Chapter 2 Carbon-based fuels

2.1 Exothermic and endothermic reactions

KEY QUESTIONS

Knowledge and understanding

1 C. C is correct as the equation is balanced and it shows a negative ΔH value. All combustion reactions are exothermic, so have a negative ΔH value. D is incorrect as ΔH is positive; B shows an unbalanced equation, and A does not have an ΔH value.

2 In an exothermic reaction, the chemical potential of the **products** is lower than that of the **reactants**. Energy is **released to** the surroundings. The sign of ΔH will be **negative**.

3 A value of ΔH is negative for exothermic reactions where the enthalpy of the products is less than that of the reactants. This means the reaction releases energy.

4 Activation energy is the energy required to break the bonds of reactants. As both endothermic and exothermic reactions have reactants, both require activation energy.

5 **a** 0.0258 kJ
  b 2.63×10^4 kJ
  c 6.6×10^6 kJ

Analysis

6 **a** There are ionic bonds in ammonium chloride between the ammonium and chloride ions. These are strong bonds that need to be broken for the reaction to occur.
  b The reaction is endothermic so it will absorb energy from the surroundings.
  c The temperature of the surroundings will decrease as the reaction proceeds.

7 **a** endothermic
  b The total enthalpy of the product (HI) is greater than that of the reactants (hydrogen gas and iodine gas).
  c The activation energy is greater than the ΔH value.

2.2 Types of fuels

KEY QUESTIONS

Knowledge and understanding

1 A fuel is a substance with stored chemical potential energy that can be released relatively easily. When natural gas burns in air it combines with oxygen to form carbon dioxide and water, releasing relatively high amounts of energy.

2 A non-renewable fuel cannot be replenished at the rate at which it is consumed. Renewable fuels are those that can be replenished at the rate at which they are consumed.

3 **a** biogas
  b The biogas is usually burned in a generator on-site to produce electrical energy.

4 **a** biodiesel
  b Biodiesel is likely to be used in a diesel engine in a vehicle.

Analysis

5 Biodiesel has been made from plants. When the plants grow, they absorb CO_2, compensating for the CO_2 produced during combustion.

6 The infrastructure to produce biogas is expensive. A farm or industry would need to be a big operation to justify the cost. The waste used is not suitable for transport to a central energy hub, therefore it is not easy for producers to share the cost.

7 Australia’s crops such as canola are used to produce food products. Widespread use of biodiesel might lead to food shortages. There is also an impact on the limited amount of fertile farming land if crop production is increased.

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2.3 Fuel sources for the body

CASE STUDY: ANALYSIS

Lavoisier and combustion

1 In respiration, glucose reacts with oxygen to form carbon dioxide and water. If glucose is burned in a flame, the reaction will be exactly the same. The equation for the reaction is:

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

2 Energy is required to melt ice. The more energy produced by the subject of the experiment, the greater the quantity of ice that will melt.

3 If a reaction was using up oxygen in a closed container, the guinea pig would struggle to breathe and appear lethargic (or die). If a reaction produced oxygen, the guinea pig would breathe and move easily.

4 Lavoisier would need to try and control the temperature of the room and minimise all heat losses from the subject and from the equipment. He would endeavour to monitor the mass of water consumed by the subject and the mass change of the air the subject breathed in and the air the subject breathed out. Perspiration, urine output and faeces output would also impact on the mass of the subject.

KEY QUESTIONS

Knowledge and understanding

1 carbon dioxide, water and sunlight

2 **a** Glucose is the molecule that can be formed in plants through photosynthesis storing energy from the Sun.
  b Glucose can be polymerised in plants to starch or to cellulose, both very important molecules. Plants can also use glucose to produce energy.
  c Glucose can be polymerised to glycogen in humans for energy storage or burned in muscle cells for energy.

3 In **cellular** respiration, glucose is used by cells to obtain energy. Aerobic respiration is an **exothermic** process in which the glucose is **oxidised** by **oxygen**. A relatively large amount of energy is **released** during aerobic respiration and can be used by the cells of the body.

Analysis

4 **a** respiration: exothermic
  b digestion of fish oil: exothermic
  c formation of cellulose from glucose in plants: endothermic
  d photosynthesis: endothermic
  e digestion of starch: exothermic

5 Carbohydrates will release less energy than fats as they are already ‘partially’ oxidised. During combustion, fuels react and bond with oxygen. As carbohydrates contain a relatively high proportion of oxygen atoms, some of the oxidation has already occurred.

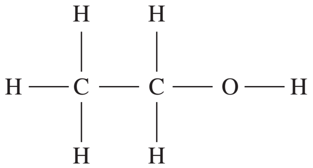
6 Oxidation, in the case of cellular respiration, involves reaction with oxygen.

2.4 Bioethanol

KEY QUESTIONS

Knowledge and understanding

1 **a**



  b Ethanol has an –OH group that can form hydrogen bonds with water, making it highly soluble.
  c $C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

2 **a** disadvantage
  b disadvantage
  c advantage
  d advantage
  e disadvantage
  f advantage

3 Molasses contains many smaller carbohydrates that can be fermented directly to ethanol. Cellulose in forest waste must first be broken down to smaller carbohydrates before fermentation occurs. The smaller carbohydrates in molasses are soluble in water, making it easier to have enzymes react with them.

4 Fermentation is a biochemical process, involving microorganisms (enzymes). If temperatures are too high, the microorganisms are destroyed and the reaction stops.

Analysis

5 An increase in the use of bioethanol-sourced E10 is likely to lower total CO_2 emissions. CO_2 emissions from the vehicle will increase with E10 use, but this impact is offset by the absorption of CO_2 during the growth of the plants used to make the bioethanol.

6 Bioethanol and biodiesel are used in vehicles. They have to be transported to where the vehicles are. Biogas is burnt in small-scale generators that can be placed easily at the site of the gas production.

