.
(b) It is only at the electrodes that electrons can be accepted in a reduction reaction (at the cathode) and lost in an oxidation reaction (at the anode), as electrons move freely through the metal/graphite but not through the molten solution.

- (c) The external power supply drives the current flow in the external circuit, which in turn drives the ion flow in the internal circuit.

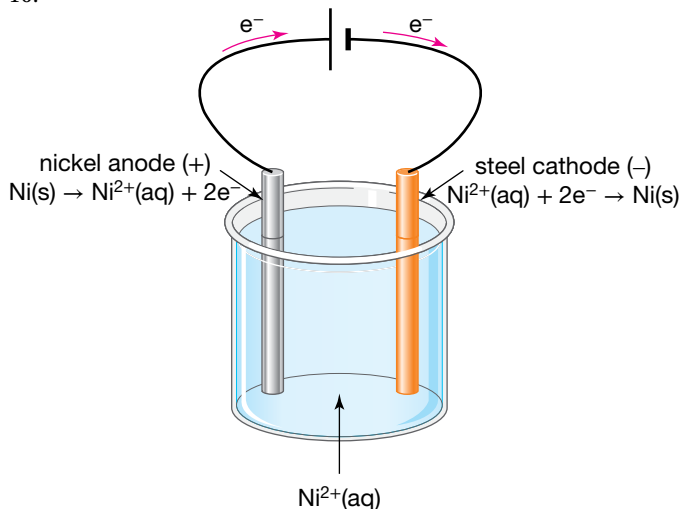
Electrolyte type	Reaction at	
	Anode (+)	Cathode (-)
NaCl(l)	$2\text{Cl}^-(\text{l}) \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$	$\text{Na}^+(\text{l}) + \text{e}^- \longrightarrow \text{Na}(\text{l})$
1 M NaCl(aq)	$2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
1 M NaCl(aq)	$\text{Cu}(\text{s}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$	$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$

5. (a) anode: bromine liquid, cathode: sodium metal, minimum cell voltage: 3.80 V
 $2\text{Na}^+(\text{l}) + 2\text{Br}^-(\text{l}) \longrightarrow 2\text{Na}(\text{l}) + \text{Br}_2(\text{l})$
 (b) anode: oxygen gas and water, cathode: aluminium metal, minimum cell voltage: 2.07 V
 $4\text{Al}^{3+}(\text{l}) + 12\text{OH}^-(\text{l}) \longrightarrow 4\text{Al}(\text{l}) + 6\text{H}_2\text{O}(\text{g}) + 3\text{O}_2(\text{g})$
 (c) anode: chlorine gas, cathode: lead metal, minimum cell voltage: 1.49 V
 $\text{Pb}^{2+}(\text{l}) + 2\text{Cl}^-(\text{l}) \longrightarrow \text{Pb}(\text{l}) + \text{Cl}_2(\text{g})$
 (d) anode: chlorine gas, cathode: magnesium metal, minimum cell voltage: 3.70 V
 $\text{Mg}^{2+}(\text{l}) + 2\text{Cl}^-(\text{l}) \longrightarrow \text{Mg}(\text{l}) + \text{Cl}_2(\text{g})$
6. (a) anode: oxygen gas and water, cathode: hydrogen gas and hydroxide ions, minimum cell voltage: 1.23 V
 $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$
 (b) anode: oxygen gas and hydrogen ions, cathode: hydrogen gas and hydroxide ions, minimum cell voltage: 2.06 V
 $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$
 (c) anode: oxygen gas and hydrogen ions, cathode: hydrogen gas and hydroxide ions, minimum cell voltage: 2.06 V
 $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$
 (d) anode: bromine liquid, cathode: zinc metal, minimum cell voltage: 1.85 V
 $\text{Zn}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq}) \longrightarrow \text{Zn}(\text{s}) + \text{Br}_2(\text{l})$
 (e) anode: iodine liquid, cathode: hydrogen gas and hydroxide ions, minimum cell voltage: 1.37 V
 $2\text{H}_2\text{O}(\text{l}) + 2\text{I}^-(\text{aq}) \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) + \text{I}_2(\text{l})$
 (f) anode: oxygen gas and hydrogen ions, cathode: hydrogen gas, minimum cell voltage: 1.23 V
 $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$
 (g) anode: oxygen gas and hydrogen ions, cathode: hydrogen gas, minimum cell voltage: 1.23 V
 $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 2\text{H}_2(\text{g})$
7. (a) (i) anode: oxygen gas and hydrogen ions
 cathode: copper, minimum cell voltage: 0.89 V
 $2\text{Cu}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Cu}(\text{s}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq})$
 (ii) anode: copper ions
 cathode: copper
 voltage: determined experimentally
Note: The reactants and products are the same.
 $\text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq})$

- (b) (i) anode: oxygen gas and hydrogen ions
 cathode: copper
 voltage: 0.89 V
 $2\text{Cu}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Cu}(\text{s}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq})$
 (ii) anode: copper ions
 cathode: copper
 voltage: determined experimentally
Note: The reactants and products are the same.
 $\text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq})$

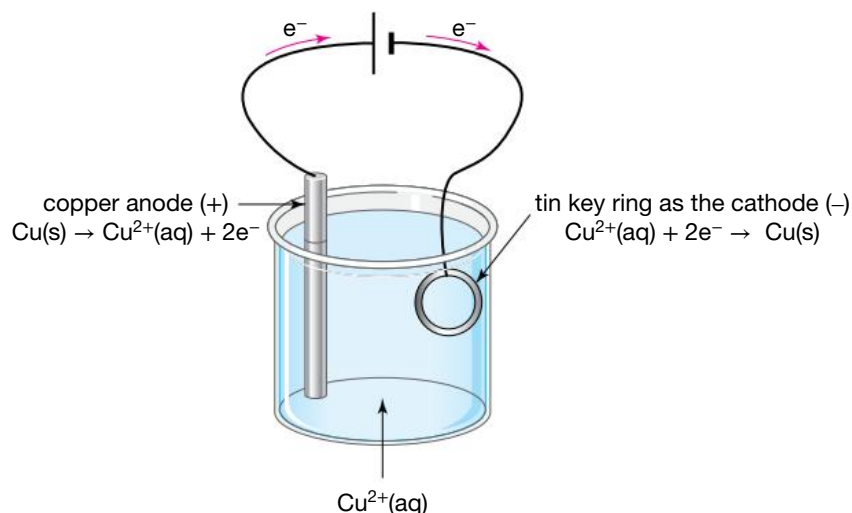
8. (a) anode: $2\text{Cl}^-(\text{l}) \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
 cathode: $\text{Na}^+(\text{l}) + \text{e}^- \longrightarrow \text{Na}(\text{l})$
 Molten sodium chloride is electrolysed using inert electrodes. The products are kept separate as the products formed would react vigorously together, especially at the elevated temperatures at which the molten cell would need to operate.
 (b) anode: $2\text{Cl}^-(\text{aq}) \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
 cathode: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
 The $\text{OH}^-(\text{aq})$ ions combine with $\text{Na}^+(\text{aq})$ ions from $\text{NaCl}(\text{aq})$ to form $\text{NaOH}(\text{aq})$. A concentrated sodium chloride solution (called a brine solution) is electrolysed using inert electrodes. The products are kept separate because they can react with each other.
9. cathode: $\text{Al}^{3+}(\text{l}) + 3\text{e}^- \longrightarrow \text{Al}(\text{l})$
 anode: $\text{C}(\text{s}) + 2\text{O}^{2-}(\text{l}) \longrightarrow \text{CO}_2(\text{g}) + 4\text{e}^-$
 The carbon cathode acts as an inert electrode and hence remains intact, whereas the carbon anode is consumed in the oxidation reaction that takes place.

10.

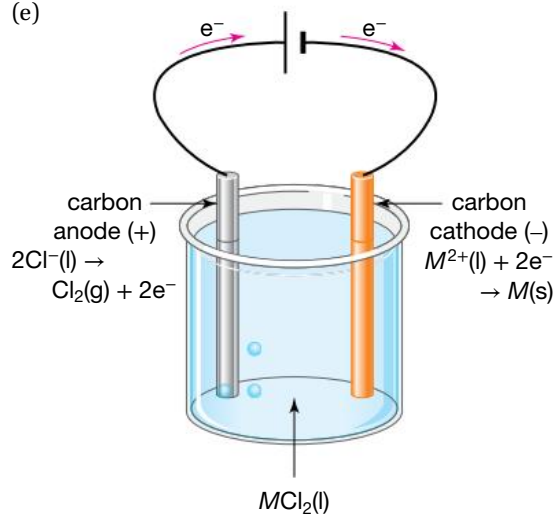


11. An object needs to be coated by a metal, M , in a reduction reaction: $M^{n+}(\text{aq}) + \text{xe}^- \longrightarrow M(\text{s})$. Reduction always takes place at the cathode.
12. (a) nickel
 (b) a nickel(II) solution

13.



14. (a) 2.0 faradays
 (b) 5.0 faradays
 (c) 1.7 faradays
 (d) 0.23 faradays
 (e) 0.014 faradays
15. (a) (i) 0.19 g (ii) 2.7 g (iii) 10 g (iv) 68 g
 (b) (i) 37 mL (ii) 0.52 L (iii) 2.0 L (iv) 13 L
16. 4.09 days
17. (a) $M^{2+}(l) + 2e^- \rightarrow M(s)$
 (b) 0.0230 mol
 (c) 55.6 g mol^{-1}
 (d) iron
 (e)



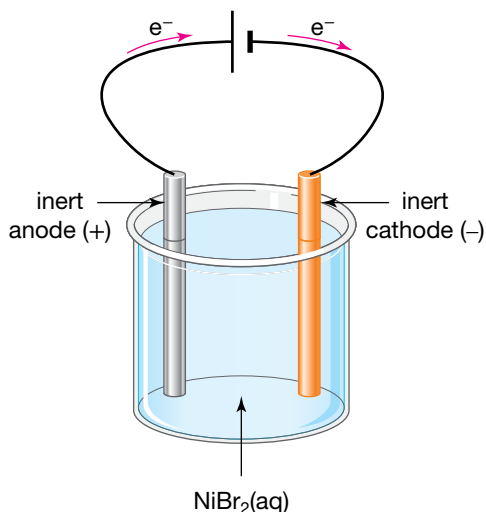
18. (a) 289 C
 (b) 0.003 00 mol
 (c) 0.001 00 mol
 (d) 3+
19. 36.3 minutes
20. (a) 19.3 g
 (b) 8.84 L
21. 39.6 s
22. (a) $V(\text{O}_2) = 0.145 \text{ L}$
 $V(\text{H}_2) = 0.289 \text{ L}$
 (b) anode: $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$
 cathode: $2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$
23. indium

24. 1.90×10^{22}
25. 47 minutes
26. (a) 1.3 tonnes
 (b) $9.2 \times 10^5 \text{ L}$
27. 1.10 g
28. 0.16 A
29. 1.28 hours
30. Lead-acid accumulators are commonly referred to as lead-acid batteries. These batteries are secondary cells and as such can be recharged. When recharged, the chemical energy that is transformed from the electrical energy used in the charging process is stored until needed.
31. (a) 2 volts
 (b) 12 V (approximately)
 (c) The anode and cathode are coated in $\text{PbSO}_4(s)$ and the concentration of sulfuric acid in the electrolyte is low (the pH of the cell is at a high value).
32. (a) devices that draw a low current and that are used only occasionally
 (b) (i) anode (-): $\text{Fe}(s) + 2\text{OH}^-(aq) \rightarrow \text{Fe}(\text{OH})_2(s) + 2e^-$
 cathode (+): $\text{NiO}(\text{OH})(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni}(\text{OH})_2(s) + \text{OH}^-(aq)$
 (ii) cathode (-): $\text{Fe}(\text{OH})_2(s) + 2e^- \rightarrow \text{Fe}(s) + 2\text{OH}^-(aq)$
 anode (+): $\text{Ni}(\text{OH})_2(s) + \text{OH}^-(aq) \rightarrow \text{NiO}(\text{OH})(s) + \text{H}_2\text{O}(l) + e^-$
- (c) iron/iron(II)hydroxide and nickel(III) oxyhydroxide/nickel(II) hydroxide
 (d) anode: iron; cathode: nickel(III) oxyhydroxide
 (e) anode: nickel(II) hydroxide; cathode: iron(II) hydroxide
33. (a) Lithium is a low-density metal that is a strong reducing agent. Its cells are relatively light, have a good shelf life and have a high energy density.
 (b) lithium during discharge:
 anode (-): $\text{CLi}_x(s) \rightarrow \text{C}(s) + x\text{Li}^+(aq) + xe^-$
 cathode (+): $\text{Li}_{1-x}\text{CoO}_2(s) + x\text{Li}^+(aq) + xe^- \rightarrow \text{LiCoO}_2(s)$
 overall: $\text{Li}_{1-x}\text{CoO}_2(s) + \text{CLi}_x(s) \rightarrow \text{C}(s) + \text{LiCoO}_2(s)$
 nickel-metal hydride during discharge:
 anode (-): $\text{MH}(s) + \text{OH}^-(aq) \rightarrow \text{M}(s) + \text{H}_2\text{O}(l) + e^-$
 cathode (+): $\text{NiO}(\text{OH})(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni}(\text{OH})_2(s) + \text{OH}^-(aq)$
 overall: $\text{NiO}(\text{OH})(s) + \text{MH}(s) \rightarrow \text{Ni}(\text{OH})_2(s) + \text{M}(s)$

Exam practice questions (page 141)

Extended response questions

1. (a)



- (b) anode: $2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{l}) + 2\text{e}^-$
 cathode: $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$
 overall equation: $2\text{Br}^-(\text{aq}) + \text{Ni}^{2+}(\text{aq}) \rightarrow \text{Br}_2(\text{l}) + \text{Ni}(\text{s})$
 (c) 1.32 V
 (d) anode: $\text{Ni}(\text{s}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$
 cathode: $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$

2. (a) 304 C
 (b) 0.001 57 mol
 (c) $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$
 Therefore, $n(\text{e}^-) = 0.003\ 15\ \text{mol}$.
 (d) $97\ 790\ \text{C mol}^{-1}$
 (e) 6.0×10^{23}
 3. 1.85 kg

Chapter 5

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1. (a) The concentration of dissolved H_2CO_3 (reactant) decreases and therefore the rate of its decomposition decreases.
 (b) It would be faster.

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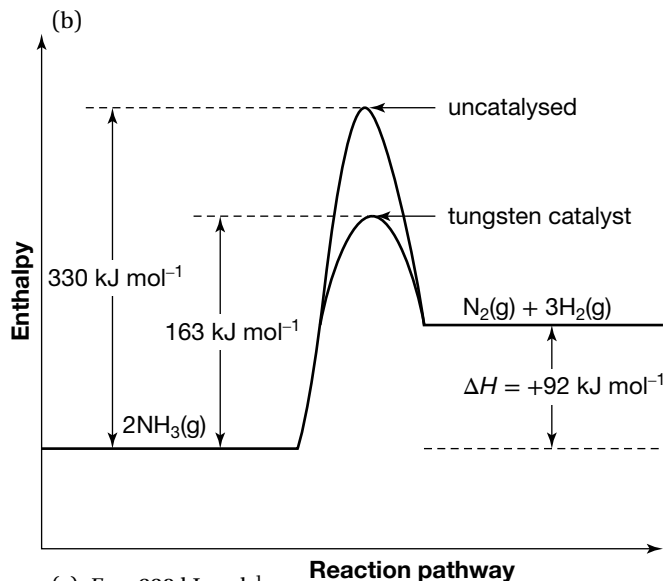
2. (a) powder, 2 M HCl, hot water bath
 (b) strip, 0.5 M HCl, cool water bath
 3. The rate will increase because the compressed gases, being more concentrated, will collide with an increased frequency, producing more successful/fruitful collisions.

Multiple choice questions

1. B 2. D 3. D 4. A 5. B 6. D 7. C 8. B 9. C

Review questions

1. A catalyst lowers the activation energy of a reaction; that is, it makes it easier to break the bonds in reactants. This is described as 'providing an alternative reaction pathway'.
 2. (a) Lipase, an enzyme, acts as a catalyst, thereby lowering the activation energy.
 (b) It is the same because catalysts are not consumed in chemical reactions.
 3. (a) A catalyst is a substance that increases the rate of a chemical reaction without itself being consumed. It provides an alternative reaction pathway with a lower activation energy.

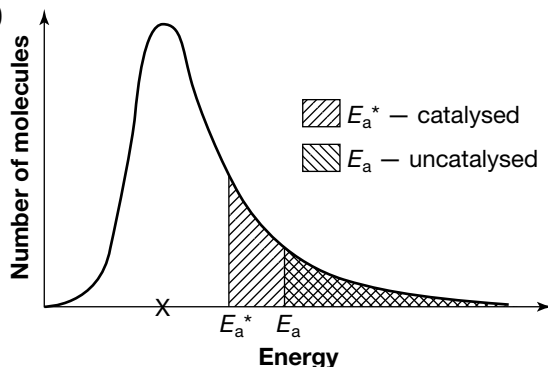


(c) $E_a = 238\ \text{kJ mol}^{-1}$

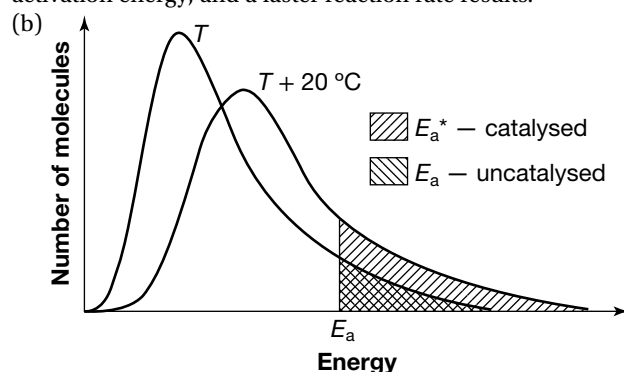
(d) $E_a = 71\ \text{kJ mol}^{-1}$

4. The addition of a catalyst changes the way in which a reaction occurs. When a solid catalyst is used, the reactant particles interact with the surface of the catalyst. This weakens (and sometimes breaks) the bonds in the reactant particles, allowing the reaction to progress faster than would have been the case without the catalyst. This change is described as 'providing an alternative pathway'. The activation energy is lowered because less energy is needed to break the bonds in the reactant particles.
 5. (a) The spilt petrol evaporates faster because it has a greater exposed surface area.
 (b) The steel wool has greater surface area and hence is more exposed to the oxygen in the air.
 (c) The manganese dioxide is acting as a catalyst; that it, it decreases the activation energy, allowing peroxide to decompose faster, producing oxygen continually.
 (d) Increased temperature causes a faster reaction due to particles colliding with more energy. The particles also have a greater kinetic energy, so move faster, hence successfully colliding with a greater frequency. This, however, is a minor effect.
 (e) Shaking allows the nail polish remover molecules to interact more rapidly with the surrounding air.
 (f) The reaction slows because the concentration of reactants decreases as they are used up.
 (g) The chemicals in the infrared film are sensitive to heat. With cooling during storage, the rate at which these chemicals react is lowered.
 6. (a) The rate decreases with time because the reactant molecules are consumed; that is, there is a progressive decrease in the frequency of successful collisions of reactant molecules.
 (b) Four reactant gas molecules are being converted into three product gas molecules, so the total gas pressure will decrease continuously.
 7. Castor sugar is finely ground and has a much greater surface area than granulated sugar. Consequently, more castor sugar particles are exposed to the sulfuric acid molecules, resulting in an increased frequency of collision between the reacting particles.

8. Particles within a container are continuously moving and hence continuously colliding with each other (and with the walls of the container). All such collisions are elastic — energy is conserved. Consequently, when these collisions occur, some particles will slow down and others will speed up, resulting in a wide range of velocities. The faster the particle's velocity, the higher is its kinetic energy. The Maxwell-Boltzmann distribution curve represents this spread of energies.
9. Reaction rates can also be increased by an increase in surface area for solid reactants, an increase in pressure for gas reactions, an increase in concentration for reactions occurring in solutions and using an appropriate catalyst.
10. (a), (c)



A catalyst provides an alternative reaction pathway with a lower activation energy. This results in an increase in the number of particles that have an energy greater than the activation energy, and a faster reaction rate results.



As the temperature is increased (for example, by 20 °C):

- the particles move faster and collide more frequently (a minor effect)
- the particles collide with more energy (the major effect).

As a consequence, when temperature is increased, there are more particles with an energy greater than the activation energy, and a faster reaction rate results.

Exam practice questions (page 154)

Extended response question

1. (a) Comparing trials 1 and 2:
Keeping $V(\text{I}^-(\text{aq}))$ constant and doubling $V(\text{S}_2\text{O}_8^{2-}(\text{aq}))$ results in a decrease in the time taken for the blue colour to appear; that is, the rate of reaction 1 is increased.
- (b) Comparing trials 1 and 3:
Keeping $V(\text{S}_2\text{O}_8^{2-}(\text{aq}))$ constant and doubling the $V(\text{I}^-(\text{aq}))$ results in a decrease in the time taken for the

blue colour to appear; that is, the rate of reaction 1 is increased.

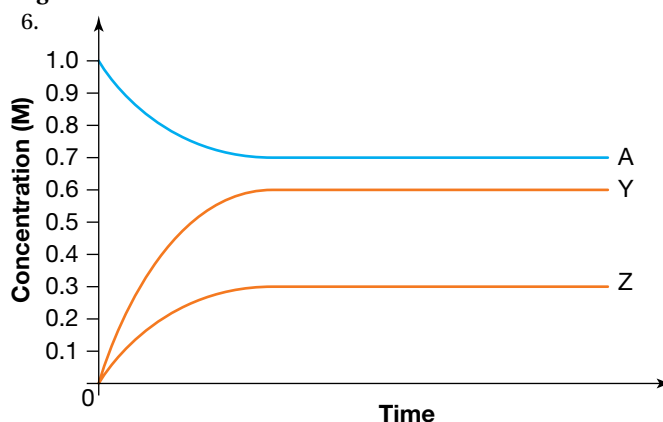
- (c) The reaction times will increase.
- (d) To be a fair test, the total volume of all solutions must be the same. Adding water as indicated ensures concentration does not become another variable in the experiment, as this would vary the frequency of collisions between reacting particles and thus affect the rate of the reaction.
- (e) To identify when reaction 1 reaches the same stoichiometric point for each trial, the appearance of the blue colour is used to indicate when the same amount of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ in each solution is used up, leaving I_2 in excess to react with starch.

Chapter 6

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- 10.0
- Experiment 2: $K_c = 0.184 \text{ M}$
Experiment 3: $K_c = 0.179 \text{ M}$
Experiment 4: $K_c = 0.174 \text{ M}$
Experiment 5: $K_c = 0.177 \text{ M}$
- 0.032 M
- 0.067
- 0.11 mol

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7. When there is a volume change, the system moves to oppose that change by producing more or fewer particles in response to a dilution or increase in concentration. For example, in $\text{N}_2(\text{g}) + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3(\text{g})$, a volume increase will cause a decrease in the total pressure. The system will then oppose this by a back reaction shifting the position of equilibrium to the left, producing more particles. In $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, a volume increase will cause a decrease in the total pressure. The system will then oppose this by a forward reaction shifting the position to the right, producing more particles.

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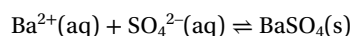
- Position of equilibrium shifts to the right.
- Position of equilibrium shifts to the right and the amount of methanol produced increases.
- raised

Multiple choice questions

1. A 2. C 3. C 4. A 5. B 6. A
7. B 8. C 9. D 10. D 11. A

Review questions

- In an irreversible reaction, the reactants form products that cannot be converted back into reactants. Only the forward reaction is possible. In a reversible reaction, as the reactants react to form products, the products can react to form reactants. Both the forward and back reactions can occur.
- The rate of a reaction measures how quickly reactants are converted into products. The extent of a reaction measures the quantity of reactants that are converted into products.
- If barium ions (from a solution of barium chloride) are added to a solution of sodium sulfate, a white precipitate of barium sulfate forms:



When the precipitate is allowed to settle to the bottom of the reaction vessel, the reaction will appear to have 'stopped'. The dynamic nature of this equilibrium reaction can be investigated if a small quantity of radioactive barium ions is later added to the solution above the precipitate. If, some time later, a small sample of barium sulfate is removed and thoroughly washed and tested, it will be found to be radioactive.

- (a) Reactants are completely converted into products.
(b) No. Due to such a very high equilibrium constant, it can be considered to be a complete reaction.

$$5. (a) K_c = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

$$(b) K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$(c) K_c = \frac{[\text{H}_2\text{O}]^2[\text{Cl}_2]^2}{[\text{HCl}]^4[\text{O}_2]}$$

$$(d) K_c = \frac{[\text{CF}_4][\text{CO}_2]}{[\text{COF}_2]^2}$$

$$(e) K_c = \frac{[\text{PF}_5]^4}{[\text{P}_4][\text{F}_2]^{10}}$$

- (a) M^{-2}
(b) no unit
(c) M^{-1}
(d) no unit
(e) M^{-7}
- Isla is correct. For example, in the reaction $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$, the equilibrium law is given by the expression:

$$K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2}$$

Since the expression comprises the equilibrium concentrations of SO_3 , SO_2 and O_2 , the unit for K_c will comprise the units of these concentrations. In this case, the unit will be $\frac{\text{M}^2 \times \text{M}}{\text{M}^2} = \text{M}$.

- It is the overall fraction of concentrations as determined by the equilibrium law that is constant, not individual concentrations within this fraction.

- (a) no unit
(b) 0.16
- (a) 0.067 M
(b) The value of K depends on the temperature.
- experiment 4
- (a) experiments 2 and 5
(b) A net forward reaction will occur in experiments 1, 3 and 6. A net back reaction will occur for experiment 4.
- 1.8 kg
- 16 M
- 4.2 M^{-1}
- 1.74
- (a) from top to bottom at the far right: C, B, A
(b) rate of forward reaction > rate of back reaction
(c) rate of forward reaction = rate of back reaction
(d) $y = 2$; $z = 3$
(e) 6.9
- The position of equilibrium would be:
(a) shifted to the left (back reaction)
(b) unchanged
(c) shifted to the left (back reaction)
(d) shifted to the right (forward reaction).
- (a) endothermic
(b) 160
- She is correct to say that an increase in pressure will cause the system to move to the right. This is because an increase in pressure will be opposed by a decrease in pressure, which will result in a forward reaction (moving to the side that has fewer moles of gas). However, assuming the temperature is kept constant, there will be no change in the value of the equilibrium constant.
- (a) 2.0
(b) 0.020 mol
(c) no effect
- It is a reaction between ammonia and oxygen to make nitrogen oxide and water.
(b) exothermic
(c) low temperature
(d) low pressure
- (a) exothermic
(b) fewer particles on the right-hand side
- (a) pressure increase
(b) lower temperature
(c) increased amount of methanol
(d) only a change in temperature
- (a) The system was in the process of reaching equilibrium.
(b) The system was at equilibrium.
(c) Some HI was removed.
(d) Some HI was added.
(e) The volume was lowered (the gas mixture was compressed).
(f) No, because there are equal numbers of moles on each side of the equation. This is clearly shown by the horizontal graph beyond 16 minutes.
- (a) 1.85 M
(b) 42.9T
(c) increase
- (a) The formation of NO is favoured by low temperatures because the reaction is exothermic; hence, more product is formed and, at low temperatures, the value of K_c is increased.

- (b) At high temperatures, the rate of the reaction will be high but the value of the equilibrium constant will be lower. At low temperatures, the rate of the reaction will be low but the value of the equilibrium constant will be high. A compromise is needed if the reaction is to operate with an acceptable rate and yield. When operating at lower temperatures to achieve an adequate yield, a catalyst is used to keep the rate at an acceptable level.
- (c) The use of high pressure requires expensive pumping equipment and stronger reaction vessels. The increase in yield that can be obtained at such high pressures does not always offset the additional costs involved with the changes in equipment and safety aspects.
28. (a) high temperatures
(b) low temperatures
(c) The $\text{ZnO/Cr}_2\text{O}_3$ catalyst allows a suitable rate to be achieved at a lower temperature. This lower temperature is preferable for maximising the extent/yield.
(d) Lower the temperature of the exit gases. Methanol, a polar molecule, will condense before both CO and H_2 . Unreacted CO , H_2 can then be recycled.
29. (a) $\text{Hb}_4 + 4\text{O}_2 \rightarrow \text{Hb}_4(\text{O}_2)_4$
(b) $\text{Hb}_4 + 4\text{CO} \rightarrow \text{Hb}_4(\text{CO})_4$
(c) $K_{(a)} = \frac{[\text{Hb}_4(\text{O}_2)_4]}{[\text{Hb}_4][\text{O}_2]^4}$, $K_{(b)} = \frac{[\text{Hb}_4(\text{CO})_4]}{[\text{Hb}_4][\text{CO}]^4}$
(d) $K_{(b)} \gg K_{(a)}$
(e) When CO is inhaled, it readily replaces O_2 in oxyhaemoglobin. Once formed, $\text{Hb}_4(\text{CO})_4$ is very stable due to the high value of the equilibrium constant for the reaction shown in (b). The stability of $\text{Hb}_4(\text{CO})_4$ prevents O_2 being carried to the cells, and cell death occurs relatively quickly.

Exam practice questions (pages 186–7)

Extended response questions

- (a) (i) darken
(ii) stay the same
(iii) lighten
(b) The addition of Br^- would cause a back reaction, resulting in the removal of Br^- .
- (a) 11.1 M^{-1}
(b) Since $Q > K_c$, a net backward reaction will occur until the reaction reaches equilibrium. Consequently, at the start of the experiment, the rate of the forward reaction < the rate of the backward reaction.
(c) $Q = K_c = 10 \text{ M}^{-1}$ because it is now at equilibrium.
(d) initial rate of forward reaction (second experiment) > initial rate of forward reaction (first experiment)
(e) initial rate of backward reaction (second experiment) > initial rate of backward reaction (first experiment)
(f) $Q = K_c = 10 \text{ M}^{-1}$ because it is now at equilibrium. The catalyst does not affect the value of K_c .
- (a) from top: C, A, B
(b) $x = 2$, $y = 2$
(c) 0.1 M
(d) addition of C as there is a vertical spike in the graph of C
(e) $K_c = 0.2 \text{ M}$. As the temperature increased, K_c increased, meaning that more product was produced. Therefore, the reaction is endothermic.

Chapter 7

Page 193

- B, A, E, F, C, D
- (a) Hypothesis: if the molecular mass of a range of different fats and oils increases then the energy content per gram of these fats and oils will increase. If access to the molecular mass of the fats and oils is not available then a more general hypothesis may be needed. If a range of different fats and oils is investigated then the energy content per gram of these fats and oils will be different.
(b) B

Page 194

- (a) B
(b) A
(c) E
(d) B or C

Page 195

- C

Page 199

- (a) independent variable: the range of pressures that were used
dependent variable: the volume of sample of gas measured at the different pressures
(b) amount in moles and the temperature
(c) to determine if the relationship between pressure and volume could be verified under different conditions of temperature and pressure
- (a) strength of the fertiliser solution
(b) weight of the shoot
(c) type of seed, type of soil/potting mix, amount of soil/potting mix, size of the pots, temperature/humidity the pots are exposed to, type of fertiliser solution, volume of fertiliser solution, time of day the fertiliser solution was added to each pot
(d) 0 g L^{-1}
(e) It is important to keep constant all factors, other than the independent variable, that might affect the measurement of the dependent variable.

Page 200

- (a) $7.5 \times 10^{-7} \text{ m}$
(b) $2.3 \times 10^{-3} \text{ mm}$
(c) $1.496 \times 10^{11} \text{ km}$
- (a) 9.275×10^5
(b) 4.5868×10^4
(c) 3.57×10^{-2}
(d) 5.629×10^{-3}
(e) 5.629×10^{-2}
(f) 1.3457×10^{-8}
- (a) 100
(b) 0.002 19
(c) 3.759
(d) 0.777
(e) 500 000
(f) 500 000
(g) 0.000 050 0

Pages 200–1

- 11.44 mL
- When reading a burette, read the volume from the top down; that is, this volume reading is between 7 and 8 mL. The actual volume reading is 7.36 mL.

Page 202

12. (a) 6
(b) 3
(c) 5
(d) 5
13. (a) 60.80
(b) 1.1
(c) 67.839
(d) 11
(e) 35.1
(f) -2.18
14. (a) 22.1 kJ
(b) 6.5×10^{-3} mol
(c) 16 g
(d) 2.2×10^3 J

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15. Systematic errors can be caused by incorrect labelling of chemicals, incorrect calibration of measurement instruments and changes in the environment that interfere with the measurement process. These can be minimised by ensuring that chemicals are correctly labelled, good equipment is used well and external influences are minimised. Random errors affect some readings and may result in higher or lower values. Random errors can be caused by imperfect methods of observation, operation or data recording, and by the uncertainties that are always present in measurement. These can be minimised by repeating experiments and collecting more data.

16.

Time (s)	Temperature (°C)
0	15.0
30	16.5
60	18.1
90	19.5
120	20.8
150	22.4
180	23.7
210	24.0
240	23.9
270	23.5
300	23.5
330	23.2

17. (a) 12.5%; interpolation
(b) 14.1%; extrapolation
(c) It would be difficult to give a reliable estimate of the ethanol level because there is no certainty that the variables will continue to behave in the same way, as a reading of 95 000 is outside the range of the graph.

Page 208

19. (a), (b) Wear appropriate safety gear such as goggles, lab coat and gloves. Complete the experiment in a fume cupboard. Know where the eyewash station is.

Pages 209–10

20. (a) (James and Stokes, 1992)
(b) James, M. and Stokes, R. (1992). *Chemical connections, Book 2*. Jacaranda Press.

Multiple choice questions

1. B 2. C 3. A 4. B 5. C 6. B 7. B

Review questions

- to minimise random error
- Independent variables are those that are changed by the experimenter while dependent variables are those that are measured in the experiment.
- All results must be recorded. Any variation that is observed can then be commented on in the discussion section of a report. Repeating the experiment several times should validate one set of data.
- suggested experiment to compare the viscosities of four fuels

Equipment:

- 4 glass tubes approximately 30 cm long and 0.5 cm wide, permanently sealed at one end and with a removable stopper at the other
- enough of each fuel to almost fill a glass tube
- 4 small funnels
- stopwatch

Method

- Label each of the four glass tubes with the name of one of the four fuels.
- Remove the stopper from one of the glass tubes. Use a small funnel to almost fill the tube with one of the fuels. Leave a space of exactly 0.5 cm at the top. Replace the stopper on the tube.
- Repeat step 2 for the other three fuels.
- Invert each of the test tubes in turn, and measure and record the time it takes for the bubble of air to rise to the top of the tube.
- (a) Stephen has not taken enough safety precautions. He should be wearing suitable protective clothing and wearing safety glasses. In addition, if possible, the experiment should be conducted in a fume hood.
(b) The experimental design is flawed. By collecting the gas in the balloon, he has created a closed system. In effect, his experiment is investigating the Law of Conservation of Mass. That there is practically no change in mass clearly shows that mass is conserved in the two experiments he conducted.
(c)
 1. Weigh a 3.00 g sample of calcium carbonate powder into a 250 mL conical flask and place cottonwool in the top of the flask to prevent the loss of any solution during the reaction.
 2. Add 50 mL of 1.0 M hydrochloric acid to a 100 mL beaker.
 3. Place both the conical flask and the beaker onto a top-loading balance and zero the balance.
 4. Remove the cottonwool, carefully pour the hydrochloric acid from the beaker into the conical flask containing the calcium carbonate, replace the cottonwool, and then place the empty beaker back on the balance.
 5. Start a stopwatch as soon as the acid is poured onto the calcium carbonate in the flask.
 6. Measure and record the mass loss every 30 seconds until no further mass loss is observed.
 7. Weigh another 3.00 g sample of calcium carbonate powder into a second 250 mL conical flask and again place cottonwool in the top of the flask to prevent the loss of any solution during the reaction.
 8. Add 50 mL of 2 M hydrochloric acid to a different 100 mL beaker.
 9. Repeat steps 3 to 6.

Chapter 8

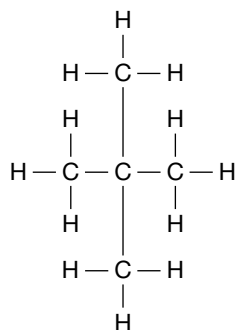
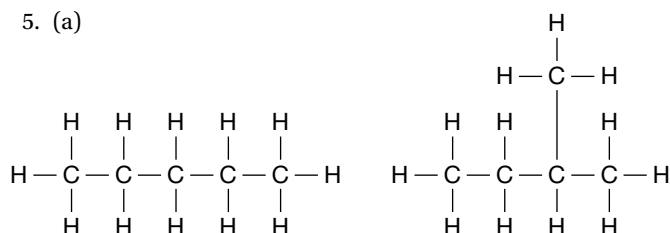
Page 217

- Organic chemistry is the branch of chemistry concerned with the study of compounds of carbon that are chemically bonded to hydrogen. Organic compounds include methane, CH_4 , ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, and benzene, C_6H_6 . Inorganic compounds include sodium chloride, NaCl , potassium oxide, K_2O , and iron(III) chloride, FeCl_3 .
- $1.13 \times 10^3 \text{ kJ}$
- C_8H_{18}

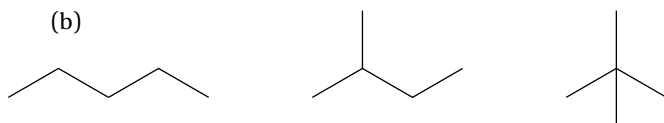
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- molecular: C_3H_8
empirical: C_3H_8
semi-structural: $\text{CH}_3\text{CH}_2\text{CH}_3$
skeletal:

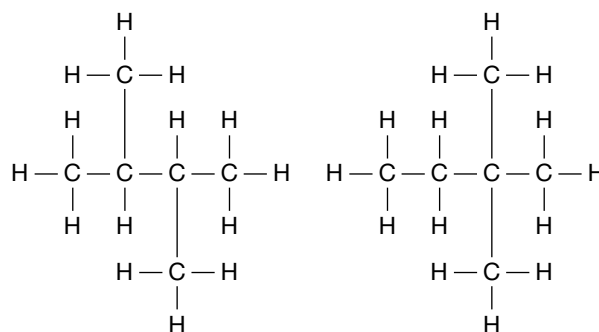
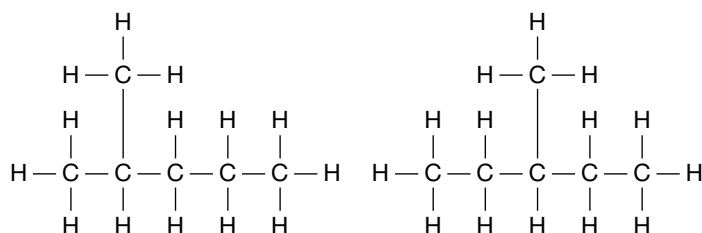
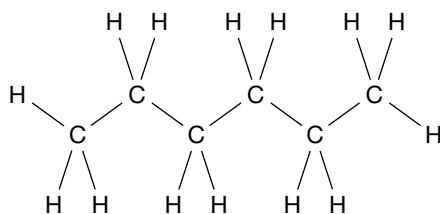
- (a)



- (b)



- There are five isomers.



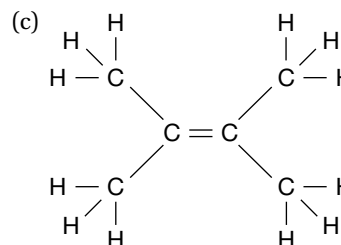
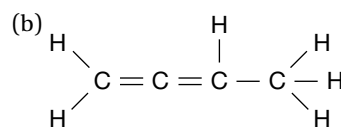
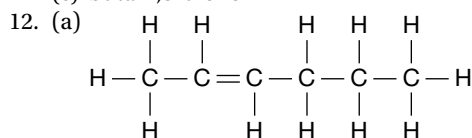
- Carbon has four outershell electrons that it can share with other atoms to form strong covalent bonds. It can also form single, double and triple covalent bonds with itself as well as ring (or cyclic) structures.