7 Bioethanol is produced as an aqueous solution. It needs to be separated from the water in the solution. Biodiesel or biogas are not produced as aqueous solutions.

2.5 Energy from the combustion of fuels

Worked example: Try yourself 2.5.1

WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

Write the equation, including state symbols, for the complete combustion of hexane (C_6H_{14}).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$C_6H_{14} + O_2 \rightarrow CO_2 + H_2O$
Balance carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$C_6H_{14} + O_2 \rightarrow 6CO_2 + 7H_2O$
Find the total number of oxygen atoms on the product side.	Total O $= (6 \times 2) + 7$ $= 19$
If this is an odd number, multiply all the coefficients in the equation by 2, except for the coefficient of oxygen.	$2C_6H_{14} + O_2 \rightarrow 12CO_2 + 14H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O$
Add state symbols.	$2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(l)$

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Worked example: Try yourself 2.5.2

WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

Write the equation, including state symbols, for the complete combustion of liquid methanol (CH_3OH).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$CH_3OH + O_2 \rightarrow CO_2 + H_2O$
Balance carbon and hydrogen atoms, based on the formula of the alcohol.	$CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$
Find the total number of oxygen atoms on the product side. Then subtract the one oxygen atom in the alcohol molecule from the total number of oxygen atoms on the product side.	Total O on product side $= (1 \times 2) + (2 \times 1)$ $= 4$ Total O on product side – 1 in alcohol $= 4 - 1 = 3$
If this is an odd number, multiply all of the coefficients in the equation by 2, except for the coefficient of oxygen.	$2CH_3OH + O_2 \rightarrow 2CO_2 + 4H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$
Add state symbols.	$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

Worked example: Try yourself 2.5.3

WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

Write an equation, including state symbols, for the incomplete combustion of liquid methanol (CH_3OH). The only carbon product is carbon monoxide.

Thinking	Working
Add oxygen as a reactant and carbon monoxide and water as the products.	$CH_3OH + O_2 \rightarrow CO + H_2O$
Balance the carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$CH_3OH + O_2 \rightarrow CO + 2H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$CH_3OH + O_2 \rightarrow CO + 2H_2O$
If oxygen gas has a coefficient that is half of a whole number, multiply all of the coefficients in the equation by 2.	$CH_3OH + O_2 \rightarrow CO + 2H_2O$
Add state symbols.	$CH_3OH(l) + O_2(g) \rightarrow CO(g) + 2H_2O(l)$

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Worked example: Try yourself 2.5.4

CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the amount of energy released when 5.40 kg of propanol (C_3H_8O) is burnt in an unlimited supply of oxygen. The molar heat of combustion of propanol is 2020 kJ mol^{-1}.

Thinking	Working
Calculate the number of moles of the compound using: $n = \frac{m \text{ (in grams)}}{M}$	$n(C_3H_8) = \frac{m}{M}$ $= \frac{5.40 \times 10^3}{60.0}$ $= 90.0$ mol
Multiply the number of moles by the heat of combustion per mole.	Energy $= n \times \Delta H_c$ $= 90.0 \times 2020$ $= 1.82 \times 10^5$ kJ

Worked example 2.5.5

CALCULATING ΔH FOR ONE EQUATION USING ANOTHER EQUATION

Carbon reacts with hydrogen according to the equation:

$$6C(s) + 3H_2(g) \rightarrow C_6H_6(g) \quad \Delta H = +49 \text{ kJ}$$

Calculate ΔH for the reaction represented by the equation:

$$3C_6H_6(g) \rightarrow 18C(s) + 9H_2(g)$$

Thinking	Working
The reaction has been reversed in the second equation, so the sign for ΔH is changed to the opposite sign.	ΔH for the second equation is negative.
Identify how the coefficients in the equation have changed.	The coefficient for C_6H_6 has tripled, as has carbon and hydrogen. All amounts have been tripled.
Identify how the magnitude of ΔH will have changed for the second equation.	ΔH will need to be tripled.
Calculate the new magnitude of ΔH. (You will write the sign of ΔH in the next step.)	$3 \times 49 = 147$ kJ
Write ΔH for the second equation, including the sign.	$\Delta H = -147$ kJ

CASE STUDY: ANALYSIS

Explosives—a blast of chemical energy

1 Exothermic. The reaction releases large amounts of energy in forms of heat, light and sound.

2 29 mol products : 4 mol reactants. An explosion occurs when liquid or solid reactants turn rapidly to a gas. With the number of moles of gaseous products being much higher than the number of moles of reactants, the change in volume is likely to be even more rapid.

3 According to the thermochemical equation for the decomposition of nitroglycerine, 4 mol of nitroglycerine reacting releases 1456 kJ energy.

$$\text{Energy released by 8 mol} = \frac{8}{4} \times 1456$$
$$= 2912 \text{ kJ}$$

4 Activation energy is always required to break bonds in the reactants so a reaction can proceed. The trigger will provide activation energy.

KEY QUESTIONS

Knowledge and understanding

1 $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

(The equation coefficients can also be shown as being double the values above to make them all whole numbers.)

2 $C_2H_5OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(l)$

3 $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l) \quad \Delta H = -3509$ kJ

4 Heat of combustion of propan-1-ol per gram $= \frac{\text{heat of combustion of propan-l-ol per mole}}{\text{molar mass}} = \frac{2021}{60} = 33.7$ kJ g^{-1}.

5 **a** energy = 250 × 55.6 = 1.39×10^4 kJ

b energy = $(9.64 \times 10^3) \times 50.5 = 4.87 \times 10^5$ kJ

c energy = $(403 \times 10^3) \times 29.6 = 1.19 \times 10^7$ kJ

6 The heat of combustion of a fuel can be defined as the heat energy released when a specified amount (e.g. 1 g, 1 L, 1 mol) of a substance burns completely in oxygen.

Analysis

7 **a** complete combustion

b Complete combustion takes the oxidation of the fuel to its limit. Incomplete combustion is only partial combustion.