Page 220

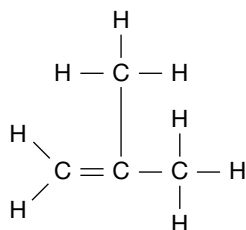
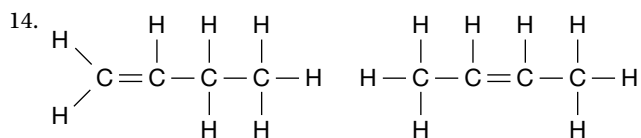
- (a) 2-methylbutane
(b) 3-ethylpentane
(c) 2,2-dimethylpropane
- (a) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$. This can also be written as $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$.
(b) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_3$. This can also be written as $\text{CH}(\text{CH}_2\text{CH}_3)_3$.
(c) $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_3$. This can also be written as $\text{C}(\text{CH}_3)_4$.
- (a) The group (or groups) attached to the longest carbon chain must be numbered to give the lowest possible value. Therefore, the correct name for this compound would be 2-methylbutane.
(b) The longest unbranched carbon chain must be chosen. Therefore, the correct name for this compound would be 2-methylbutane.

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- (a) but-1-ene
(b) 2-methylpropene
(c) buta-1,3-diene

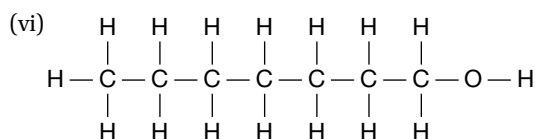
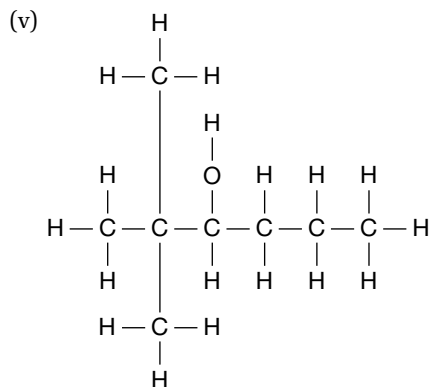
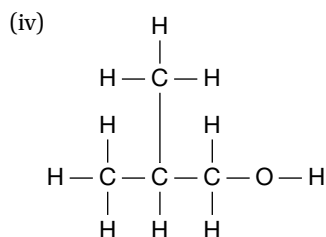
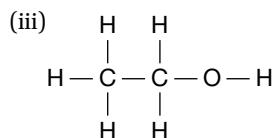
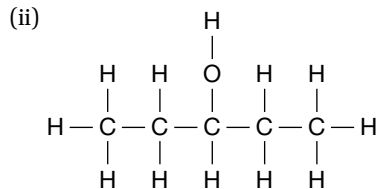
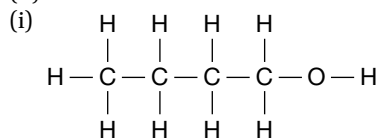


- C_nH_{2n} . Alkenes have double bonds between two carbon atoms. This cannot be achieved if there is only one carbon atom.

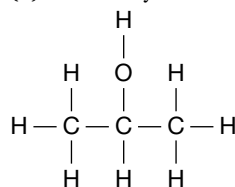


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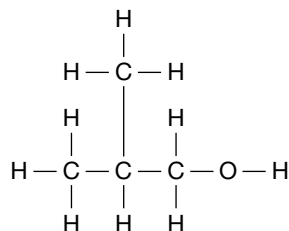
15. (a) $C_nH_{2n+2}O$
 (b) *Note:* The O—H bonds must be shown.



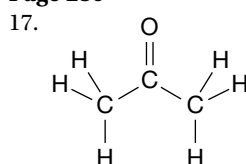
16. (a) secondary alcohol



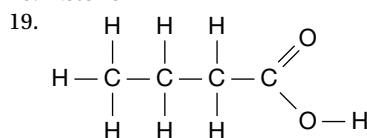
- (b) primary alcohol



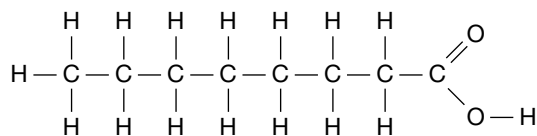
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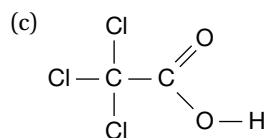
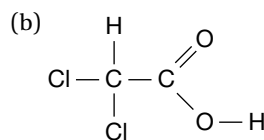
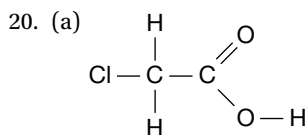
18. ketone



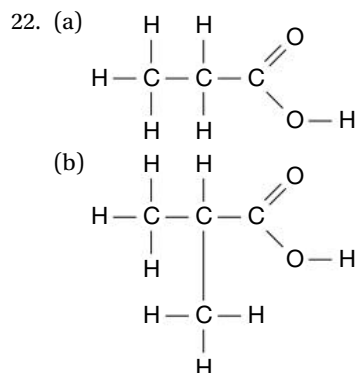
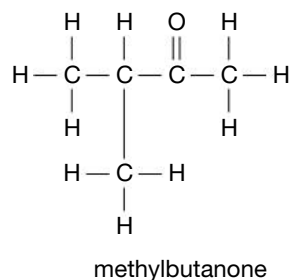
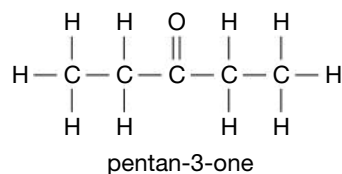
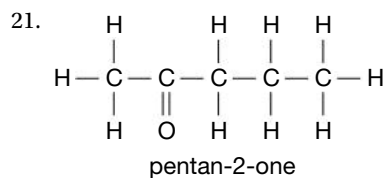
butanoic acid



octanoic acid



Tetrachloroethanoic acid is not possible as the end carbon must be bonded to another carbon to create the 'ethane' component, therefore leaving only three potential bonds to be formed between the end carbon and chlorine, rather than the four that would be required for the *tetra-* prefix.

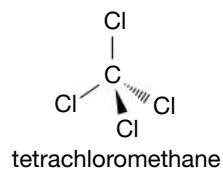
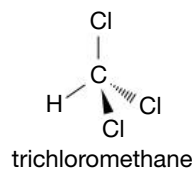
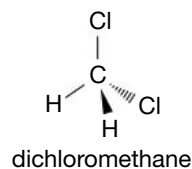
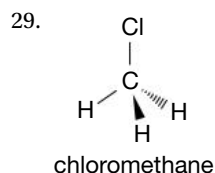
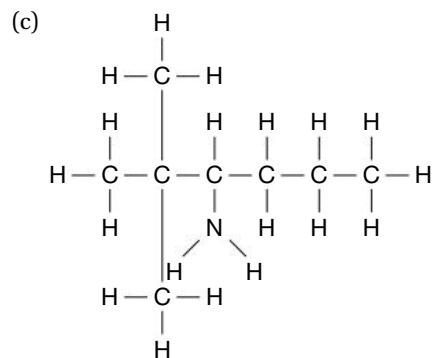
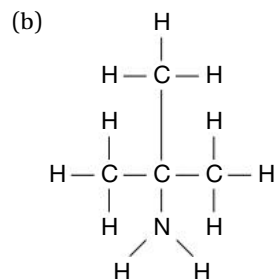
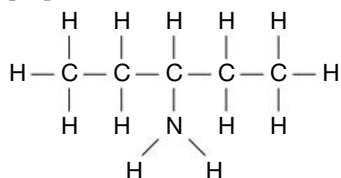


Pages 231–2

23. methyl ethanoate
 24. $\text{HCOOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (or $\text{HCOO}(\text{CH}_2)_3\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_3\text{COOH}$)
 25. ethyl methanoate

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26. (a) 4,4,4-trichlorobut-1-ene
 (b) 1-chloro-2-methylbut-2-ene
 27. (a) propan-2-amine (b) butan-1-amine
 28. (a)



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30. $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 31. (a) 3-methylpentanoic acid
 (b) 1-aminopropan-2-ol

Multiple choice questions

1. D 2. A 3. B 4. D 5. B 6. C 7. G and H
 8. B 9. B 10. B 11. D 12. B 13. A 14. D 15. C
 16. C 17. A 18. B 19. D

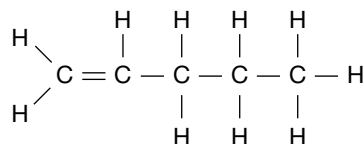
Review questions

- (a) a compound comprising only carbon and hydrogen atoms
- (b) a family of carbon compounds where each member of the family differs from the preceding member by a $-\text{CH}_2-$ group.
- (c) a hydrocarbon containing only single $\text{C}-\text{C}$ covalent bonds
- (d) a hydrocarbon containing one or more double $\text{C}=\text{C}$ or triple $\text{C}\equiv\text{C}$ covalent bonds
- (e) molecules with the same molecular formula but different structural formulas

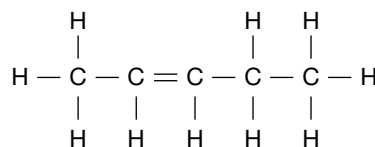
2. An alkane as a hydrocarbon containing only single C—C covalent bonds. An alkene is a hydrocarbon containing one or more double C=C covalent bonds.

	Alkanes	Alkenes
Elemental content	carbon and hydrogen	carbon and hydrogen
General formula	C_nH_{2n+2}	C_nH_{2n}
Bonding	contain only single C—C bonds	contain at least one double C=C bond
Type of hydrocarbon	saturated hydrocarbons	unsaturated hydrocarbons
Source	natural component of crude oil (petroleum)	produced from crude oil by a process called cracking

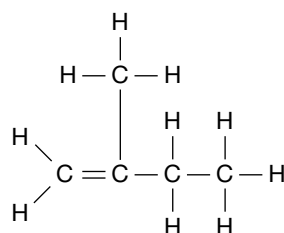
3. (a) pent-2-ene
 (b) chloroethene
 (c) dichloro-difluoromethane
 (d) ethanol
 (e) 2,2-dimethylpropane
 (f) hexan-2-ol
 (g) 1,1-dibromo-2,2-dichloroethane
4. There are five compounds.



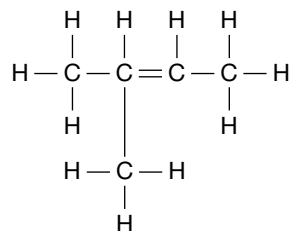
pent-1-ene



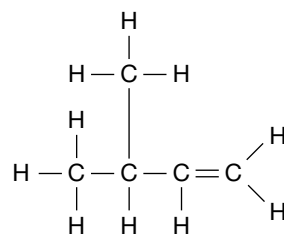
pent-2-ene



2-methylbut-1-ene

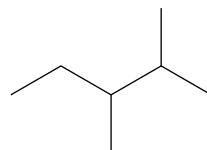


2-methylbut-2-ene

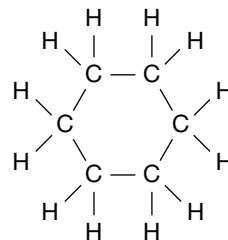


3-methylbut-1-ene

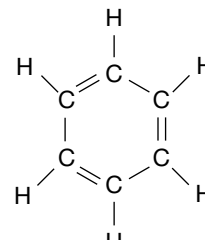
5. While alkanes readily undergo combustion and can react with chlorine in the presence of UV light, they are relatively unreactive. However, when functional groups are attached to an alkane, the greater reactivity of the functional group means that many more chemical reactions can occur.
6. (a), (c) hexane
 (d), (e), (g) 3-methylhexane
 (b), (f), (h) heptane
7. C_5H_{10} , cyclopentane
- 8.



9. 1,5-dibromo-2-methylpentane
- 10.



cyclohexane

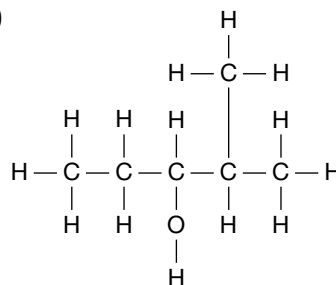


benzene

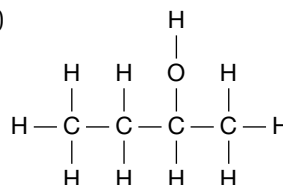
Similarity: They both have cyclic structures involving six carbon atoms.

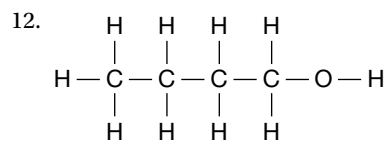
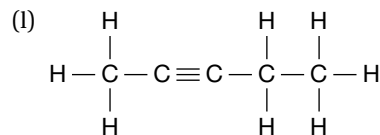
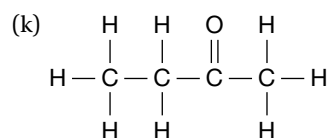
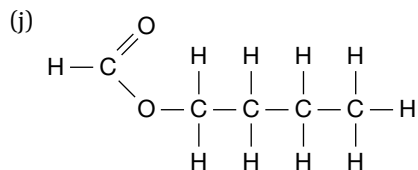
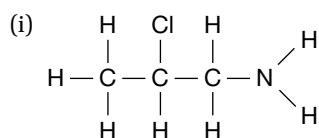
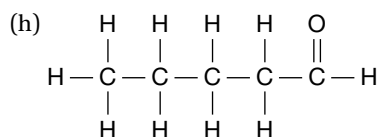
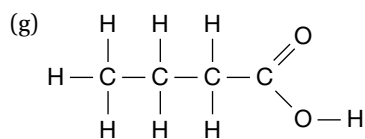
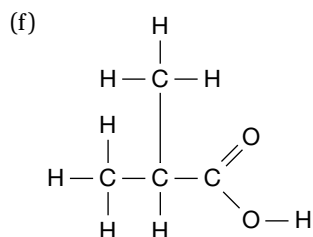
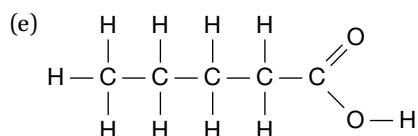
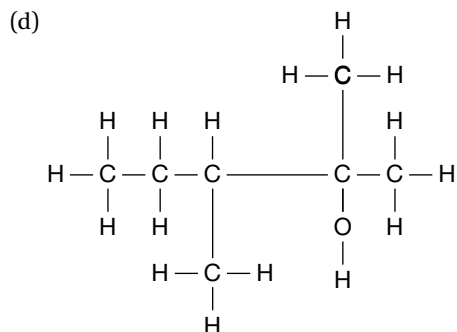
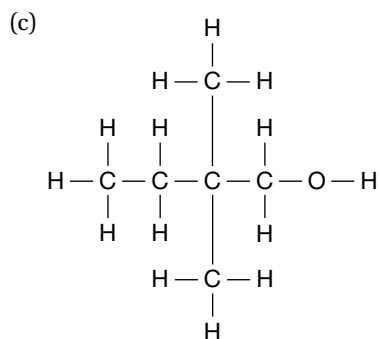
Differences: In cyclohexane, the carbon atoms are joined by single bonds, each carbon atom is bonded to two hydrogen atoms and the atoms do not lie in the same plane. In benzene, the six electrons in the three double bonds are shared by all the carbon atoms in the ring, each carbon atom is bonded to one hydrogen atom and all atoms lie in the same plane.

11. (a)

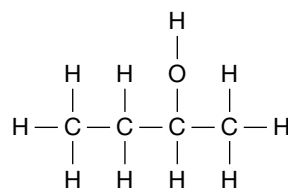


- (b)

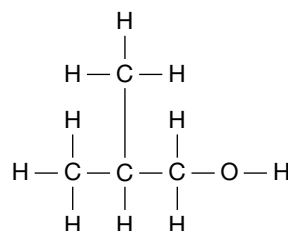




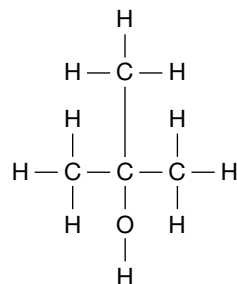
butan-1-ol



butan-2-ol



2-methylpropan-1-ol



2-methylpropan-2-ol

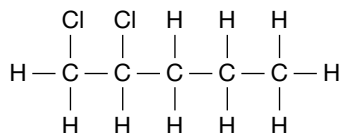
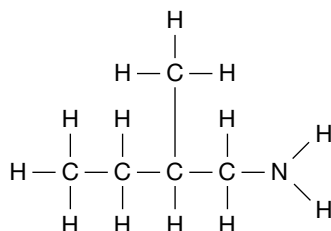
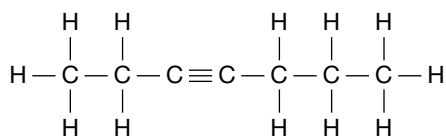
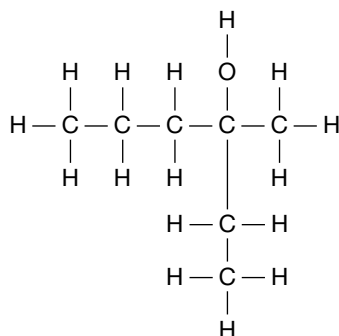
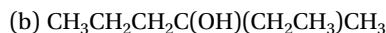
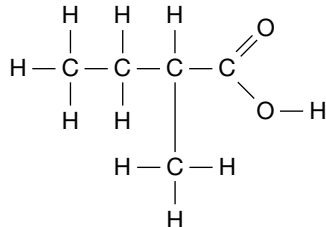
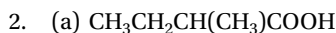
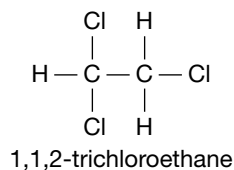
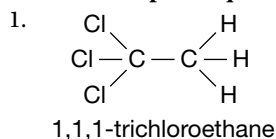
13. (a) hexanoic acid
 (b) 2,2-dimethylbutan-1-ol
 (c) 2,2,2-trichloroethane-1,1-diol
 (d) octan-2-ol
 (e) 2-bromoethanol
 (f) 2-methylpropanoic acid
 (g) methyl propanoate
 (h) pentyl ethanoate
 (i) 1,2-dichloroethane
 (j) 1,1-dichloroethane
 (k) ethanamine
 (l) propan-2-amine

Exam practice questions (page 240)

Multiple choice questions

1. B 2. A 3. C 4. D

Extended response questions



Chapter 9

Page 243

- (a) dispersion forces and hydrogen bonding
(b) dispersion forces only

(c) dispersion forces and dipole-dipole attraction

(d) dispersion forces and hydrogen bonding

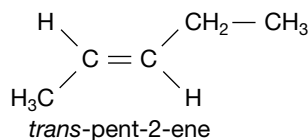
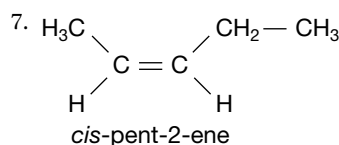
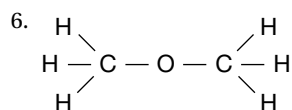
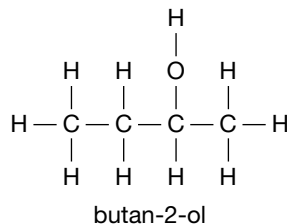
- (a) CH_3CH_3 (b) CH_3OH (c) $\text{CH}_3\text{CH}_2\text{Cl}$

Pages 247–8

- achiral: (a), (b), (d), (f), (i); chiral: (c), (e), (g), (h)

- three

-



- optical isomers (enantiomers)

Page 250

- Intramolecular: Hydrocarbons are held together by strong C—C and C—H covalent bonds.
Intermolecular: Being non-polar, there are only weak dispersion forces between hydrocarbon molecules.
- As a molecule increases in size (in molecular mass), there are more dispersion forces, so the overall strength of the dispersion forces between such molecules increases.
- (a) The forces of attraction (dispersion forces but primarily hydrogen bonding) between the molecules of the straight-chain alcohol propan-1-ol are stronger than those between the molecules of the branched alcohol propan-2-ol. This occurs because the branched chain molecules are unable to get as close to each other and the intermolecular forces operate over a larger distance. Consequently, propan-1-ol is less easily vaporised than propan-2-ol.
(b) propan-1-ol

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- propane, pentane, propan-1-ol, pentan-1-ol

Compound	Relative molecular mass	Intermolecular force			Boiling temperature (°C)
		Dispersion	Dipole-dipole	Hydrogen bonding	
propane	44	✓	✗	✗	−42
pentane	72	✓	✗	✗	36
propan-1-ol	60	✓	✗	✓	97
pentan-1-ol	88	✓	✗	✓	138

Propane is the smallest molecule, and its only intermolecular force is weak dispersion forces. Pentane,

while being larger than propan-1-ol (hence has greater dispersion forces), has a lower boiling point because propan-1-ol also has hydrogen bonding between its molecules. Propan-1-ol and pentan-1-ol both have dispersion forces and hydrogen bonding between their molecules but, because pentan-1-ol is the larger of the two molecules, it has greater dispersion forces and hence a higher boiling point.