8 **a** Photosynthesis is an endothermic process as sunlight is required for energy and the enthalpy of reaction is a positive value.

b The energy change is half of the original as the reaction has been halved. 1402 kJ of energy is released, so ΔH will be –1402 kJ. ΔH needs to be negative as the equation has been reversed.

9 The energy released to form steam will be less than the energy released to form water. The thermochemical equation for the reaction in which liquid water turns into steam is:

$H_2O(l) \rightarrow H_2O(g) \quad \Delta H = +40.7$ kJ

So the combustion of octane to form carbon dioxide and steam will release 9 × 40.7 = 366.3 kJ less energy than the combustion of octane to form carbon dioxide and liquid water:

$C_8H_{18}(g) + 12\frac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g); \Delta H = -5083.7$ kJ

Chapter 2 Review

REVIEW QUESTIONS

Knowledge and understanding

1 B. Biodiesel is blended in with petrodiesel and is used as a fuel for diesel engines in trucks and other transport. The other options are more likely to be used for electricity generation or providing heat for cooking.

2 C. Animal manure is a renewable resource whereas the other options are all fossil fuels.

3 D. Ethanol has a lower energy density than petrol, so E10 will also have a lower energy density. E10 still produces $CO_2(g)$ when it burns and there are limits to the volume that can be produced.

4 C. All reactions involve breaking the bonds in the reactants. This is the activation energy. Options A and B only apply some of the time, depending upon whether it is exothermic or endothermic. D is incorrect as the highest point of the energy profile diagram is not relevant.

5 **a** ice melting to water: endothermic

b candle burning: exothermic

c reaction that causes the surroundings to drop in temperature: endothermic

d reaction with a negative value of ΔH: exothermic

6 The formation of fossil fuels is a process that occurs over millions of years. The organic matter produced by plants and animals undergoes complex changes as it is subjected to heat and pressure under tonnes of mud and sand. Once the current reserves of fossil fuels have been used, they will not be replaced in the foreseeable future.

7 **a** Heat of combustion of ethanol = 1360 kJ mol^{-1}

$0.74 \times 1360 = 1.01 \times 10^3$ kJ of energy is released when 0.74 mol of ethanol is burnt.

b Heat of combustion of ethanol = 29.6 kJ g^{-1}

12.6 × 29.6 = 373 kJ of energy is released when 12.6 g of ethanol is burnt.

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8 **a** The combustion of hydrogen is a reaction between hydrogen and oxygen gases. For the reaction to occur the covalent bonds in hydrogen and the covalent bonds in oxygen must be broken.

b The covalent bonds in water are formed.

c The combustion of hydrogen is exothermic, so the energy released when the bonds in water form will be greater than the energy required to break the bonds in hydrogen and oxygen gases.

d The temperature of the surroundings will increase as the reaction is exothermic.

9 **a** $6CO_2(g) + 6H_2O(l) \xrightarrow{\text{sunlight}} C_6H_{12}O_6(aq) + 6O_2(g)$

b glucose

c $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

10 **a** Many possibilities such as sugarcane waste, wheat husks and fruit waste.

b $C_6H_{12}O_6(aq) \rightarrow 2C_2H_6O(aq) + 2CO_2(g)$

c The distillation column is used to purify the ethanol solution, separating the water and ethanol.

11 $C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -1360 \text{ kJ}$

12 **a** methane and carbon dioxide

b The composition of biogas depends on the original material from which it is sourced and the method of decomposition.

13 **a** True

b False. The activation energy of the endothermic process is always higher than that of the reverse exothermic process.

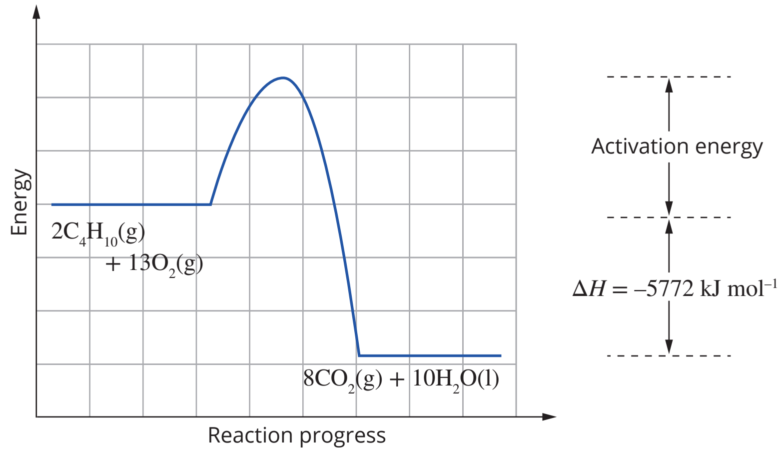
c False. It varies whether the activation energy is high or not, depending upon the bonds that need to be broken.

d False. This statement is too general. While there may be some fuels that have low activation energies, such fuels would be quite dangerous to store. The majority of fuels do not have low activation energies.

14 Reversing a chemical reaction involves the same bonds as the forward reaction, but the bonds that were formed are now broken and the bonds that were broken are reformed. The overall energy change has the same magnitude for both processes.

15 **a** For this exothermic reaction, the overall energy of the bonds in the products will be less than the overall energy of the bonds in the reactants.

b



16 **a** $C_3H_7OH(l) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ or $2C_3H_7OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)$

b $C_5H_{12}(l) + \frac{11}{2}O_2(g) \rightarrow 5CO(g) + 6H_2O(l)$ or $2C_5H_{12}(l) + 11O_2(g) \rightarrow 10CO(g) + 12H_2O(l)$

Application and analysis

17 The formula of the biodiesel will be $C_{15}H_{31}COOCH_3$, or $C_{17}H_{34}O_2$

$$C_{17}H_{34}O_2(l) + \frac{49}{2}O_2(g) \rightarrow 17CO_2(g) + 17H_2O(l)$$

$$\text{Or } 2C_{17}H_{34}O_2(l) + 49O_2(g) \rightarrow 34CO_2(g) + 34H_2O(l)$$

18 **a** exothermic because ΔH is negative

b $\Delta H = 2 \times -2619 = -5238$ kJ

19 $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta H = -572$ kJ or $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286$ kJ

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20 The combustion of biodiesel produces CO_2.
For example:

$$C_{18}H_{36}O_2(l) + 26O_2(g) \rightarrow 18CO_2(g) + 18H_2O(l)$$

However, a similar amount of CO_2 is absorbed by the canola during photosynthesis while the crop grows:

$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{sunlight}} C_6H_{12}O_6(aq) + 6O_2(g)$$

The farming equipment required and the transport of the canola also produce CO_2 emissions, so the use of biodiesel is not completely carbon neutral.

21 Biogas is formed through the action of anaerobic bacteria on organic matter. Anaerobic bacteria operate in the absence of oxygen. Methane is the most abundant component of biogas, followed by carbon dioxide and then a mix of other gases in low percentages.

22

Advantages	Disadvantages
fewer particulate emissions than natural gas	can only be used on site
renewable	raw material needs to be heated in winter
less reliance on fossil fuels	cheese waste previously used as a fertiliser
fewer net CO_2 emissions than natural gas	
lower sulfur content than natural gas	

23 **a** exothermic

b activation energy forward reaction:

$$400 - 300 = 100 \text{ kJ}$$

activation energy back reaction:

$$400 - 100 = 300 \text{ kJ}$$

c 300 – 100 = 200 kJ. It is the reverse of the forward reaction.

24 **a** **i** heat of combustion of octane = 5460 kJ mol^{-1}

$$n(C_8H_{18}) = \frac{1000}{114} = 8.77 \text{ mol}$$

$$8.77 \times 5460 = 4.79 \times 10^4 \text{ kJ}$$

ii heat of combustion of butane = 2880 kJ mol^{-1}

$$n(C_4H_{10}) = \frac{1000}{58} = 17.2 \text{ mol}$$

$$17.2 \times 2880 = 4.95 \times 10^4 \text{ kJ}$$

iii heat of combustion of ethane = 1560 kJ mol^{-1}

$$n(C_2H_6) = \frac{1000}{30} = 33.3 \text{ mol}$$

$$33.3 \times 1560 = 5.19 \times 10^4 \text{ kJ}$$

b The data shows that the heat of combustion in kJ/kg decreases slightly as the alkane molecule gets longer.

25 **a** Because the reaction is exothermic, 1 mol of CO(g) and 0.5 mol of O_2(g) (the reactants) has a higher enthalpy value than 1 mol of CO_2(g) (the products).

b **i** –566 kJ. The equation provided has been doubled. The value of ΔH is also doubled.

ii +566 kJ. The equation provided has been reversed and doubled. The sign of ΔH must be reversed and its value doubled also.

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Chapter 3 Obtaining energy from fuels

3.1 Stoichiometry involving combustion of fuels

Worked example: Try yourself 3.1.1

MASS–MASS STOICHIOMETRIC PROBLEMS

Calculate the mass of carbon dioxide, in kg, produced when 3.60 kg of butane (C_4H_{10}) burns completely in oxygen.

Thinking	Working
Write a balanced equation for the reaction.	$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$
As the quantity of the known substance is a mass, calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_4H_{10}) = \frac{3.60 \times 10^3}{58.0}$ $= 62.1$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(CO_2) = \frac{8}{2} \times 62.1$ $= 248.3$ mol
Calculate the mass of the unknown substance using: $m = n \times M$	$m(CO_2) = 248.3 \times 44.0$ $= 10924$ g $= 10.9$ kg

Worked example: Try yourself 3.1.2

MASS–VOLUME STOICHIOMETRIC CALCULATIONS AT SLC

Calculate the volume of carbon dioxide, in L, produced when 300 g of butane (C_4H_{10}) is burned completely in oxygen. The gas volume is measured at SLC.

Thinking	Working
Write a balanced chemical equation for the reaction.	$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$
As the quantity of the known substance is a mass, calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_4H_{10}) = \frac{300}{58.0}$ $= 5.17$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(CO_2) = \frac{8}{2} \times 5.17$ $= 20.7$ mol
Calculate the volume of the unknown substance using: $V = n \times V_m$	$V(CO_2) = 20.7 \times 24.8$ $= 513$ L

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Worked example: Try yourself 3.1.3

GAS VOLUME–VOLUME CALCULATIONS

Methane gas (CH_4) is burned in a gas stove according to the following equation:

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

If 50 mL of methane is burned in air, calculate the volume of CO_2 gas produced under constant temperature and pressure conditions.

Thinking	**Working**
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(CH_4)} = \frac{1}{1}$
The temperature and pressure are constant, so volume ratios are the same as mole ratios.	$\frac{V(CO_2)}{V(CH_4)} = \frac{1}{1}$
Calculate the volume of the unknown substance using: $V(\text{unknown}) = \text{mole ratio} \times V(\text{known})$	$V(CO_2) = \frac{1}{1} \times 50$ $= 50$ mL

Worked example: Try yourself 3.1.4

USING A THERMOCHEMICAL EQUATION TO CALCULATE ENERGY RELEASED BY THE COMBUSTION OF A FUEL

Calculate the heat energy released, in MJ, when 10.0 kg of ethane undergoes complete combustion.