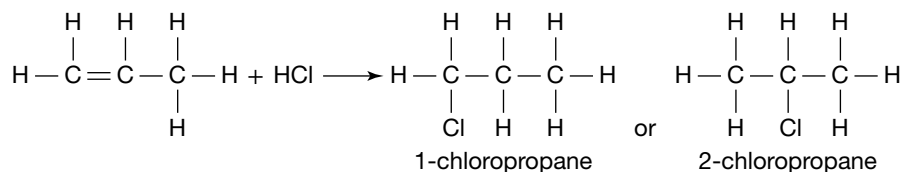
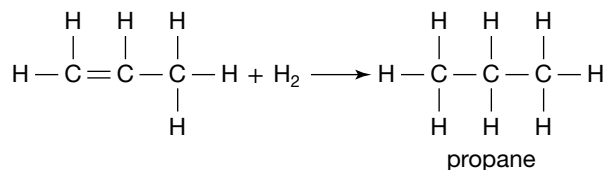
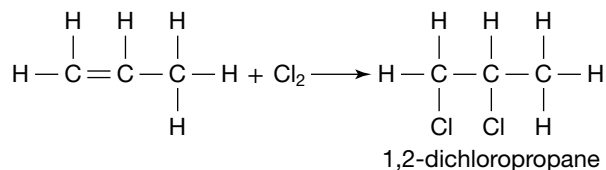
13. Both methanol and ethanol are soluble in water because they can form hydrogen bonds with water molecules. Methane and ethane, as non-polar molecules, are unable to form hydrogen bonds with water molecules and hence are insoluble.
14. The presence of one or more chlorine atoms does not always result in a polar molecule. For example:
 - Methane does not have a permanent dipole and hence is non-polar.
 - Chloromethane has a permanent dipole and hence is a polar molecule.
 - Dichloromethane has a permanent dipole and hence is a polar molecule.
 - Trichloromethane has a permanent dipole and hence is a polar molecule.
 - Tetrachloromethane does not have a permanent dipole and hence is non-polar.
15. The dispersion forces between both butanamide ($M = 87$) and ethyl ethanoate ($M = 88$) are very similar because their relative molecular masses are very similar. Dispersion forces can therefore be discounted as causing a difference in the boiling points. Butanamide has a higher boiling point than ethyl ethanoate because it has hydrogen bonding between its molecules, while ethyl ethanoate has weaker dipole-dipole attraction between its molecules.

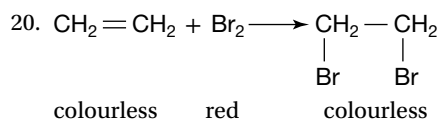
Page 256

16. $2\text{C}_8\text{H}_{18}(\text{l}) + 25\text{O}_2(\text{g}) \longrightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{g})$
17. $2\text{C}_3\text{H}_6(\text{l}) + 9\text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
18. There are nine possible products: bromoethane, 1,1-dibromoethane, 1,2-dibromoethane, 1,1,1-tribromoethane, 1,1,2-tribromoethane, 1,1,1,2-tetrabromoethane, 1,1,2,2-tetrabromoethane, pentabromoethane and hexabromoethane.

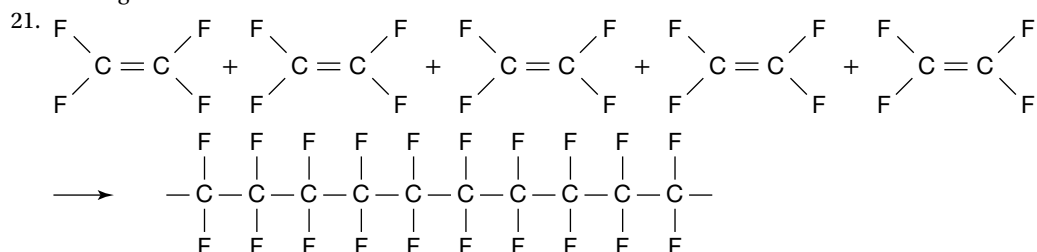
Page 258

19.



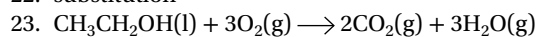


If bromine was added to ethane, the red colour of the bromine would remain as there would be no reaction. However, if bromine was added to ethene, the bromine would undergo an addition reaction with the ethene turning the reaction mixture colourless.



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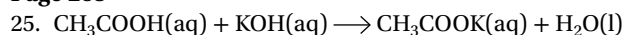
22. substitution



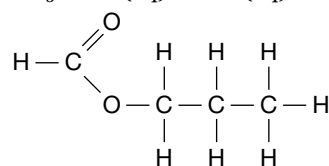
24. (a) 3-methylbutan-1-ol

(b) 3-methylbutanoic acid

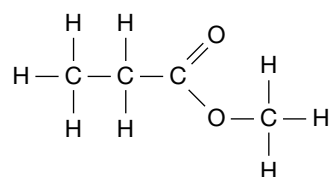
Page 263



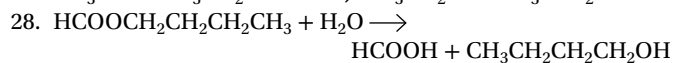
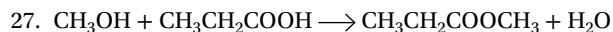
26.



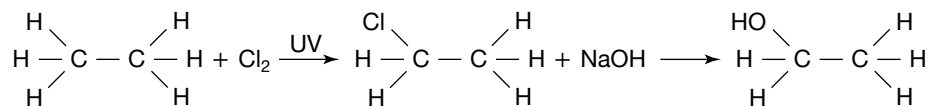
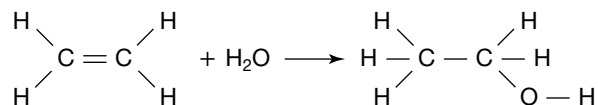
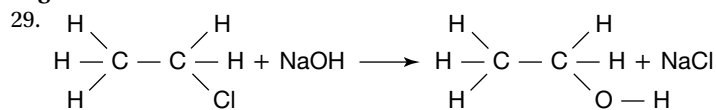
propyl methanoate

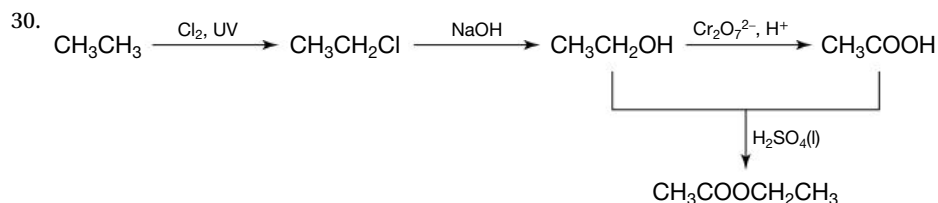


methyl propanoate



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31. 86.6%
 32. 181 g
 33. (a) 100%
 (b) It is much higher (100% compared with 51.1%).
 (c) the addition reaction between ethene and water
 (d) reaction rate, yield of the reaction, availability of reactants, cost of reactants, cost of completing the reaction, environmental impact (fermentation of glucose produces the greenhouse gas CO_2)
 34. method 2
 35. 53.8%

Multiple choice questions

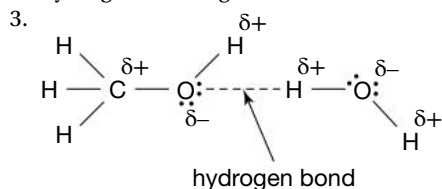
1. C 2. B 3. B 4. C 5. C 6. B 7. B 8. B
 9. B 10. A 11. D 12. C 13. D 14. D 15. C 16. A
 17. D 18. D 19. A 20. C 21. A 22. D 23. C 24. C
 25. B

Review questions

1.

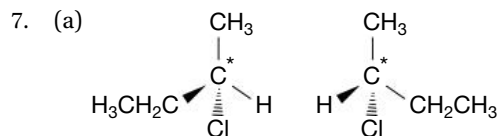
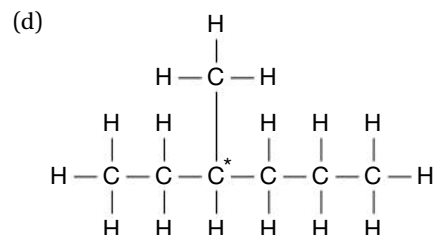
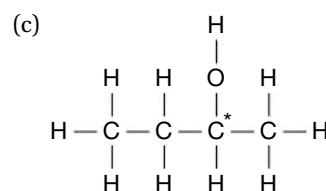
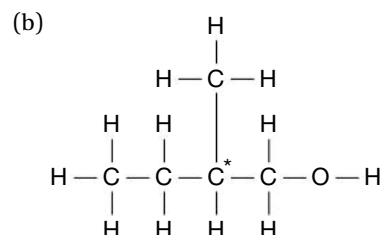
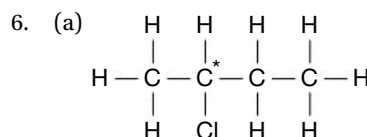
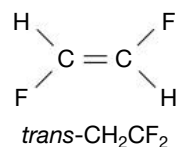
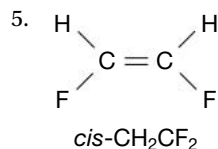
	Intermolecular bonding		
	Dispersion	Dipole-dipole	Hydrogen bonding
(a)	✓	✓	
(b)	✓	✓	
(c)	✓		
(d)	✓		✓
(e)	✓		
(f)	✓	✓	
(g)	✓	✓	
(h)	✓		✓

2. Given that their molar masses are similar, the strength of the dispersion forces between the molecules in both substances would be similar. Propan-1-ol would therefore have the higher boiling point because it would also have hydrogen bonding between its molecules.



The polar —OH group is attracted to the polar water molecule, forming hydrogen bonds.

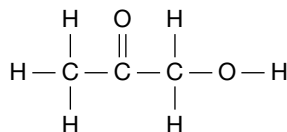
4. (a) decrease
 (b) increase
 (c) increase
 (d) increase



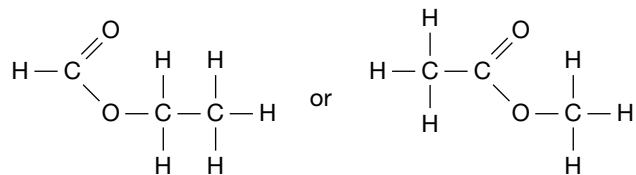
- (b) The chiral carbon atom (marked as * above) must be bonded to four different atoms (or groups of atoms).

8. (a) stereoisomerism — optical isomers
 (b) stereoisomerism — *cis-trans* isomers
 (c) structural isomerism — positional isomers

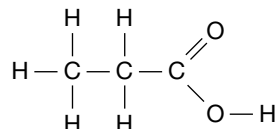
9. X



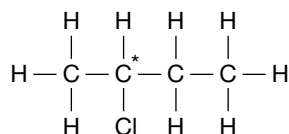
Y



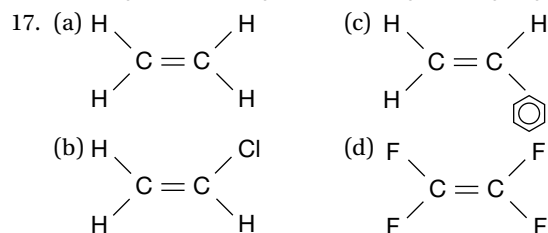
Z



10. (a) carboxyl group, benzene ring
 (b) The chiral carbon is the carbon next to the C=O.
 11. The molecule is 2-chlorobutane. The carbon atom marked as * below is a chiral carbon as it has four different atoms (groups of atoms) attached to it.

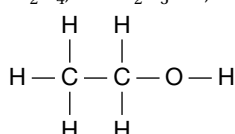


12. $\text{H}_2\text{NCH}_2\text{COOH}$, an amino acid called glycine, contains both an acidic carboxyl functional group and a basic amino functional group, so it can act as both an acid and a base.
 As a base in water: $\text{H}_2\text{NCH}_2\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{N}^+\text{CH}_2\text{COOH} + \text{OH}^-$
 As an acid in water: $\text{H}_2\text{NCH}_2\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{NCH}_2\text{COO}^- + \text{H}_3\text{O}^+$
 13. (a) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$
 (b) 4.8 kg
 14. A reaction in which an atom is replaced by another atom or group is known as a substitution reaction.
 $\text{CH}_4 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{HBr}$
 $\text{CH}_3\text{Br} + \text{Br}_2 \rightarrow \text{CH}_2\text{Br}_2 + \text{HBr}$
 $\text{CH}_2\text{Br}_2 + \text{Br}_2 \rightarrow \text{CHBr}_3 + \text{HBr}$
 $\text{CHBr}_3 + \text{Br}_2 \rightarrow \text{CBr}_4 + \text{HBr}$
 15. Ultraviolet light (or heat) is required for substitution reactions.
 16. (a) $\text{H}_2\text{C}=\text{CH}_2 + \text{HI} \rightarrow \text{CH}_3\text{CHI}$
 (b) $\text{H}_2\text{C}=\text{CHCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$
 (c) $\text{H}_2\text{C}=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCH}_2\text{Br}$
 (d) $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_2\text{ClCHClCH}_2\text{CH}_3$
 (e) $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
 (f) $\text{CH}_3\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl}$
 (g) $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$
 (h) $\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

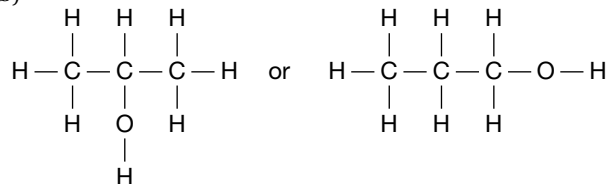


18. X = C_2H_4 ; Y = $\text{C}_2\text{H}_5\text{OH}$; Z = Br_2

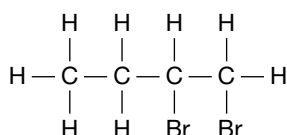
19. (a)



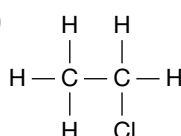
(b)



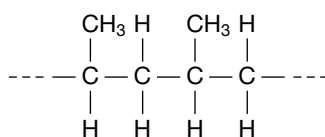
(c)



(d)

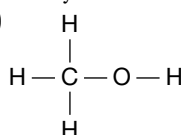


(e)

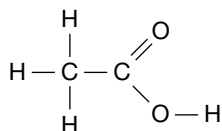


20. (a) methyl ethanoate

(b)

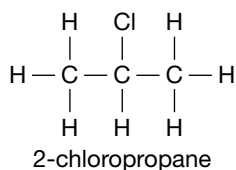
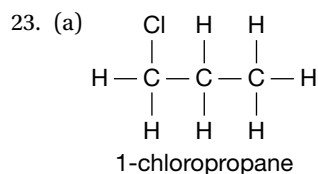


methanol



ethanoic acid

21. A small quantity of a solution containing bromine is added to the hydrocarbon sample in a test tube and then the test tube is shaken carefully side to side. If the colour of the bromine solution remains, the hydrocarbon is saturated; if the colour of the bromine solution disappears, the hydrocarbon is unsaturated.
 22. $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{g})$
 $\text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{Cl}(\text{g})$
 $\text{C}_2\text{H}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_2\text{ClCH}_2\text{Cl}(\text{g})$
 Other answers are possible.



(b) When HCl is added to but-2-ene, a symmetrical molecule, the Cl atom will always end up on the number 2 carbon atom.

24. 349 L

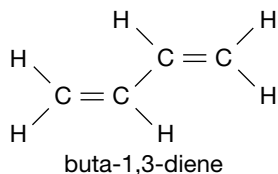
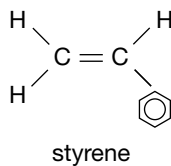
25. (a) a small molecule that can be joined to other similar or identical molecules to produce a much larger molecule (polymer)

(b) propene

(c) catalytic cracking of compounds obtained from petroleum/crude oil

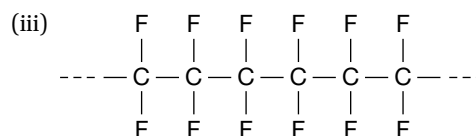
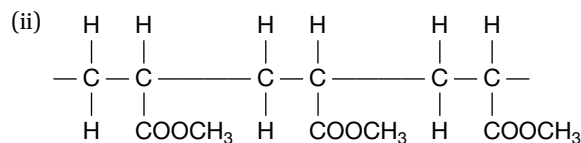
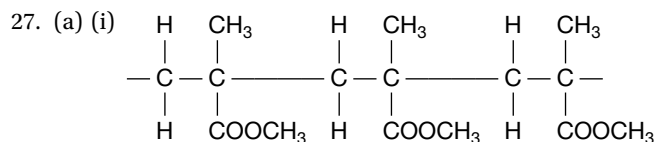
(d) ethene

26. (a) They both contain a double C=C bond.

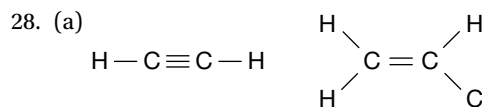


(b) catalytic cracking of compounds obtained from petroleum/crude oil

(c) benzene (specifically ethyl benzene)

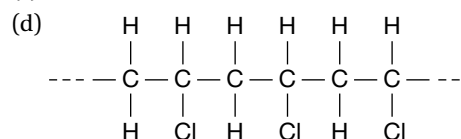


(b) polymethylmethacrylate (Perspex — a rigid shatterproof plastic used in, for example, in fume hoods)
polyvinylchloride (PVC — plumbing pipes)
polytetrafluoroethene (Teflon — non-stick surfaces on cookware)



(b) 513 g

(c) addition

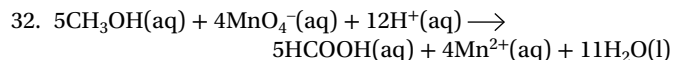
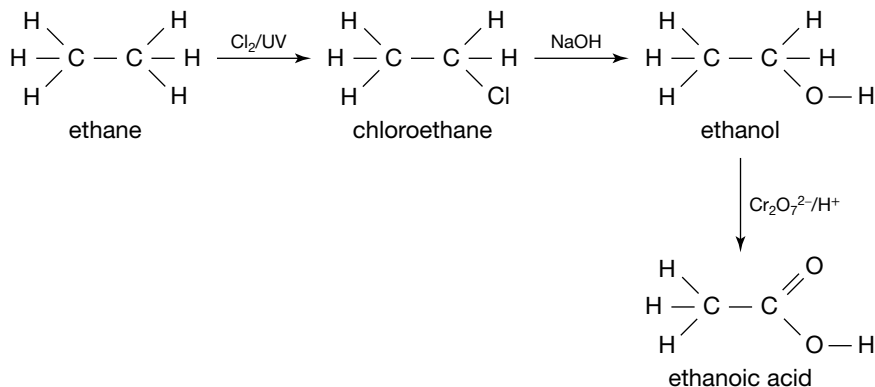


29. (a) yes

(b) yes

30. condensation reaction; reactants: carboxylic acid and alcohol; products: ester and water

31.