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l) \qquad \Delta H = -3120 \text{ kJ}$$

Thinking	**Working**
As the quantity of the known substance is a mass, calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_2H_6) = \frac{1.00 \times 10^4}{30.0}$ $= 333$ mol
Using the thermochemical equation, find the relationship between the number of moles of fuel burned and energy released.	x kJ is released by 333 mol 3120 kJ is released by 2 mol
Calculate the energy released by the fuel in kilojoules.	By proportion: $\frac{x}{3120} = \frac{333}{2}$ $x = \frac{333}{2} \times 3120$ $= 520\,000$ kJ
Convert the energy released to MJ. 1 MJ = 10^3 kJ Express the answer to the correct number of significant figures. 10.0 kg of ethane in question has 3 significant figures. Therefore, 3 significant figures are given in the answer.	520 000 kJ = 520 MJ

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Worked example: Try yourself 3.1.5

USING A THERMOCHEMICAL EQUATION TO CALCULATE THE AMOUNT OF FUEL THAT MUST BE BURNED TO PRODUCE A PARTICULAR AMOUNT OF ENERGY

What volume of methane, measured at SLC, burns completely to provide 5.00×10^3 kJ?

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890 \text{ kJ}$$

Thinking	**Working**
Using the thermochemical equation, write a relationship between the number of moles of fuel burned and energy released.	x mol releases 5.00×10^3 kJ 1 mol releases 890 kJ
Calculate the amount of the fuel that must have been burnt to produce the energy.	By proportion: $\frac{x}{1} = \frac{5.00 \times 10^3}{890}$ $x = \frac{5.00 \times 10^3}{890} \times 1$ $= 5.62$ mol
Calculate the volume of the fuel, at SLC.	$V(CH_4) = n \times V_m$ $= 5.62 \times 24.8$ $= 139$ L

Worked example: Try yourself 3.1.6

CALCULATING THE VOLUME OF GREENHOUSE GASES RELEASED

What is the volume of greenhouse gases released when 10.8 L of methane (CH_4) undergoes complete combustion in oxygen? Assume all reactants and products are in the gaseous state, and the temperature and pressure remain constant.

Thinking	**Working**
Write a balanced chemical equation for the reaction.	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$
Identify the volume ratio between methane and greenhouse gases produced (CO_2 and H_2O).	$\frac{V(\text{greenhouse gases})}{V(CH_4)} = \frac{3}{1}$
Calculate the volume of greenhouse gases produced.	$V(\text{greenhouse gases}) = \frac{3}{1} \times V(CH_4)$ $= \frac{3}{1} \times 10.8$ $= 32.4$ L
Establish the final volumes of greenhouse gases released.	$V(CH_4) = 0$ L $V(CO_2 + H_2O) = 32.4$ L

CASE STUDY: ANALYSIS

Bioethanol as a fuel for cars to reduce greenhouse gases

Analysis

1 $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g) \qquad \Delta H = -1360$ kJ

2 **a** $m(C_2H_5OH) = 1.00$ kg

$$= 1.00 \times 10^3 \text{ g}$$

$$n(C_2H_5OH) = \frac{m}{M}$$

$$= \frac{1.00 \times 10^3}{46.0}$$

$$= 21.7 \text{ mol}$$

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$$\frac{n(CO_2)}{n(C_2H_5OH)} = \frac{2}{1}$$

$$n(CO_2) = \frac{2}{1} \times n(C_2H_5OH)$$

$$= \frac{2}{1} \times 21.7$$

$$= 43.5 \text{ mol}$$

$$m(CO_2) = n \times M$$

$$= 43.5 \times 44.0$$

$$= 1913 \text{ g}$$

$$= 1.91 \text{ kg}$$

b $V(CO_2) = n \times V_m$

$$= 43.5 \times 24.8$$

$$= 1078 \text{ L}$$

$$= 1.08 \times 10^3 \text{ L}$$

3 **a** $\text{density} = \frac{m(\text{in g})}{V(\text{in mL})}$

so $m(C_2H_5OH) = d \times V(\text{in mL})$

$$= 0.785 \times 50.0 \times 1000$$

$$= 39\,250 \text{ g}$$

$$= 39.3 \text{ kg}$$

b $n(C_2H_5OH) = \frac{m}{M}$

$$= \frac{39250}{46.0}$$

$$= 853 \text{ mol}$$

Reaction of 1 mol C_2H_5OH generates 1360 kJ.

So, reaction of 853 mol C_2H_5OH generates x kJ.

By proportion:

$$\frac{x}{1360} = \frac{853}{1}$$

$$x = \frac{853}{1} \times 1360$$

$$= 1\,160\,080 \text{ kJ}$$

$$= 1160 \text{ MJ}$$

Energy released = 1.16×10^3 MJ

4 From the equation, 2 moles of CO_2 are released when 1360 kJ of energy is generated.

So x mole of CO_2 is released when 1.00 kJ of energy is generated.

By proportion: $\frac{x}{2} = \frac{1.00}{1360}$

$$x = \frac{1.00}{1360} \times 2$$

$$= 0.001\,471 \text{ mol}$$

$$n(CO_2) = 0.001\,471 \text{ mol}$$

$$m(CO_2) = n \times M$$

$$= 0.001\,471 \times 44.0$$

$$= 0.0647 \text{ g}$$

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KEY QUESTIONS

Knowledge and understanding

1 a $\frac{n(O_2)}{n(CO)} = \frac{1}{2}$

$n(O_2) = \frac{1}{2} \times n(CO)$

$= \frac{1}{2} \times 2$

$= 1$ mol

b $n(O_2) = \frac{1}{2} \times n(CO)$

$= \frac{1}{2} \times 6$

$= 3$ mol

c The reactants and product in the equation are all in the gaseous state. Therefore, the mole ratio is also a volume ratio.

$\frac{V(O_2)}{V(CO)} = \frac{1}{2}$

$V(O_2) = \frac{1}{2} \times V(CO)$

$= \frac{1}{2} \times 1.5$

$= 0.75$ L

2 a The coefficient in front of methane is a 1, so 1.00 mol of methane must undergo combustion to release 890 kJ.

b 1.00 mol of carbon dioxide, 2.00 mol of H_2O (according to their coefficients in the equation).

c CH_4, CO_2 and H_2O are all greenhouse gases.