% yield = 79.8%

33. In this addition reaction, all reactant atoms finish up in the product.

34. 75.7%

Exam practice questions (page 273)

Multiple choice questions

1. A 2. C 3. D 4. B

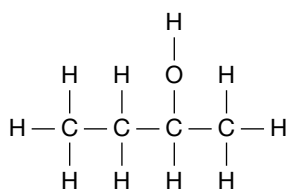
Extended response questions

1. (a) (i)
- ```

 H H H H H H
 | | | | |
---C---C---C---C---C---C---
 | | | | |
 Cl Cl Cl Cl Cl Cl

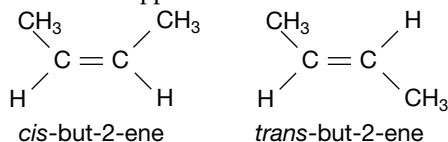
```
- (ii)
- ```

  H   H   H   H   H   H
  |   |   |   |   |
---C---C---C---C---C---C---
  |   |   |   |   |
  H   CN  H   CN  H   CN
  
```
- (b) addition polymerisation
2. (a) ester (c) pentan-1-ol
(b) cosmetics, perfume, solvent (d) condensation polymerisation
3. (a)

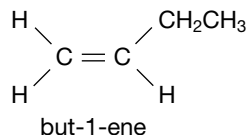


butan-2-ol

- (b) The but-2-ene molecule has a hydrogen atom and a CH_3 group on each carbon. The methyl group can be positioned on the same or opposite sides of the double bond.



The but-1-ene molecule has two hydrogen atoms on one of its carbon atoms and hence cannot form *cis* and *trans* isomers.



- (c) It is an alkene.
(d) It is an addition reaction (using HCl).

Chapter 10

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1. (a) 2 (b) 35.5
2. (a)
- ```

 H H H H
 | | | |
H---C---C---C---C---H
 | | | |
 H H H H
butane

```
- ```

  H   H   H
  |   |   |
H---C---C---C---H
  |   |   |
  H   C   H
   / \
  H   H
methylpropane
  
```

- (b) butane fragment ions: $[\text{CH}_3\text{CH}_2\text{CH}_2]^+$, $[\text{CH}_3\text{CH}_2]^+$, $[\text{CH}_3]^+$
methylpropane fragment ions: $[\text{CH}_3\text{CHCH}_3]^+$, $[\text{CH}_3\text{CH}]^+$, $[\text{CH}_3]^+$
3. (a) Z
(b) Peak X is $[\text{CH}_3]^+$. Peak Y is $[\text{CH}_3\text{CO}]^+$.

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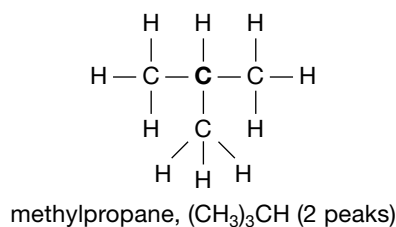
4. (a) $\text{C}=\text{O}$ at $1600\text{--}1750\text{ cm}^{-1}$, O--H at $2500\text{--}3300\text{ cm}^{-1}$, C--H at $1470\text{--}1350\text{ cm}^{-1}$
(b) IR spectrum for compound B
(c) $M(\text{CH}_3\text{COOH}) = 60$; $M(\text{CH}_3\text{CH}_2\text{COOH}) = 74$
5. compound X = carboxylic acid (peaks at $2500\text{--}3300\text{ cm}^{-1}$ and 1700 cm^{-1}); compound Y = alcohol (peak at $3200\text{--}3550\text{ cm}^{-1}$)

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- 6.
- ```

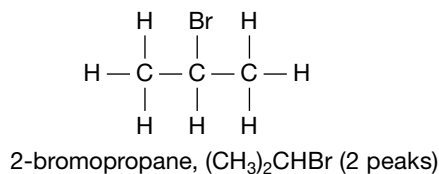
 H H H H
 | | | |
H---C---C---C---C---H
 | | | |
 H H H H
butane, CH3CH2CH2CH3 (2 peaks)

```



- 7.
- ```

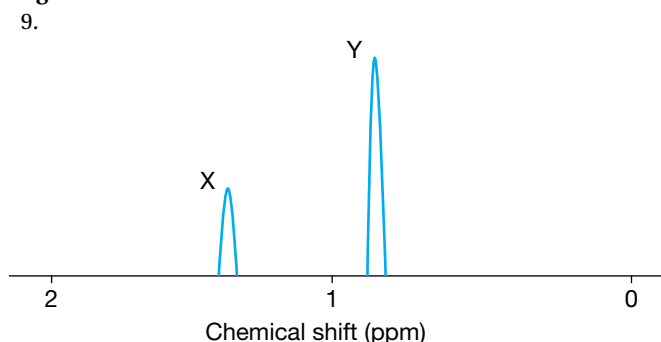
  H   H   Br
  |   |   |
H---C---C---C---H
  |   |   |
  H   H   H
1-bromopropane, CH3CH2CH2Br (3 peaks)
  
```



The number of peaks in the ^{13}C NMR spectrum is used to distinguish between the structures.

8. 2

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There would be two signals: one (Y) for the two CH_3 groups at $\delta = 0.8\text{--}1.0$ and another (X) for CH_2 at $\delta = 1.2\text{--}1.4$. The areas under the peaks X and Y would be in the ratio 1 : 3.

10. 4

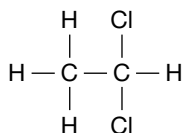
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11. The peak cluster around $\delta = 3.5$ is a quartet as there are three hydrogen atoms on the neighbouring carbon atom. The number of peaks = (number of H atoms on the neighbouring C atom) + 1 = 4 (a quartet).

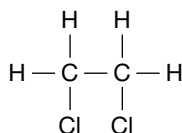
Pages 292–3

Hydrogen set or atom	Splitting pattern	Relative peak height	Chemical shift (ppm)
$\text{CH}_3\text{CH}_2\text{COOH}$	triplet	3	0.8–1.0
$\text{CH}_3\text{CH}_2\text{COOH}$	quartet	2	2.1–2.7
$\text{CH}_3\text{CH}_2\text{COOH}$	singlet	1	9–13

13.



1,1-dichloroethane, CH_3CHCl_2

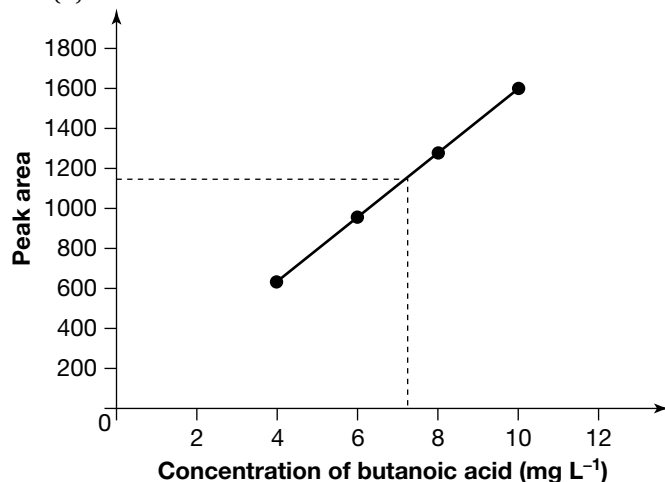


1,2-dichloroethane, $\text{CH}_2\text{ClCH}_2\text{Cl}$

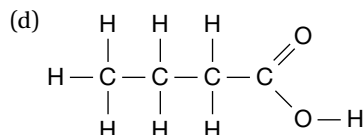
1,1-dichloroethane contains two different carbon environments, whereas 1,2-dichloroethane has only one, due to the symmetry of the molecule. Therefore, the proton NMR spectrum is for 1,1-dichloroethane.

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14. (a) methanol
(b)



(c) 7.2 mg L^{-1}



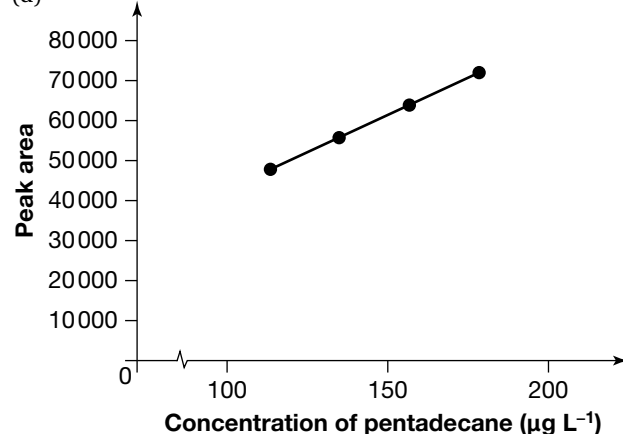
15. (a) alkanes
(b) As a non-polar hydrocarbon, it is not soluble in water.
(c) For a solution with a concentration of $120 \mu\text{g L}^{-1}$,
 $V_1 = 5.0 \text{ mL}$. Add 5.00 mL of pentadecane solution to a

10.0 mL volumetric flask. Then carefully add hexane (5.00 mL) up to the calibration line on the volumetric flask.

Volumes needed for the four solutions

c_2 (pentadecane) ($\mu\text{g L}^{-1}$)	V_2 (mL)	c_1 ($\mu\text{g L}^{-1}$)	V (hexane) (mL)
120	10.0	240	5.00
140	10.0	240	4.17
160	10.0	240	3.33
180	10.0	240	2.50

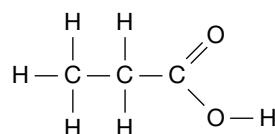
(d)



- (e) verification standard 1: 6.00×10^5
verification standard 2: 6.80×10^5

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16. (a) $\text{C}_3\text{H}_6\text{O}_2$
(b) A: $m/z = 74$, $[\text{C}_3\text{H}_6\text{O}_2]^+$; B: $m/z = 57$, $[\text{C}_3\text{H}_5\text{O}]^+$;
C: $m/z = 45$, $[\text{COOH}]^+$; D: $m/z = 29$, $[\text{C}_2\text{H}_5]^+$
(c) (i) $2500\text{--}3300 \text{ cm}^{-1} \Rightarrow \text{OH}$ in a carboxylic acid
(ii) $1670\text{--}1750 \text{ cm}^{-1} \Rightarrow \text{a C=O group}$
(iii) $1000\text{--}1300 \text{ cm}^{-1} \Rightarrow \text{a C—O bond}$
(d), (e) propanoic acid



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17. 0.0999 M
18. (a) $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$
(b) 0.0860 M
(c) The reacting solutions are colourless. The indicator is needed to detect the end point.
(d) Yes. The concentration is now accurately known. (Note: This solution must be used immediately because it will react with carbon dioxide in the atmosphere and so its concentration will change.)

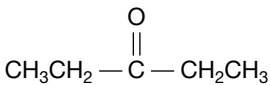
Pages 310–11

19. 0.124 M
20. 40.4 g L^{-1}

Multiple choice questions

1. D 2. C 3. B 4. C 5. B 6. A 7. C 8. C
9. A 10. C 11. D 12. D 13. A 14. B 15. C 16. C
17. B 18. D 19. B 20. B

Review questions

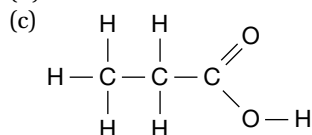
- (a) $m/z = 86$
(b) $m/z = 57$
(c) $[\text{CH}_3\text{CH}_2]^\bullet$
(d) 
- $\text{C}_2\text{H}_4\text{O}_2$
- Ethanoic acid has a peak in the region $2500\text{--}3300\text{ cm}^{-1}$ due to the O—H (acid). Ethanoic anhydride has no peak in this region.
- (a) Butanoic acid has a peak in the region $2500\text{--}3300\text{ cm}^{-1}$ due to O—H (acid) and a peak in the region $1670\text{--}1750\text{ cm}^{-1}$ due to $\text{C}=\text{O}$. Butan-1-ol has a peak in the region $3200\text{--}3550\text{ cm}^{-1}$ due to O—H (alcohol) but no peak in the region $1670\text{--}1750\text{ cm}^{-1}$.
(b) The main difference is there are more peaks in the $1000\text{--}1100\text{ cm}^{-1}$ region for the longer molecule of butanoic acid.

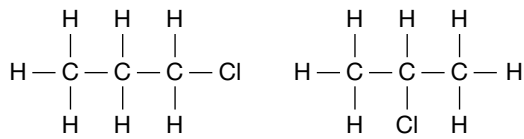
5. R

Method	Type of radiation	Basis of analysis	Method	Type of analysis
IR	infrared light	change in vibrational energy level of functional groups in molecules	analysis of IR spectrum	identify functional groups in molecules
NMR	radio waves	change in spin state of ^1H or ^{13}C nucleus	analysis of NMR spectrum	identify different H or C environments

- The different connectivities of atoms in a molecule produce different numbers, shapes and sizes for peaks, depending on whether it is ^{13}C NMR or high- or low-resolution ^1H NMR. The relative height of the integration/peak represents the number of nuclei in that environment. The splitting represents the number of adjacent protons (for ^1H NMR). The position of the peak reflects the degree of shielding/deshielding.
- (a) $\text{R}-\text{CH}_3$ (1.0 ppm); R_2-CH_2 (1.3 ppm); $\text{R}-\text{COOH}$ (10.5 ppm)

(b) 4

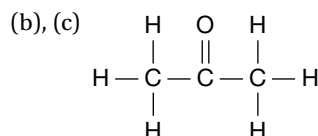
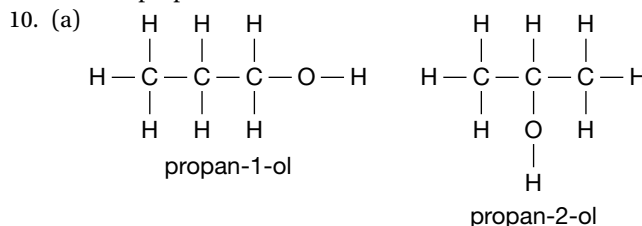


- 

1-chloropropane 2-chloropropane

Compound	Number of groups of peaks for ^1H NMR	Number of peaks for ^{13}C NMR
1-chloropropane	3	3
2-chloropropane	2	2

The isomer represented by these two spectra is 2-chloropropane.



Primary alcohols (propan-1-ol) are oxidised firstly to aldehydes and then to carboxylic acids, while secondary alcohols (propan-2-ol) are oxidised to ketones. Based on this evidence, compound B could be $\text{CH}_3\text{CH}_2\text{CHO}$ (propanal) or propanone (CH_3COCH_3). Since the proton NMR of B has only 1 peak, there is only 1 H environment. This indicates that the compound is the symmetrical ketone, rather than the aldehyde. The mass spectrum has a peak at $m/z = 43$, which could be $[\text{CH}_3\text{CO}]^+$. Thus compound B must be propanone (CH_3COCH_3).

(d) $\text{CH}_3\text{COCH}_3^+ \rightarrow \text{CH}_3\text{CO}^\bullet + \text{CH}_3^+$

(e) 2 peaks

- (a), (b) The mobile phase passes over and through the stationary phase and carries the components of the mixture to be separated.
(c) The solvent dissolves the components of the mixture to form the mobile phase.
(d) The retention time is a measure of the time it takes for the various components of the mixture to travel through the column.
(e) The column is the narrow diameter tube that contains the stationary phase.
(f) When using HPLC, a set of standards of known concentration is used to plot a calibration curve of concentration against peak area.
(g) A chromatogram is a visible record that shows the result of the HPLC separation.
- Separation occurs through the processes of adsorption and desorption onto and from the surface of the stationary phase. The larger the surface area, the greater is the degree of adsorption and desorption, producing better separation.
- Most likely, yes. However, there is a low probability that it is another substance with the same retention time under the same conditions. Repeating the analysis using a different column or solvent would give the same retention time only if the two substances are in fact the same.
- (a) The peak would have the same retention time as the standards.
(b) to determine the relationship between concentration and peak area (a calibration curve), thus enabling the unknown concentration of other samples to be determined by interpolation
(c) true
- (a) compound E
(b) compound A

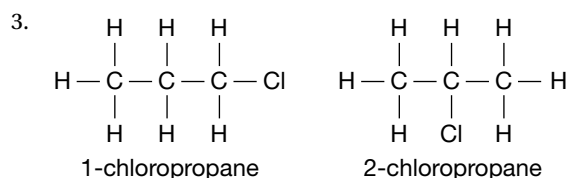
16. 1.7 g. Accurately weigh the mass required. Transfer this to a volumetric flask, making certain that the transfer is complete. Add enough water to dissolve it. Add further water up to the mark. Mix thoroughly to ensure a uniform concentration is attained.
17. (a) A burette is typically a fixed piece of equipment. It can deliver accurate volumes. A pipette is typically a movable piece of equipment. It can pick up and deliver accurate volumes. It is more suited to smaller volumes.
 (b) An aliquot is the volume dispensed by a pipette. A titre is the volume delivered by a burette.
 (c) The end point is where the indicator changes colour. The equivalence point is where the reactants are present in their stoichiometric proportions.
 (d) A primary standard is a pure substance that can be weighed out and then made into a solution of accurately known concentration. A standard solution is any solution for which the concentration is known accurately.
 (e) Deliquescence is the absorption of so much atmospheric moisture that the substance dissolves in it. Efflorescence is the giving off of water molecules.
 (f) Quantitative analysis determines the amounts of substances that are present. Qualitative analysis identifies the substances that are present.
18. (a), (b) All are important, but cost is probably the least important. For this reason, there may be occasions where an expensive standard is used because no cheaper alternative is available.
19. (a) $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
 (b) $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
 (c) $5\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) \rightarrow 5\text{Fe}^{3+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
 (d) 0.007 76 M
 (e) An indicator is not required for this reaction as it is a redox reaction that is self-indicating. The permanganate ion is purple and the manganese ion is colourless.
20. (a) $\text{CH}_3\text{COOC}_6\text{H}_4\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{COOC}_6\text{H}_4\text{COONa}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 (b) 0.431 g
21. 0.143 M
22. (a) 0.006 20 M
 (b) 0.109 g
 (c) 52.0 mg/100 g
23. (a) $2\text{HCl}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 $c(\text{HCl}) = 0.1030 \text{ M}$
 (b) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 $c(\text{NaOH}) = 0.1070 \text{ M}$
 (c) $2\text{NaOH}(\text{aq}) + \text{H}_2\text{C}_2\text{O}_4(\text{aq}) \rightarrow \text{Na}_2\text{C}_2\text{O}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
 $c(\text{H}_2\text{C}_2\text{O}_4)$ in the spot removal solution = 0.5559 M

Exam practice questions (pages 320–1)

Extended response questions

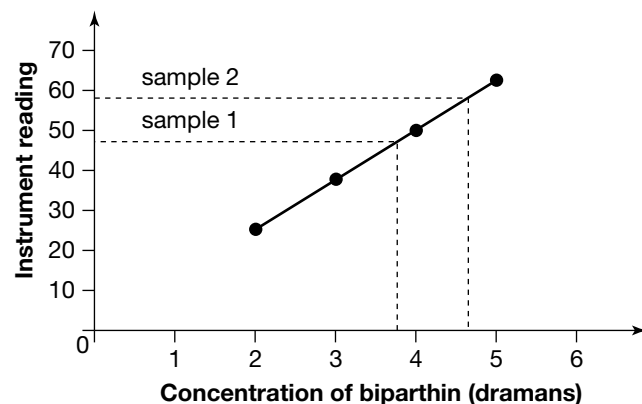
1. (a) chromatography — HPLC
 (b) mass spectroscopy (as long as they were thermally stable)
 (c) IR and NMR
2. Spectrum A is ethanol.
 $m/z = 46 [\text{CH}_3\text{CH}_2\text{OH}]^+$ — the molecular ion peak
 $m/z = 31 [\text{CH}_2\text{OH}]^+$
 $m/z = 29 [\text{CH}_3\text{CH}_2]^+$
 Spectrum B is ethanoic acid.

$m/z = 60 [\text{CH}_3\text{COOH}]^+$ — the molecular ion peak
 $m/z = 45 [\text{COOH}]^+$
 $m/z = 43 [\text{CH}_3\text{CO}]^+$



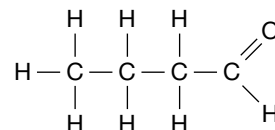
Compound	Number of hydrogen environments	Relative peak height	Splitting
1-chloropropane a b c $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	3	a : b : c 3 : 2 : 2	a : b : c triplet : sextet : triplet
2-chloropropane a b a $\text{CH}_3\text{CHClCH}_3$	2	a : b 6 : 1	a : b doublet : septet

4. (a)

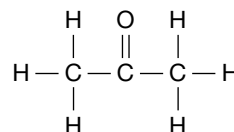


- (b) food sample no. 1 = 3.8 dramans; food sample no. 2 = 4.6 dramans
 (c) Don't eat any food corresponding to food sample no. 2.

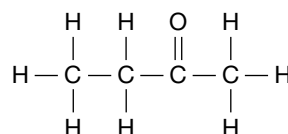
5.



butanal

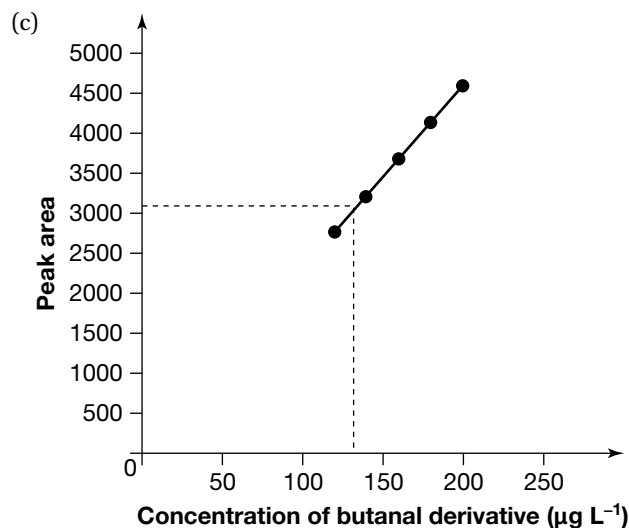


propanone



butanone

- (b) between 120 and 140 $\mu\text{g L}^{-1}$



$c(\text{butanal})$ in the diluted sample = $133 \mu\text{g L}^{-1}$

(d) 13.3 mg L^{-1}

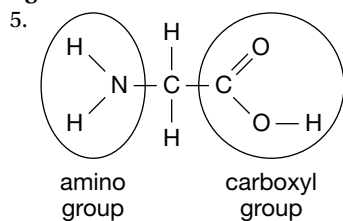
(e) Different compounds interact differently with both the mobile phase and the stationary phase. It is necessary to experimentally derive the conditions that best separate this component from the compound under investigation.

Chapter 11

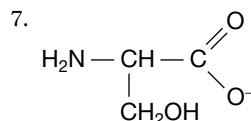
Page 327

1. Fat-soluble vitamins are stored in the body in fat deposits and within the liver, remaining in the body until needed. By comparison, water-soluble vitamins do not remain in the body and must be obtained from food on a regular basis.
2. As fat-soluble vitamins are stored by the body, they can accumulate. The accumulation of fat-soluble vitamins may cause toxicity. This is observed for vitamins A and D more than other fat-soluble vitamins.
3. (a) This vitamin is a non-polar molecule (the single —OH group would have no effect on the overall polarity of the molecule) and so it would be fat soluble.
(b) This vitamin is a highly polar molecule (many —OH groups) and so would be water soluble.
4. $\text{C}_6\text{H}_8\text{O}_6$

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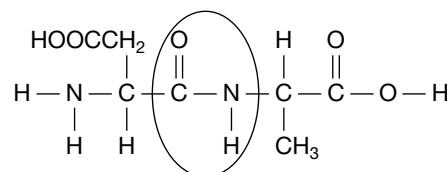
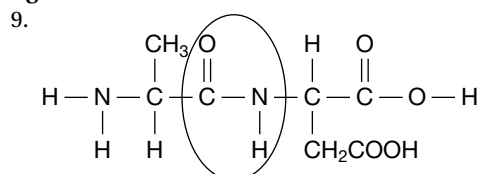


6. Glycine does not have four different atoms bonded to its central carbon atom and so does not have a chiral carbon.



8. aspartic acid and glutamic acid

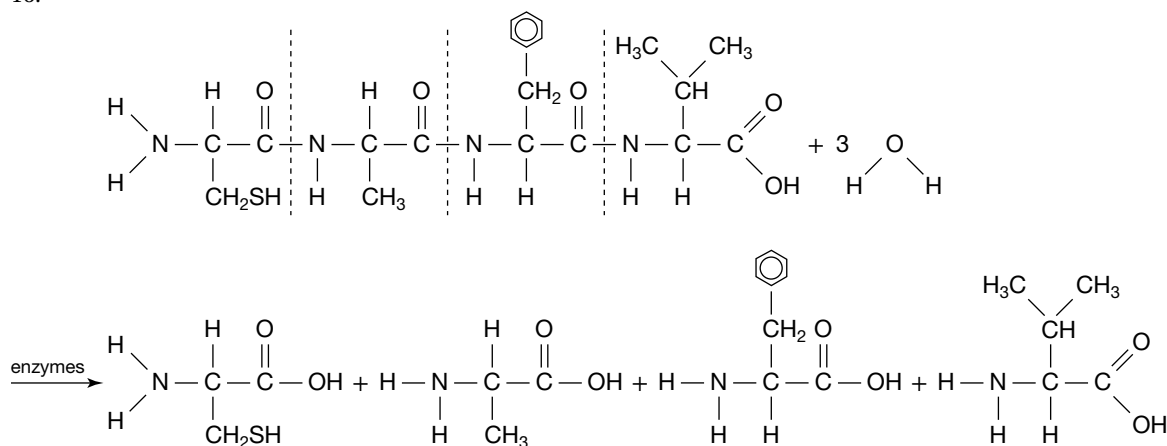
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10. 204.0 g mol^{-1}
11. hydrogen bonding
12. hydrogen bonding

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13. Similarities: They both explain how substrates react with the active site of an enzyme.
Differences: In the lock-and-key model, only a substrate with the shape that exactly matches (is complementary to) the shape of the active site can be catalysed. In the induced fit model, the active site can change its shape in the presence of the substrate to become complementary to the substrate.
14. Coenzymes are non-protein molecules that assist the functioning of an enzyme by providing the atoms or electrons needed for the reaction.
15. When the temperature is raised beyond the optimum range of an enzyme, the enzyme begins to denature as the bonds responsible for its structure are compromised.



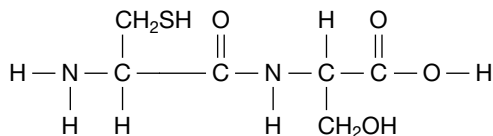
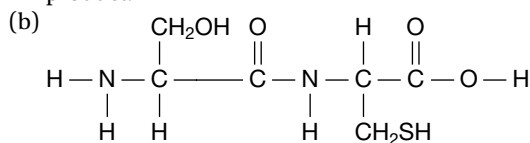
17. CON_2H_4 ; $M = 60.0 \text{ g mol}^{-1}$

Multiple choice questions

1. B 2. A 3. D 4. A 5. A 6. D 7. D 8. A
 9. D 10. C 11. C 12. C 13. C 14. B 15. A 16. C
 17. B 18. D 19. B 20. A 21. B 22. B

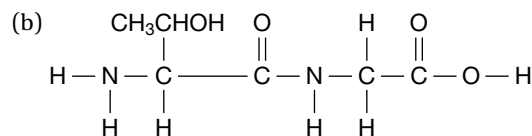
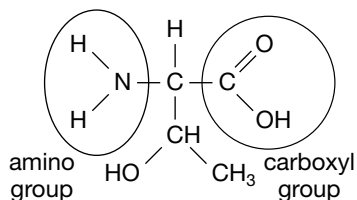
Review questions

- (a) A vitamin is an organic compound required in the diet because it cannot be synthesised by the body.
 (b) Vitamins are essential for growth and nutrition.
- It is possible to have a deficiency of vitamin C because it is water soluble (due to the presence of several —OH groups) and so is not retained by the body. By comparison, vitamin D is a fat-soluble vitamin (long carbon chain and only one —OH group present) and so it can accumulate in the body. Consequently, excess vitamin D in the body can result in toxicity, while the lack of a constant supply of vitamin C in the diet can lead to deficiency conditions such as scurvy.
- (a) hydroxyl, carbonyl and amino groups
 (b) water soluble
- (a) It is a condensation reaction and water is the other product.



5. The central carbon atom is chiral; it has four different atoms or groups of atoms bonded to it.

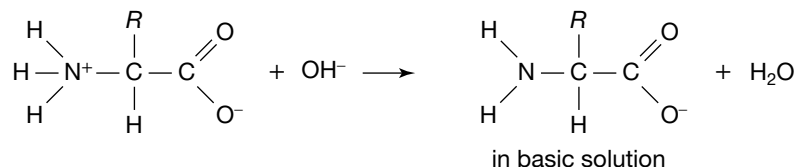
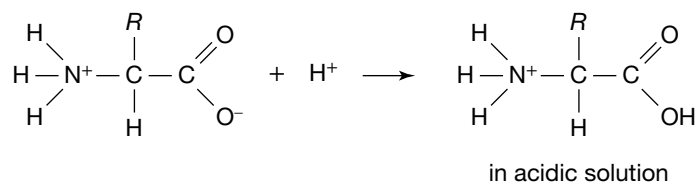
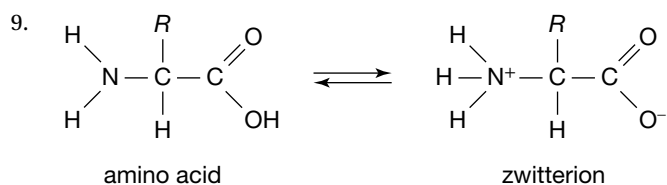
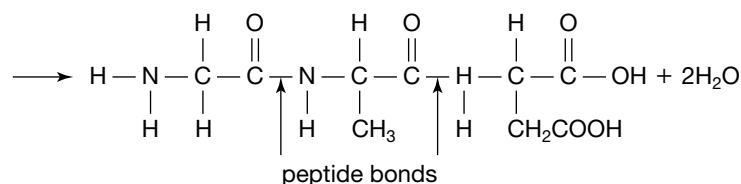
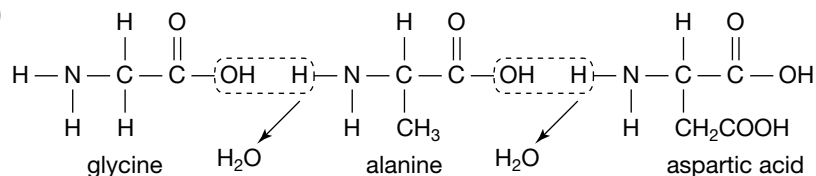
6. (a)



The other substance formed is water.

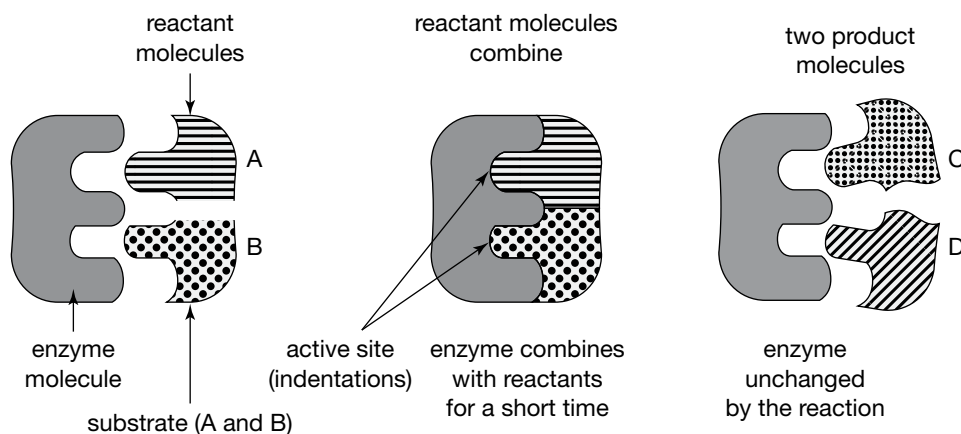
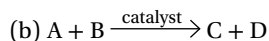
- Threonine contains a chiral carbon (it has four different atoms or groups of atoms bonded to it), whereas glycine does not contain a chiral carbon (there are two hydrogens attached to the central carbon).
- to prevent infection, act as hormones, regulate body functions, act as catalysts
- (a) hydrogen bonding between the peptide links on different parts of the protein chain
 (b) dispersion forces, covalent bonds (disulfide bridge), dipole-dipole interactions

8. (a) 6
(b) 27
(c)



In acidic solutions, the zwitterion accepts a proton, whereas, in basic solutions, the zwitterion donates a proton.

10. Enzymes can speed reactions to a much greater degree than inorganic catalysts. Enzymes operate under much milder conditions. Enzymes operate within narrower temperature and pH ranges. Enzymes are much more selective.
11. (a) An enzyme is a biological catalyst. It is a complex protein that increases the rate of a chemical reaction without being changed.
(b) Each enzyme is specific and catalyses a particular reaction. It interacts with a substance called the substrate.
(c) Enzymes each have a unique three-dimensional shape that is determined by the nature of the bonding and side chains in the protein. The reactant molecule (substrate) fits into a region in this shape that is called the active site.
(d) A coenzyme is a non-protein compound that is necessary for the functioning of an enzyme.
12. (a) An enzyme is said to fit together with a substrate like a lock and key. The substrate fits perfectly into the shape produced by the relevant enzyme. Bonds form between the substrate and the active site in the enzyme that weaken bonds within the substrate. The two parts of the substrate separate from the enzyme.



13. Enzymes are organic protein molecules while coenzymes are organic non-protein molecules. Enzymes act as catalysts while coenzymes assist some enzymes to act as catalysts.
14. (a) Denaturation is an alteration of a protein's shape that makes the protein unable to carry out its usual function.
(b) Denaturation can be caused by heat, a change in pH, a change in salt concentration or the presence of heavy metals.
15. (a) The acid build-up via the production of lactic acid causes the milk protein caseinogen to denature. The proteins unfold and interact with each other, clumping together. The presence of these lumps is called curdling.
(b) The acid disrupts the bonds in the secondary and tertiary structures but not the strong covalent peptide bonds in the primary structure. New bonds form between the unwound chains of the protein. This formation of a new structure is called coagulation.
16. (a) Digestive enzymes are proteins. It is important to wash at normal room temperatures so the proteins are not denatured.
(b) Digestive enzymes are used to remove biological stains containing starches, lipids or proteins from clothes.
(c) The specific shape of the enzyme allows the bonding of the substrate (biological molecule) to the active site and decreases the activation energy by providing an alternative pathway for the hydrolysis of starches, lipids and proteins. The resulting sugars, fatty acids, glycerol and amino acids are removed during the rest of the washing process.
17. If hot water is used to remove the blood, it can cause the blood protein to denature and coagulate. In this process, the protein molecules bind to the fibres of the material, making them harder to remove.
18. (a) Pineapple contains an enzyme called bromelain. Enzymes and acids from fruits such as pineapples can denature muscle and connective proteins in meat so that it is more tender.
(b) The enzyme is denatured when the can is heated during the canning process.

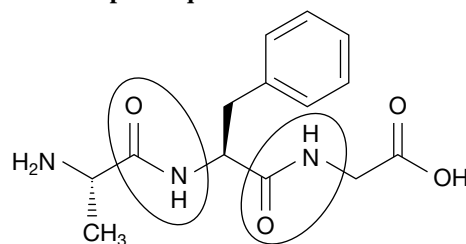
Exam practice questions (pages 344–5)

Multiple choice questions

1. B 2. C 3. B 4. B 5. C

Extended response questions

1.



The amino acids are (from left to right): alanine, phenylalanine and glycine.

2. (a)
$$\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{OH} \\ | \\ \text{CH}_2 \\ | \\ \text{OH} \end{array} \quad \text{or} \quad \begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}_3\text{N}^+-\text{C}-\text{C}-\text{O}^- \\ | \\ \text{CH}_2 \\ | \\ \text{OH} \end{array}$$
- (b)
$$\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}_3\text{N}^+-\text{C}-\text{C}-\text{OH} \\ | \\ \text{CH}_2 \\ | \\ \text{OH} \end{array}$$
- (c)
$$\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{O}^- \\ | \\ \text{CH}_2 \\ | \\ \text{OH} \end{array}$$
- (d)
$$\begin{array}{c} \text{CH}_2\text{OH} \quad \text{O} \quad \text{H} \quad \text{O} \\ | \quad || \quad | \quad || \\ \text{H}-\text{N}-\text{C}-\text{C}-\text{N}-\text{C}-\text{C}-\text{O}-\text{H} \\ | \quad | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$$

$$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \quad \text{O} \\ | \quad || \quad | \quad || \\ \text{H}-\text{N}-\text{C}-\text{C}-\text{N}-\text{C}-\text{C}-\text{O}-\text{H} \\ | \quad | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{CH}_2\text{OH} \end{array}$$

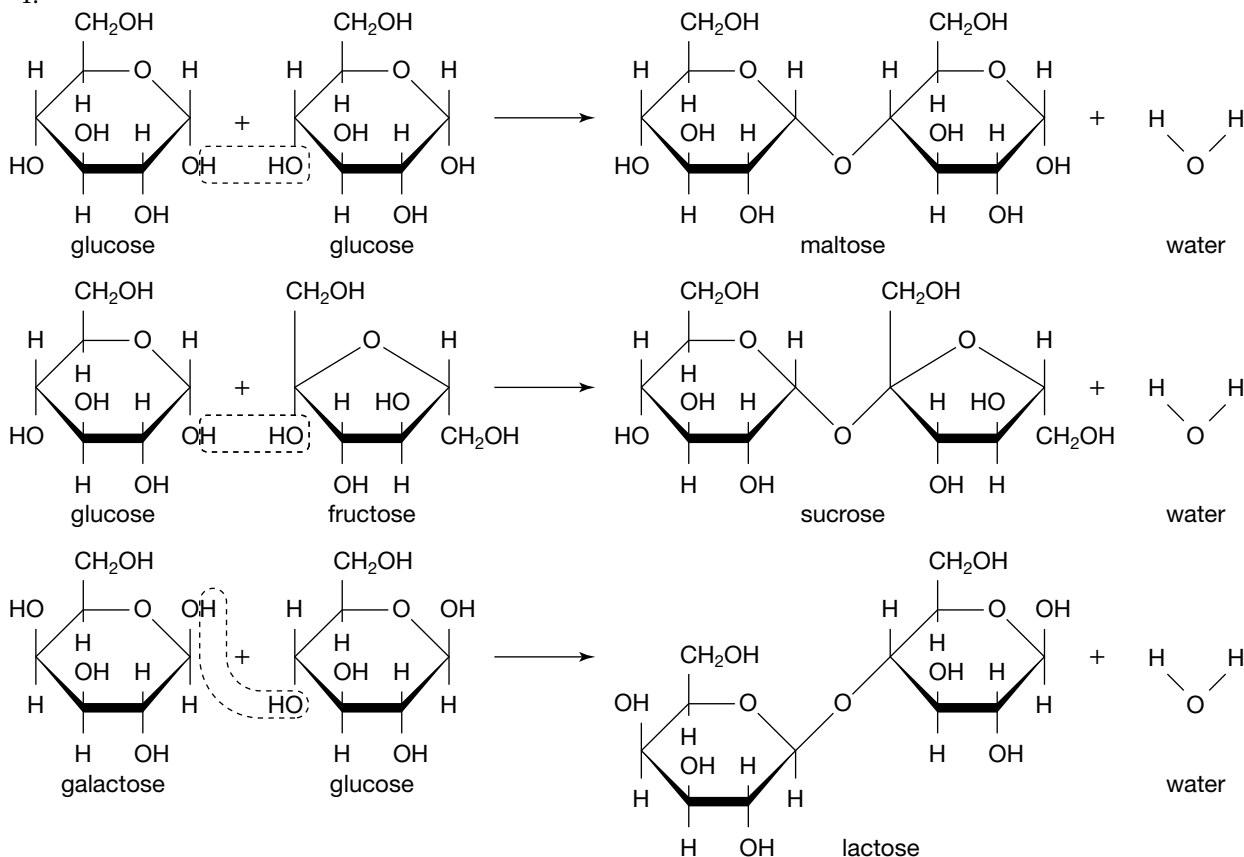
3. Inorganic catalysts operate under variable conditions.