When 890 kJ of energy is released, 1 mol of CH_4 is consumed.

$m(CH_4) = n \times M$

$= 1 \times 16.0$

$= 16.0$ g

When 890 kJ of energy is released, 1 mol of carbon dioxide is produced.

$m(CO_2) = n \times M$

$= 1 \times 44.0$

$= 44.0$ g

When 890 kJ of energy is released, 2 mol of water are produced.

$m(H_2O) = n \times M$

$= 2 \times 18.0$

$= 36.0$ g

The net mass of greenhouse gases released = mass of CO_2 + mass of H_2O

$= 44.0 + 36.0$

$= 80.0$ g

3 a From the thermochemical equation, 2 mol C_2H_6 releases 3120 kJ of energy.

By proportion: $\frac{x}{3120} = \frac{3.00}{2}$

$x = \frac{3.00}{2} \times 3120$

$= 4.68 \times 10^3$ kJ

$= 4.68$ MJ

b $n(C_2H_6) = \frac{m}{M}$

$= \frac{100}{30.0}$

$= 3.33$ mol

From the thermochemical equation, 2 mol C_2H_6 releases 3120 kJ of energy.

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By proportion: $\frac{x}{3120} = \frac{3.33}{2}$

$$x = \frac{3.33}{2} \times 3120$$
$$= 5.20 \times 10^3 \text{ kJ}$$
$$= 5.20 \text{ MJ}$$

c $n(C_2H_6) = \frac{V}{V_m}$

$$= \frac{10.0}{24.8}$$
$$= 0.403 \text{ mol}$$

From the thermochemical equation, 2 mol C_2H_6 releases 3120 kJ of energy.

By proportion: $\frac{x}{3120} = \frac{0.403}{2}$

$$x = \frac{0.403}{2} \times 3120$$
$$= 0.629 \text{ MJ}$$

Analysis

4 **a** $\frac{n(O_2)}{n(C_8H_{18})} = \frac{25}{2}$

$$n(C_8H_{18}) = \frac{200}{114.0}$$
$$= 1.75 \text{ mol}$$
$$n(O_2) = \frac{25}{2} \times 1.75$$
$$= 21.9 \text{ mol}$$
$$m(O_2) = 21.9 \times 32.0$$
$$= 702 \text{ g}$$

b $\frac{n(CO_2)}{n(C_8H_{18})} = \frac{16}{2}$

$$n(C_8H_{18}) = \frac{200}{114.0}$$
$$= 1.75 \text{ mol}$$
$$n(CO_2) = \frac{16}{2} \times 1.75$$
$$= 14.0 \text{ mol}$$
$$m(CO_2) = 14.0 \times 44.0$$
$$= 618 \text{ g}$$

5 **a** $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$

b $\frac{n(CO_2)}{(C_3H_8)} = \frac{3}{1}$

$$n(C_3H_8) = \frac{8.00}{44.0}$$
$$= 0.182 \text{ mol}$$
$$n(CO_2) \text{ produced} = \frac{3}{1} \times 0.182$$
$$= 0.545 \text{ mol}$$
$$m(CO_2) \text{ produced} = 0.545 \times 44.0$$
$$= 24.0 \text{ g}$$

c $\frac{n(O_2)}{n(C_3H_8)} = \frac{5}{1}$

$$n(C_3H_8) = \frac{8.00}{44.0}$$
$$= 0.182 \text{ mol}$$

$$n(O_2)\text{ consumed} = \frac{5}{1} \times 0.182\text{ mol}$$
$$= 0.909\text{ mol}$$
$$V(O_2)\text{ consumed} = 0.909 \times 24.8$$
$$= 22.5\text{ L}$$

6 $$n(C_8H_{18}) = \frac{250.0}{114.0}$$
$$= 2.193\text{ mol}$$

From the thermochemical equation, 2 mol C_8H_{18} release 10 900 kJ.

By proportion: $$\frac{x}{10\,900} = \frac{2.193}{2}$$
$$x = \frac{2.193}{2} \times 10\,900$$
$$= 11\,951\text{ kJ}$$
$$= 11.95\text{ MJ}$$

Energy released = 11.95 MJ

7 **a** $$n(C_4H_{10}) = \frac{m}{M}$$
$$= \frac{10.0}{58.0}$$
$$= 0.172\text{ mol}$$

From the thermochemical equation, 2 mol C_4H_{10} release 5772 kJ of energy.

By proportion: $$\frac{0.172}{2} = \frac{x}{5772}$$
$$x = \frac{0.172}{2} \times 5772$$
$$= 498\text{ kJ}$$

Energy produced = 498 kJ

b $$n(C_4H_{10}) = \frac{V}{V_m}$$
$$= \frac{0.100}{24.8}$$
$$= 0.004\,03\text{ mol}$$

From the thermochemical equation, 2 mol C_4H_{10} release 5772 kJ of energy.

By proportion: $$\frac{0.004\,03}{2} = \frac{x}{5772}$$
$$x = \frac{0.004\,03}{2} \times 5772$$
$$= 11.6\text{ kJ}$$

Energy released = 11.6 kJ

8 **a** From the thermochemical equations:

1 mol methane releases 890 kJ

2 mol methanol releases 1450 kJ

so 1 mol methanol releases $\frac{1450}{2} = 725$ kJ

The first experiment using 1 mol of methane releases the most energy.

b From the first equation, 1 mol of CO_2 is released when 890 kJ of energy is released.

By proportion: $$\frac{x}{1} = \frac{2000}{890}$$
$$x = \frac{2000}{890} \times 1$$
$$= 2.25\text{ mol}$$

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From the second equation, 2 mol of CO_2 are released when 1450 kJ of energy is released.

By proportion: $\frac{x}{2} = \frac{2000}{1450}$

$$x = \frac{2000}{1450} \times 2$$
$$= 2.759 \text{ mol}$$

The combustion of methanol will release more carbon dioxide to produce the same amount of energy as methane.