Pressures can range from 1 atm to 250 atm, and temperatures can range from low (25 °C) to high (e.g. 600 °C). Enzymes operate under much milder conditions (37 °C). Inorganic catalysts are not selective. Platinum can catalyse a wide range of reactions. Enzymes are very selective. Each reaction in the body requires a specific enzyme.

Chapter 12

Page 351

1.



2. (a) hydroxyl
(b) hydroxyl and ether
(c) amino, carboxyl, amide and ester
3. As aspartame is around 200 times sweeter than sucrose, far less aspartame would be needed to provide the same degree of sweetness as sucrose. Consequently, the contribution to the energy content of the food from the sweetener component would be reduced.
4. Aspartame is a dipeptide (phenylalanine and aspartic acid) methyl ester.

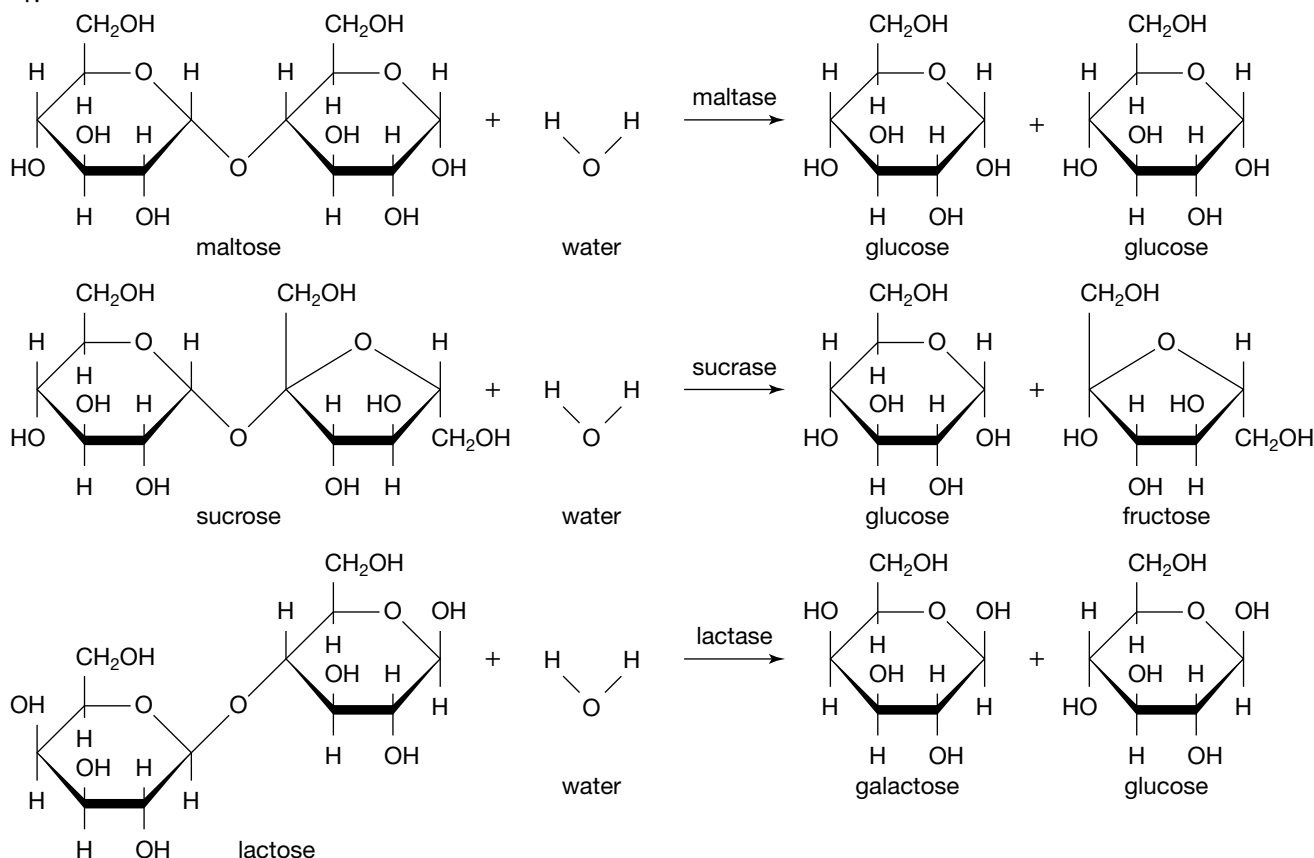
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5. Starch is a condensation polymer of α -D-glucose, while cellulose is a condensation polymer of β -D-glucose. In starch, the α -D-glucose monomers link up regularly when they polymerise, while, in cellulose, alternate β -D-glucose monomers are inverted when they link up. Starch comprises two different polymers: amylose (linear polymer chains) and amylopectin (branched polymer chains). Cellulose comprises only one type of unbranched polymer chain that forms extensive hydrogen bonds to other unbranched polymer chains.

6. (a) starch (c) glycogen (e) cellulose
 (b) cellulose (d) starch

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7.



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8. Lactose is soluble in milk as milk has a high water content. Lactose can readily form hydrogen bonds with water molecules. Butter and cheese have a lower water content and a higher fat content and as a consequence the polar lactose molecule is less soluble in butter and cheese.

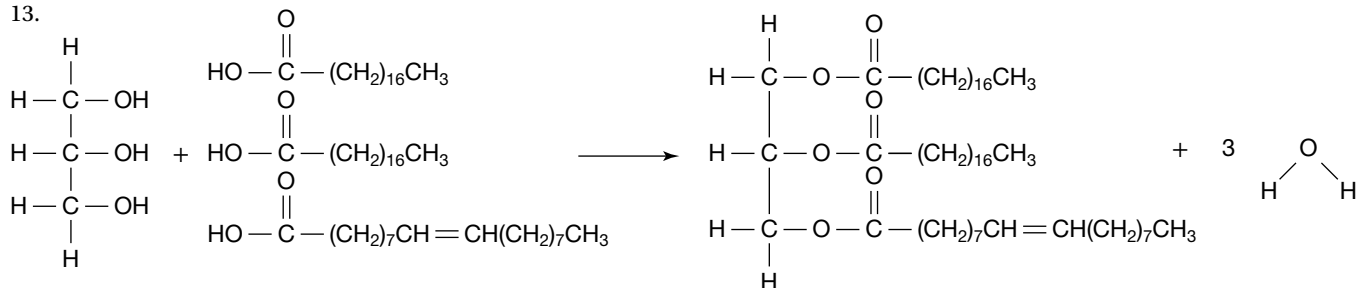
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9. 90 mg dL⁻¹

Pages 360-1

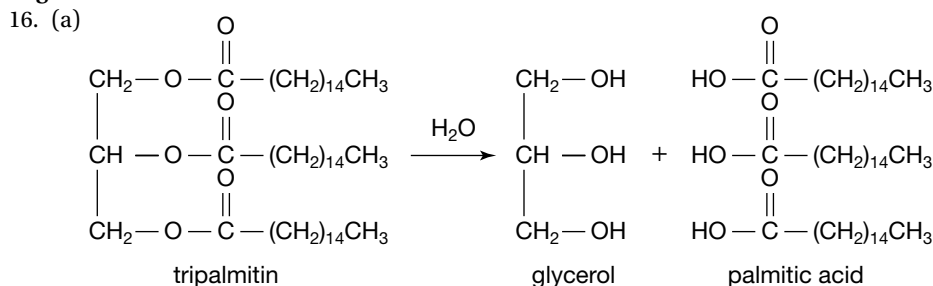
10. (a) stearic acid
 (b) oleic acid
11. Lipids are insoluble because of their long non-polar hydrocarbon chains. As water is a polar molecule, lipids and water do not bond or share electrons in any way.
12. oils, because they would have a greater degree of unsaturation (more double bonds)

13.



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14. Oxygen (from the air) readily reacts across the double bonds present in unsaturated fats.
15. (a) $\text{C}_6\text{H}_8\text{O}_6(\text{aq}) \rightarrow \text{C}_6\text{H}_6\text{O}_6(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$
 (b) This is an oxidation reaction; there is a loss of electrons and gain in oxidation number.
 (c) Two hydroxyl groups are oxidised to two carbonyl groups.

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- (b) ester, hydroxyl, carboxyl
17. (a) $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}(\text{s}) + 23\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2(\text{g}) + 16\text{H}_2\text{O}(\text{l})$
 (b) $2\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}(\text{l}) + 52\text{O}_2(\text{g}) \rightarrow 36\text{CO}_2(\text{g}) + 34\text{H}_2\text{O}(\text{l})$

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18. 0.492°C
19. (a) The student would use an electric heater, connected into an electric circuit, to pass a known quantity of energy (E) through 100.0 mL of water (using the same total volume as used in the experiment) in the same calorimeter used for the experiment. The energy (E) released from the electric heater = VIt (where V = voltage, I = current and t = time in seconds). The calibration factor (CF) can then be calculated from the relationship:

$$\text{CF} = \frac{E}{\Delta T} = \frac{VIt}{\Delta T}$$

where ΔT = change in temperature of the 100 mL of water.

- (b) $\Delta H = -54.9 \text{ kJ mol}^{-1}$
 (c) to ensure that all of the acid had reacted
 (d) There would be no change as amount in moles of the limiting reactant would not change.
 (e) Random errors might involve measurement of the solution volume and temperature, and not stirring the reaction mixture during the reaction. Random errors can be minimised by repeating experiments. Another error is heat losses due to insufficient insulation.

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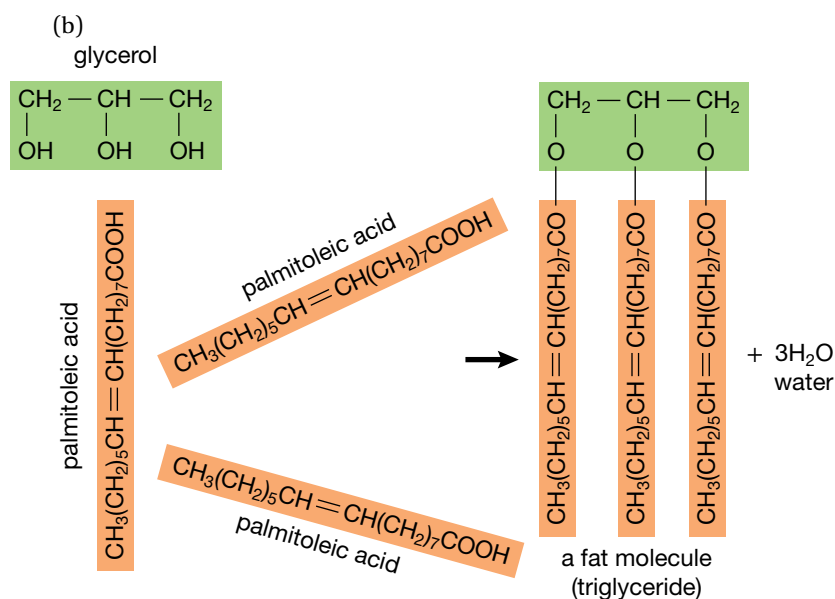
20. (a) $1.18 \times 10^3 \text{ J } ^\circ\text{C}^{-1}$
 (b) $3.01 \times 10^3 \text{ J g}^{-1}$
 (c) The reaction involves gases as reactants and/or products. All reactants and products must be contained to determine the overall energy transfers in the reaction.
 (d) Cereal is a mixture and consequently does not have a molar mass.

Multiple choice questions

1. C 2. C 3. B 4. C 5. B 6. D 7. C 8. C
 9. B 10. D 11. C 12. A 13. A 14. D 15. A 16. C
 17. D 18. B 19. B 20. A 21. C 22. B 23. D 24. C
 25. B 26. B 27. C 28. D 29. C 30. B

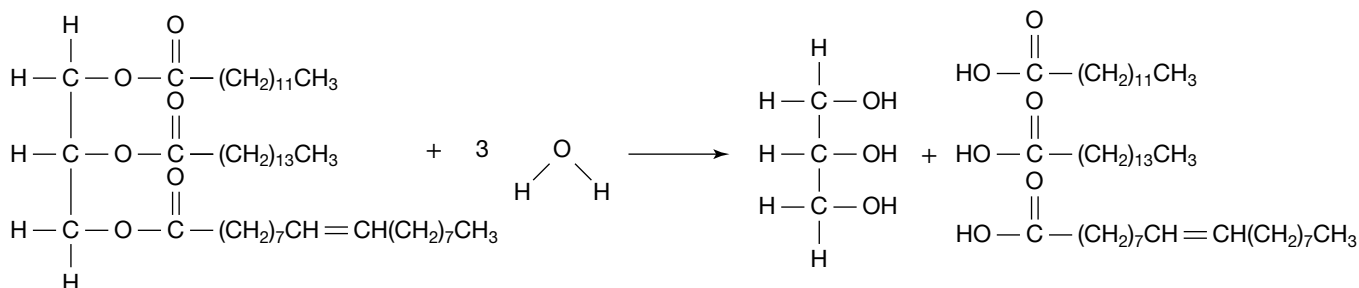
Review questions

- $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- The two components of starch are amylose and amylopectin. They are both polymers formed from the monomer α -D-glucose. Amylose consists of linear chains arranged in a helical structure. The glycosidic links connect C1 of one glucose molecule to C4 of the next glucose molecule. Amylopectin is a longer and branched molecule where the branches are formed by glycosidic links connecting C1 of a glucose molecule in one linear chain to C6 of a glucose molecule in another linear chain.
- $1.04 \times 10^5 \text{ g mol}^{-1}$
- These symptoms are typical of lactose intolerance. People with lactose intolerance suffer from a lack of the enzyme lactase, which is required for the hydrolysis of lactose. Those more likely to experience lactose intolerance tend to be people with Asian, African, native American, South American, southern European and Australian Aboriginal heritage.
- In cellulose, the arrangement of the linear polysaccharide chains formed from β -D-glucose monomers is such that there is extensive hydrogen bonding between the chains. Humans do not have the ability to easily hydrolyse cellulose. However, cellulose does provide fibre that assists the passage of food through the digestive system.
- (a) glucose
 (b) Low glycaemic foods are digested more slowly and hence provide energy over a longer period of time.
 (c) After activity, a high GI food would enable depleted energy stores to be more quickly filled.
 (d) Amylose is more slowly digested and accordingly has a lower GI; that is, the greater the proportion of amylose to amylopectin, the lower is the GI value of the food.
- (a) It has one double bond and is a long-chain carboxylic acid.

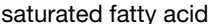


(c) In an esterification reaction, the alcohol functional group of one molecule reacts in a condensation reaction with the carboxyl functional group of a carboxylic acid to form the ester functional group. When a triglyceride forms in a reaction between glycerol (a triol) and three fatty acid molecules, three ester groups form; it is an esterification reaction.

8.



9. Butter is harder and less spreadable than margarine because butter has a high proportion of saturated fatty acids, whereas margarines are made from higher proportions of polyunsaturated fatty acids. Molecules with straight chains as in saturated fatty acids are able to get closer, allowing for more extensive dispersion forces between the hydrocarbon chains, which makes them more rigid (harder) and less manoeuvrable (spreadable) than margarine.
10. The polar —OH groups on carbohydrates form hydrogen bonds with water. The long hydrocarbon side chains in fats are non-polar and so do not form bonds with water.
11. Fatty acids can be saturated (have only single C—C bonds), monounsaturated (have one double C=C double bond) or polyunsaturated (have more than one double C=C double bonds). The examples on the next page show a saturated and polyunsaturated fatty acid molecule. The double bond(s) in unsaturated fats make these fats more susceptible to oxidation than saturated fats because oxygen (in the air) reacts across the double bond. Consequently, foods containing unsaturated fats are more likely to become rancid.



21. (a) 17.3 kJ g^{-1}
(b) The biscuit is a mixture (not a pure substance) and consequently does not have a molar mass.
(c) Not all of the food that is ingested is completely digested and so not all of the energy will be absorbed.
22. Glucose is a disaccharide formed from a condensation reaction of one glucose molecule and one fructose molecule. Assuming that the heat of combustion of fructose is the same as that of glucose, the approximate heat of combustion of sucrose would be slightly less than $2 \times 2816 = 5632 \text{ kJ mol}^{-1} \approx 5600 \text{ kJ mol}^{-1}$.

Exam practice questions (page 375)

Multiple choice questions

1. A 2. B 3. A 4. A

Extended response questions

1. 39.9 kJ g⁻¹
2. (a) $5.36 \times 10^3 \text{ J g}^{-1}$
(b) There would be random errors associated with uncertainty in the measurement of the current, voltage, time and temperature for the calibration. There would also be random errors with the measurement of the mass and temperature in the combustion process. The consequence of random error is to obtain a result that can vary either above or below the expected result. The effects of random error can be minimised by repeating measurements. Other factors are incomplete reaction and insulation issues.

Glossary

- absolute zero:** the lowest temperature that is theoretically possible; 0 K
- acid rain:** rain that has a pH lower than 5
- activation energy:** the minimum energy required by reactants in order to react
- active site:** a region on an enzyme that binds to a protein or other substance during a reaction
- addition polymerisation:** the process in which monomers with at least one double bond react together to form a polymer by addition reactions
- addition reactions:** reactions in which one molecule bonds covalently with another molecule without losing any other atoms
- adsorption:** the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface
- alcohols:** hydrocarbons containing the —OH functional group
- aliphatic:** describes organic compounds in which carbon atoms form open chains
- aliquot:** the liquid from a pipette
- alkaline fuel cell:** fuel cell that converts oxygen (from the air) and hydrogen (from a supply) into electrical energy and heat
- alkanes:** simple, saturated binary compounds of carbon and hydrogen atoms with single bonds between the carbon atoms. The general formula for all members of this homologous series is C_nH_{2n+2} .
- alkenes:** the family of hydrocarbons that contain one carbon-carbon double bond
- alkynes:** the family of hydrocarbons with one carbon-carbon triple bond
- amide linkage:** linkage formed when a carboxyl group reacts with an amino group in a polymerisation reaction
- amino acids:** molecules that contain an amine and a carboxyl group
- amphoteric:** describes a substance that can act as either an acid or a base
- analytes:** the components of a sample
- anode:** the electrode at which oxidation occurs. In a galvanic cell, it is the negative electrode, since it is the source of negative electrons for the circuit. If the reducing agent is a metal, it is used as the electrode material.
- aromatic:** describes a compound that contains at least one benzene ring and is characterised by the presence of alternating double bonds within the ring
- aspartame:** a common artificial sweetener
- base peak:** the most abundant ion in a mass spectrum
- benzene:** an aromatic hydrocarbon with the formula C_6H_6
- biodiesel:** a fuel produced from vegetable oil or animal fats and combined with an alcohol, usually methanol
- bioethanol:** ethanol produced from plants, such as sugarcane, and used as an alternative to petrol
- biogas:** fuel produced from the fermentation of organic matter
- bomb calorimeter:** apparatus used to measure the heat of combustion of a substance
- burette:** a graduated glass tube for delivering known volumes of a liquid, especially in titrations
- button cells:** small, long-life cells used in devices such as calculators, hearing aids, pacemakers, cameras and watches
- calibration:** the process of finding a relationship between two unknown quantities
- calorimeter:** apparatus used to measure heat changes during a chemical reaction or change of state
- calorimetry:** method used to determine the changes in energy of a system by measuring heat exchanges with the surroundings
- carbohydrates:** general name for a class of carbon compounds that include sugars, starch and cellulose. Carbohydrates contain the elements carbon, hydrogen and oxygen.
- carboxyl group:** the —COOH functional group, which has weakly acidic properties
- carboxylic acids:** hydrocarbons containing the —COOH functional group
- catalyst:** a substance that alters the rate of a reaction without a change in its own concentration
- catenate:** to link atoms of the same element into longer chains
- cathode:** the electrode at which reduction occurs. In a galvanic cell, it is the positive electrode, since the negative electrons are drawn towards it and then consumed by the oxidising agent, which is present in the electrolyte.

- cell potential difference:** the difference between the reduction potentials of two half-cells
- cellulose:** the most common carbohydrate and a condensation polymer of D-glucose. Humans cannot hydrolyse cellulose, so it is not a source of energy.
- chain isomers:** a type of structural isomer that involves more branching
- change in enthalpy:** the amount of energy released or absorbed in a chemical reaction
- chemical thermodynamics:** the branch of chemistry concerned with the quantities of heat evolved or absorbed during chemical reactions
- chiral centre:** an asymmetric carbon atom
- chiral:** describes compounds containing an asymmetric carbon atom or chiral centre. The molecule cannot be superimposed upon its mirror image.
- chromatogram:** a chart that results from analysis by chromatography
- cis-trans isomers:** types of stereoisomers that are formed when the same two different groups are bonded to each of the carbon atoms in a carbon-carbon double bond. A *cis* isomer has identical groups on the same side of the double bond; a *trans* isomer has the groups on opposite sides.
- coenzymes:** organic non-protein molecules required to temporarily and loosely bind with the protein molecule to form an active enzyme
- concentration fraction:** essentially, the concentrations of the products divided by the concentrations of the reactants, including the coefficients of each component in the reaction
- concordant:** describes titres that are within a defined volume of each other, such as 0.10 mL
- condensation polymerisation:** step-growth polymerisation in which two monomers combine and a smaller molecule is eliminated
- condensation reactions:** reactions in which molecules react and link together by covalent bonding with the elimination of a small molecule, such as water or hydrogen chloride, from the bond that is formed
- conjugate redox pair:** two species that differ only by a certain number of electrons
- control:** a standard of comparison for checking or verifying the results of an experiment
- controlled variables:** the experimental element that is constant and unchanged throughout the course of an investigation
- COOH:** the carboxyl functional group
- covalent bonds:** bonds involving the sharing of electron pairs between atoms
- cracking:** the process of breaking down complex chemical compounds by heating them
- cyclohexane:** a pungent saturated cyclic hydrocarbon C_6H_{12} found in petroleum
- denaturation:** change in the structure or function of a large molecule, such as a protein
- denaturing:** loss of structure or function of a protein at extreme temperature or pH
- dependent variables:** variables whose variation does depend on that of another
- desorption:** the removal of a substance from or through a surface; the opposite of adsorption
- diastereomers:** a type of stereoisomer.
Diastereomerism occurs when two or more stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent (related) stereocentres and are not mirror images of each other.
- dipolar ion:** an ion containing equal positive and negative charges
- direct methanol fuel cell:** a new technology that is powered by pure methanol
- disaccharides:** two sugar molecules (monosaccharides) bonded together
- dry cell (Leclanché cell):** an electrochemical cell in which the electrolyte is a paste, rather than a liquid
- efficiency:** (of energy conversion) the ratio between useful energy output and the energy input
- electrical potential:** the ability of a galvanic cell to produce an electric current
- electrochemical cell:** cell that generates electrical energy from chemical reactions
- electrochemical series:** a series of chemical elements arranged in order of their standard electrode potentials
- electrodes:** a solid used to conduct electricity in a galvanic half-cell
- electrolysis:** the decomposition of a chemical substance (in solution or the molten state) by the application of electrical energy
- electrolytes:** liquids that can conduct electricity
- electrolytic cell:** an electric cell in which a non-spontaneous redox reaction is made to occur by the application of an external potential difference across the electrodes
- electroplating:** adding a thin metal coating by electrolysis
- eluent:** a substance used as a solvent in separating materials
- enantiomers:** chiral molecules that are non-superimposable mirror images of one another
- end point:** the experimentally determined equivalence point at which the indicator just changes colour or the pH curve becomes vertical
- endothermic:** describes a chemical reaction in which energy is absorbed from the surroundings
- enhanced greenhouse effect:** the increasing concentrations of greenhouse gases
- enthalpy:** a thermodynamic quantity equivalent to the total heat content of a system
- enzymes:** proteins that catalyse chemical reactions

equilibrium constant: the value of the concentration fraction at equilibrium; also called the equilibrium constant, K_c

equilibrium law: the relationship between the concentrations of the products and the reactants, taking into account their stoichiometric values

equilibrium reaction: a reaction where a chemical equilibrium is reached. This is the state in which both reactants and products are present in concentrations that have no further tendency to change with time.

equivalence point: where two reactants have reacted in their correct mole proportions in a titration

essential amino acids: amino acids that cannot be synthesised by animals from materials in their diets and therefore must be supplied directly in the diet

ester: an organic compound formed from a condensation reaction between an alcohol and a carboxylic acid

exothermic: describes a chemical reaction in which energy is released to the surroundings

external circuit: circuit composed of all the connected components within an electrolytic or a galvanic cell to achieve desired conditions

extrapolation: estimation of values of data outside the known data range

Faraday constant: a constant that represents the amount of electric charge carried by 1 mole of electrons

Faraday's first law of electrolysis: The amount of current passed through an electrode is directly proportional to the amount of material released from it.

Faraday's second law of electrolysis: When the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

fatty acids: a long-chain carboxylic acid

fingerprint region: the lower end of the infrared spectrum

flashpoint: the temperature at which a particular organic compound gives off sufficient vapour to ignite in air

fossil fuel: fuel formed from once-living organisms

fuel cell: an electrochemical cell that produces electrical energy directly from a fuel

fuel: a substance that burns in air or oxygen to release useful energy

functional group: a group of atoms attached to or part of a hydrocarbon chain that influence the physical and chemical properties of the molecule

functional isomerism: isomers containing different functional groups

general gas equation: $PV = nRT$, where pressure is in kilopascals, volume is in litres and temperature is in Kelvin

global warming: a gradual increase in the overall temperature of the Earth's atmosphere

glycaemic index: a figure representing the relative ability of a carbohydrate food to increase the level of glucose in the blood

glycogen: the storage form of glucose in animals. It has a similar structure to amylopectin but is even more highly branched.

glycosidic link: a particular type of ether bond

greenhouse effect: a natural process that warms the Earth's surface. When the sun's energy reaches the Earth's atmosphere, some of it is reflected back to space and the rest is absorbed and re-radiated by greenhouse gases.

greenhouse gases: gases that contribute to the greenhouse effect by absorbing infrared radiation

haemoglobin: the oxygen-carrying pigment and predominant protein in red blood cells

half-cell: one half of a galvanic cell containing an electrode immersed in an electrolyte that may be the oxidising agent or the reducing agent depending on the oxidising strength of the other cell to which it is connected

Hall-Héroult: the method of aluminium production used in primary aluminium smelters throughout the world

heat content: a thermodynamic quantity equivalent to the total heat content of a system

heat of reaction: the heat evolved or absorbed during a chemical reaction taking place under conditions of constant temperature and of either constant volume or, more often, constant pressure

homologous series: a series of organic compounds that have the same structure but in which the formula of each molecule differs from the next by a CH_2 group

HPLC: high-performance liquid chromatography; method used to separate the components of a mixture

hydrocarbons: compounds containing only carbon and hydrogen atoms

hydrogenation: the addition of hydrogen to unsaturated compounds, such as fatty acids

hydrolysis: the chemical breakdown of a compound due to reaction with water

hydroxyl group: the $-\text{OH}$ functional group

independent variables: variables whose variation does not depend on that of another

indicator: a chemical compound that changes color and structure when exposed to certain conditions and is therefore useful for chemical tests

induced fit model: model of enzyme action where, in the presence of a substrate, the active site may change in order to fit the substrate's shape

infrared: describes spectroscopy that deals with the infrared region of the electromagnetic spectrum

internal circuit: a circuit within a conductor.

Anions flow to the anode and cations flow to the cathode.

interpolation: estimation of values of data between two known values

iodine number: number used to measure the degree of unsaturation in triglycerides

Kelvin: the SI base unit of thermodynamic temperature, equal in magnitude to the degree Celsius

kinetic molecular theory of gases: Gas particles are in continuous, random motion. Collisions between gas particles are completely elastic.

Law of Conservation of Energy: Energy cannot be created or destroyed but only changed from one form into another or transferred from one object to another.

Le Châtelier's principle: When a change is made to an equilibrium system, the system moves to counteract the imposed change and restore the system to equilibrium.

lead-acid accumulator: a battery with lead electrodes using dilute sulfuric acid as the electrolyte; each cell generates about 2 volts

lipids: substances such as a fat, oil or wax that dissolve in alcohol but not in water

lithium cells: cells that use lithium anodes and can produce a high voltage

lithium ion cell: a battery where lithium ions move from the negative electrode to the positive electrode during discharge and back when charging

lock-and-key model: model of enzyme action where only molecules with complementary shapes can react with the enzyme

mass spectrometry: the investigation and measurement of the masses of isotopes, molecules and molecular fragments by ionising them and determining their trajectories in electric and magnetic fields

membrane cell: cell used for the electrolysis of brine

metabolism: the chemical processes that occur within a living organism in order to maintain life

minerals: inorganic substances required in various amounts for normal bodily functions

mobile phase: the liquid or gas that flows through a chromatography system, moving the materials to be separated at different rates over the stationary phase

molar gas volume: the volume occupied by a mole of a substance at a given temperature and pressure. At STC, 1 mole of gas occupies 24.8 litres.

monomer: a molecule that links with other monomers to form a polymer

monosaccharides: the simplest form of carbohydrate, consisting of one sugar molecule

mono-unsaturated fatty acids: fatty acids containing only one double carbon-carbon bond

natural gas: a source of alkanes (mainly methane) of low molecular mass

negative ΔH : A negative change in enthalpy indicates an exothermic reaction.

non-renewable energy sources: energy sources that are being used up faster than they can be produced

—OH: the hydroxyl functional group

oligosaccharides: three to ten monosaccharides bonded together

organic chemistry: the study of carbon-containing compounds and their properties

oxidation numbers: numbers used to find an oxidising agent and a reducing agent by a change in perceived valency

oxidation: an increase in the oxidation number; a loss of electrons

oxidising agents (oxidants): electron acceptors

pascal (Pa): unit of pressure

peptide linkage: linkage formed when a carboxyl group reacts with an amino group in a polymerisation reaction

petroleum: viscous, oily liquid composed of crude oil and natural gas that was formed by geological processes acting on marine organisms over millions of years; a mixture of hydrocarbons used to manufacture other fuels and many other chemicals

pipette: a slender tube for transferring or measuring small quantities of liquid

polymerisation: a process of reacting monomer molecules together in a chemical reaction to form polymer chains

polymers: giant molecules formed by repeated monomers that have been joined by covalent bonds

polypeptides: many amino acid residues bonded together

polysaccharides: more than 10 monosaccharides bonded together

polyunsaturated fatty acids: fatty acids containing more than one double carbon-carbon bond

positional isomers: isomers where the position of the functional group differentiates the compounds

positive ΔH : A positive change in enthalpy indicates an endothermic reaction.

pressure: the force per unit area that one region of a gas, liquid or solid exerts on another

primary alcohols: an alcohol in which the carbon atom that carries the —OH group is attached to only one alkyl group

primary cells: an electrolytic cell in which the cell reaction is not reversible

primary standard: a substance used in volumetric analysis that is of such high purity and stability that it can be used to prepare a solution of accurately known concentration

- primary structure:** the order of amino acids in a protein molecule
- proteins:** large molecules composed of one or more long chains of amino acids
- proton exchange membrane fuel cell (PEMFC):** a fuel cell being developed for transport applications as well as for stationary fuel cell applications and portable fuel cell applications
- qualitative analysis:** an investigation used to identify the presence or absence of elements, ions or molecules in a sample
- quantitative analysis:** an investigation used to determine the amount of a given element or compound in a known weight or volume of material
- quaternary structure:** structure formed when individual protein molecules link together in a particular spatial arrangement
- reaction quotient:** essentially, the concentrations of the products divided by the concentrations of the reactants, including the coefficients of each component in the reaction
- rechargeable:** describes a battery that is an energy storage device; it can be charged again after being discharged by applying DC current to its terminals
- recharging:** forcing electrons to travel in the reverse direction and, because the discharge products are still in contact with the electrodes, the original reactions are reversed
- redox reactions:** reactions that involve the transfer of one or more electrons between chemical species
- reducing agents (reductants):** electron donors
- reduction potential:** a measure of the tendency of an oxidising agent to accept electrons and so undergo reduction
- reduction:** a decrease in the oxidation number; a gain of electrons
- renewable energy sources:** energy sources that can be produced faster than they are used
- retention time:** the time taken for each component of a sample to travel from the injection port to the end of the column
- salt bridge:** a component that provides a supply of mobile ions that balance the charges built up in the half-cells of a galvanic cell during reaction
- sample:** a substance to be analysed
- saturated fatty acids:** fatty acids containing only single carbon-carbon bonds
- saturated hydrocarbons:** hydrocarbons containing only single carbon-carbon bonds
- secondary alcohols:** an alcohol in which the carbon atom that carries the —OH group attached is joined directly to two alkyl groups, which may be the same or different
- secondary cells:** electrolytic cells in which the cell reaction is reversible
- secondary fuel:** a fuel that is produced from another energy source
- secondary structure:** structure formed from hydrogen bonding between carboxyl and amino groups in a protein molecule
- spectroscopy:** the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic radiation
- standard cell potential difference:** the measured cell potential difference, under standard conditions, when the concentration of each species in solution is 1 M, the pressure of a gas, where applicable, is 1 atm, and the temperature is 25 °C (298 K).
- standard hydrogen half-cell:** used as a standard reference electrode
- standard laboratory conditions (SLC):** 100 kPa and 25 °C
- standard solution:** a solution that has a precisely known concentration
- standard temperature and pressure (STP):** 1 atm and 0 °C
- starch:** a condensation polymer of α -D-glucose that is made up of two polymers: amylose and amylopectin
- stationary phase:** a solid with a high surface area, or a finely divided solid coated with liquid. It shows different affinities for various components of a sample mixture when separating them by chromatography.
- stereoisomers:** two or more compounds differing only in the spatial arrangements of their atoms
- structural isomers:** molecules that have the same molecular formula but different structural formulas
- substitution reactions:** reactions in which one or more atoms of a molecule are replaced by different atoms
- substrate:** the substance on which an enzyme acts
- sustainable energy:** energy that meets present needs without compromising the ability of future generations to meet their own needs
- tertiary structure:** structure formed from side-group interaction, including hydrogen bonding, ionic bonding, dipole-dipole interactions and disulfide bridges, in a protein molecule
- thermochemical equation:** a balanced stoichiometric chemical equation that includes the enthalpy change
- thermochemistry:** the branch of chemistry concerned with the quantities of heat evolved or absorbed during chemical reactions
- titrant:** a solution of known concentration
- titration curve:** curve used to measure the volume of a titrant against pH
- titration:** process used to determine the concentration of a substance by using a pipette to deliver one substance and a burette to deliver another

- substance until they have reacted exactly in their mole ratios
- titre:** the volume delivered by a burette
- transesterification:** the reaction between an ester of one alcohol and a second alcohol to form an ester of the second alcohol and an alcohol from the original ester
- universal gas constant:** a physical constant used in many thermochemical equations and relationships, denoted by R , where $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
- universal gas equation:** $PV = nRT$, where pressure is in kilopascals, volume is in litres and temperature is in Kelvin
- unsaturated hydrocarbons:** hydrocarbons containing at least one double carbon-carbon bond
- variable:** an element, feature or factor that is liable to vary or change
- viscosity:** a measure of a fluid's resistance to flow
- vitamins:** organic compounds that are needed in minute quantities on a regular basis as part of a healthy diet
- volumetric analysis:** determination of the concentration, by volume, of a substance in a solution, such as by titration
- yield:** amount of product
- zinc-air cell:** cell that uses oxygen from the air as a reactant
- zwitterion ion:** a dipolar ion containing equal positive and negative charges

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Periodic table of the elements

Periodic Table of Elements									
Alkali metals		Alkaline earth metals							
↓		↓							
Group 1		Group 2							
Period 2	3 Lithium Li 6.9	4 Beryllium Be 9.0							
	11 Sodium Na 23.0	12 Magnesium Mg 24.3							
Period 3			Transition metals						
			Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9
Period 4									
	19 Potassium K 39.1	20 Calcium Ca 40.1	21 Scandium Sc 45.0	22 Titanium Ti 47.9	23 Vanadium V 50.9	24 Chromium Cr 52.0	25 Manganese Mn 54.9	26 Iron Fe 55.8	27 Cobalt Co 58.9
Period 5									
	37 Rubidium Rb 85.5	38 Strontium Sr 87.6	39 Yttrium Y 88.9	40 Zirconium Zr 91.2	41 Niobium Nb 92.9	42 Molybdenum Mo 96.0	43 Technetium Tc (98)	44 Ruthenium Ru 101.1	45 Rhodium Rh 102.9
Period 6									
	55 Caesium Cs 132.9	56 Barium Ba 137.3	57–71 Lanthanoids	72 Hafnium Hf 178.5	73 Tantalum Ta 180.9	74 Tungsten W 183.8	75 Rhenium Re 186.2	76 Osmium Os 190.2	77 Iridium Ir 192.2
Period 7									
	87 Francium Fr (223)	88 Radium Ra (226)	89–103 Actinoids	104 Rutherfordium Rf (261)	105 Dubnium Db (262)	106 Seaborgium Sg (266)	107 Bohrium Bh (264)	108 Hassium Hs (267)	109 Meitnerium Mt (268)

Lanthanoids

57 Lanthanum La 138.9	58 Cerium Ce 140.1	59 Praseodymium Pr 140.9	60 Neodymium Nd 144.2	61 Promethium Pm (145)	62 Samarium Sm 150.4	63 Europium Eu 152.0

Actinoids

89 Actinium Ac (227)	90 Thorium Th 232.0	91 Protactinium Pa 231.0	92 Uranium U 238.0	93 Neptunium Np (237)	94 Plutonium Pu (244)	95 Americium Am (243)

The period number refers to the number of the outermost shell containing electrons.

			Non-metals				Halogens	Noble gases
			Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
			5 Boron B 10.8	6 Carbon C 12.0	7 Nitrogen N 14.0	8 Oxygen O 16.0	9 Fluorine F 19.0	10 Neon Ne 20.2
Group 10	Group 11	Group 12	13 Aluminium Al 27.0	14 Silicon Si 28.1	15 Phosphorus P 31.0	16 Sulfur S 32.1	17 Chlorine Cl 35.5	18 Argon Ar 39.9
28 Nickel Ni 58.7	29 Copper Cu 63.5	30 Zinc Zn 65.4	31 Gallium Ga 69.7	32 Germanium Ge 72.6	33 Arsenic As 74.9	34 Selenium Se 79.0	35 Bromine Br 79.9	36 Krypton Kr 83.8
46 Palladium Pd 106.4	47 Silver Ag 107.9	48 Cadmium Cd 112.4	49 Indium In 114.8	50 Tin Sn 118.7	51 Antimony Sb 121.8	52 Tellurium Te 127.6	53 Iodine I 126.9	54 Xenon Xe 131.3
78 Platinum Pt 195.1	79 Gold Au 197.0	80 Mercury Hg 200.6	81 Thallium Tl 204.4	82 Lead Pb 207.2	83 Bismuth Bi 209.0	84 Polonium Po (210)	85 Astatine At (210)	86 Radon Rn (222)
110 Darmstadtium Ds (271)	111 Roentgenium Rg (272)	112 Copernicium Cn (285)		114 Flerovium Fl (289)	Metals ←	116 Livermorium Lv (292)	The elements in the purple cells adjacent to the bold black border are neither metals nor non-metals. They are called metalloids.	

64 Gadolinium Gd 157.3	65 Terbium Tb 158.9	66 Dysprosium Dy 162.5	67 Holmium Ho 164.9	68 Erbium Er 167.3	69 Thulium Tm 168.9	70 Ytterbium Yb 173.1	71 Lutetium Lu 175.0

96 Curium Cm (247)	97 Berkelium Bk (247)	98 Californium Cf (251)	99 Einsteinium Es (252)	100 Fermium Fm (257)	101 Mendelevium Md (258)	102 Nobelium No (259)	103 Lawrencium Lr (262)