3.2 Determination of limiting reactants or reagents

Worked example: Try yourself 3.2.1

IDENTIFYING LIMITING AND EXCESS REACTANTS

8.00 g of butane (C_4H_{10}) is burned completely in 20.0 L of oxygen at SLC. The equation for the reaction is:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$$

a Which reactant is the limiting reactant?

b Calculate the amount, in mol, of the excess reactant that remains unreacted.

Thinking	Working
a Calculate the number of moles of each reactant using $n = \frac{m}{M}$ or $n = \frac{V}{V_m}$ or $n = \frac{pV}{RT}$. The formula chosen will depend on the quantity and conditions provided for each reactant.	$n(C_4H_{10}) = \frac{m}{M}$ $= \frac{8.00}{58.0}$ $= 0.138$ mol $n(O_2) = \frac{V}{V_m}$ $= \frac{20.0}{24.8}$ $= 0.806$ mol
Choose one reactant and use the coefficients of the equation to find the amount of the other reactant needed for the first to completely react.	$n(O_2)$ needed to react $= \frac{13}{2} \times n(C_4H_{10})$ $= \frac{13}{2} \times 0.138$ $= 0.897$ mol
Compare the values for the second reactant of amount required and amount actually present to determine which is the limiting factor.	0.897 mol of O_2 is needed for all of the butane to react. There is 0.806 mol of O_2 present. Therefore the butane will be in excess. O_2 is the limiting reactant.
b Use the mole ratio and amount of limiting reactant to determine the amount of excess reactant involved in the reaction.	$n(O_2)$ that reacted = 0.806 mol $\frac{n(C_4H_{10})}{n(O_2)} = \frac{2}{13}$ $n(C_4H_{10}) = \frac{2}{13} \times 0.806$ $= 0.124$ mol
Determine the amount of excess reactant left over after the limiting reactant has been consumed.	$n(C_4H_{10})$ in excess $= n(C_4H_{10})$ initially $- n(C_4H_{10})$ reacted $= 0.138 - 0.124$ $= 0.014$ mol

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Worked example: Try yourself 3.2.2

STOICHIOMETRY CALCULATIONS INVOLVING LIMITING AND EXCESS REACTANTS

150 g of propanol (C_3H_7OH) burns in 200.0 g of oxygen gas. The equation for the reaction is:

$$2C_3H_7OH(g) + 9O_2(g) \longrightarrow 6CO_2(g) + 8H_2O(g)$$

Calculate the volume, in L, of carbon dioxide formed at 120 kPa and 20°C.

Thinking	Working
Calculate the number of moles of each reactant using $n = \frac{m}{M}$ or $n = \frac{V}{V_m}$ or $n = \frac{pV}{RT}$. The formula chosen will depend on the quantity and conditions provided for each reactant.	$n(C_3H_7OH) = \frac{m}{M}$ $= \frac{150}{60.0}$ $= 2.50$ mol $n(O_2) = \frac{m}{M}$ $= \frac{200.0}{32.0}$ $= 6.25$ mol
Identify the limiting reactant.	$n(C_3H_7OH)$ needed to react $= \frac{2}{9} \times n(O_2)$ $= \frac{2}{9} \times 6.25$ $= 1.39$ mol As there is 2.50 mol C_3H_7OH present, the propanol is in excess. O_2 is the limiting reactant
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known (limiting reactant)}}$	$\frac{n(CO_2)}{n(O_2)} = \frac{6}{9}$
Calculate the number of moles of the unknown substance using: n(unknown) = mole ratio × n(known)	$n(CO_2) = \frac{6}{9} \times 6.25$ $= 4.17$ mol
Calculate the required quantity of the unknown substance using $m = n \times M$, $V = n \times V_m$ or $V = \frac{nRT}{p}$ as appropriate. The choice will depend on the required quantity and provided conditions.	The volume of a gas at non-standard conditions needs to be calculated, so the formula chosen is $V = \frac{nRT}{p}$ $V(CO_2) = \frac{4.17 \times 8.31 \times 293}{120}$ $= 84.5$ L

KEY QUESTIONS

Knowledge and understanding

1 **D** Calculate the number of moles of iron and oxygen.
B Refer to the balanced equation
E Use mole ratios to determine which reactant is limiting.
C Calculate the number of moles of iron oxide that forms.
A Calculate the mass of iron oxide that forms.

2

Propane molecules available	Oxygen molecules available	Carbon dioxide molecules produced	Propane molecules in excess	Oxygen molecules in excess
2	15	6	0	5
300	1200	720	60	0
2.5 mol	10 mol	6 mol	0.5 mol	0 mol

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Explanation. From the balanced equation, 1 mol of propane reacts with 5 mol of oxygen to produce 3 mol of carbon dioxide.

- 2 propane molecules will need 10 oxygen molecules to fully react. There are 15 oxygen molecules. Therefore, oxygen is in excess. The 2 propane molecules will react with 10 oxygen molecules to produce 6 carbon dioxide molecules. All the propane molecules are reacted. There are 15 – 10 = 5 oxygen molecules in excess.
- 300 propane molecules will need 1500 oxygen molecules to fully react. There are only 1200 oxygen molecules. Therefore, propane is in excess. The 1200 oxygen molecules will react with 240 oxygen molecules to produce 720 carbon dioxide molecules. All the oxygen molecules are reacted. There are 300 – 200 = 60 propane molecules in excess.
- 2.5 mol propane will need 12.5 mol of oxygen to fully react. There is 10 mol of oxygen. Therefore, propane is in excess. The 10 mol oxygen will react with 2 mol propane to produce 6 mol carbon dioxide. All oxygen has reacted. There is 2.5 – 2 = 0.5 mol propane in excess.

Analysis

3

$$\begin{aligned} n(F_2) &= \frac{m}{M} \\ &= \frac{42.0}{38.0} \\ &= 1.105 \text{ mol} \\ n(P) &= \frac{m}{M} \\ &= \frac{29.0}{31.0} \\ &= 0.935 \text{ mol} \end{aligned}$$

$$\frac{n(P)}{n(F_2)} = \frac{2}{3}$$

For 1.11 mol F_2, to react completely, it requires $1.105 \times \frac{2}{3}$ = 0.737 mol P. There is 0.935 mol P, so P is in excess. F_2 is the limiting reagent.

$$\frac{n(PF_3)}{n(F_2)} = \frac{2}{3}$$

$$\begin{aligned} n(PF_3) &= n(F_2) \times \frac{2}{3} \\ &= 1.105 \times \frac{2}{3} \\ &= 0.737 \text{ mol} \\ m(PF_3) &= n \times M \\ &= 0.737 \times 88.0 \\ &= 64.8 \text{ g} \end{aligned}$$

4 **a**

$$\begin{aligned} n(C_2H_5OH) &= \frac{m}{M} \\ &= \frac{7.0}{46.0} \\ &= 0.152 \text{ mol} \\ n(O_2) &= \frac{m}{M} \\ &= \frac{30.0}{32.0} \\ &= 0.938 \text{ mol} \end{aligned}$$

For 0.152 mol of ethanol to completely react it will require $\frac{3}{1} \times 0.152$ = 0.456 mol of oxygen. There is 0.928 mol of oxygen present so oxygen is in excess. Ethanol is the limiting reactant.

0.456 mol of O_2 will react.

$$\begin{aligned} n(O_2) \text{ in excess} &= n(O_2) \text{ initially} - n(O_2) \text{ reacted} \\ &= 0.938 - 0.456 \\ &= 0.482 \text{ mol} \\ m(O_2) \text{ in excess} &= n \times M \\ &= 0.482 \times 32.0 \\ &= 15.4 \text{ g} \end{aligned}$$

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b $$\frac{n(CO_2)}{n(C_2H_5OH)} = \frac{2}{1}$$

$$n(CO_2) = \frac{2}{1} \times n(C_2H_5OH)$$

$$= \frac{2}{1} \times 0.152$$

$$= 0.304 \text{ mol}$$

$$m(CO_2) = n \times M$$

$$= 0.304 \times 44.0$$

$$= 13.4 \text{ g}$$

c $$\frac{n(H_2O)}{n(C_2H_5OH)} = \frac{3}{1}$$

$$n(H_2O) = \frac{3}{1} \times n(C_2H_5OH)$$

$$= \frac{3}{1} \times 0.152$$

$$= 0.456 \text{ mol}$$

$$m(H_2O) = n \times M$$

$$= 0.456 \times 18.0$$

$$= 8.21 \text{ g}$$

d Once the reaction is complete the following masses are present:

Products:

$m(CO_2)$ = 13.4 g

$m(H_2O)$ = 8.21 g

Reactants:

$m(C_2H_5OH)$ = 0 g (as was limiting reactant)

$n(O_2)$ in excess = 0.482 mol

$m(O_2)$ in excess = 15.4 g (from part **a**)

Total mass present = 13.4 + 8.21 + 15.4 = 37.0 g

Note: As mass is conserved in a chemical reaction, the total mass after the reaction is the same as the total mass of reactants,

5 $$n(C_2H_5OH) = \frac{m}{M}$$

$$= \frac{23.0}{46.0}$$

$$= 0.500 \text{ mol}$$

$$n(O_2) = \frac{V}{V_m}$$

$$= \frac{10.0}{24.8}$$

$$= 0.403 \text{ mol}$$

$$\frac{n(C_2H_5OH)}{n(O_2)} = \frac{1}{3}$$

For 0.403 mol of oxygen to completely react it will require $\frac{1}{3} \times 0.403$ = 0.134 mol of ethanol. There is 0.500 mol of ethanol present, so ethanol is in excess. Oxygen is the limiting reactant.

$$\frac{n(CO_2)}{n(O_2)} = \frac{2}{3}$$

$$n(CO_2) = \frac{2}{3} \times n(O_2)$$

$$= \frac{2}{3} \times 0.403$$

$$= 0.269 \text{ mol}$$

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$$V(CO_2) = n \times V_m$$
$$= 0.134 \times 24.8$$
$$= 6.67 \text{ L}$$

6 $$n(C_3H_7OH) = \frac{m}{M}$$
$$= \frac{8.50}{60.0}$$
$$= 0.142 \text{ mol}$$
$$n(O_2) = \frac{pV}{RT}$$
$$= \frac{120 \times 20.0}{8.31 \times 303}$$
$$= 0.953 \text{ mol}$$
$$\frac{n(C_3H_7OH)}{n(O_2)} = \frac{2}{9}$$

For 0.142 mol of propanol to completely react it will require $\frac{9}{2} \times 0.142 = 0.638$ mol of oxygen. There is 0.953 mol of oxygen present, so oxygen is in excess. Propanol is the limiting reactant.

$$\frac{n(CO_2)}{n(C_3H_7OH)} = \frac{6}{2}$$
$$n(CO_2) = \frac{6}{2} \times n(C_3H_7OH)$$
$$= \frac{6}{2} \times 0.142$$
$$= 0.425 \text{ mol}$$
$$V(CO_2) = \frac{nRT}{p}$$
$$= \frac{0.425 \times 8.31 \times 303}{120}$$
$$= 8.92 \text{ L}$$

3.3 Calculating heat energy released

Worked example: Try yourself 3.3.1

CALCULATING THE ENERGY REQUIRED TO HEAT A MASS OF WATER USING SPECIFIC HEAT CAPACITY

Calculate the heat energy, in kJ, needed to increase the temperature of 375 mL of water by 45.0°C.

Thinking	**Working**
Change the volume of water, in mL, to mass of water, in g. Remember that the density of water is 1.0 g mL^{-1}, so 1 mL of water has a mass of 1 g.	375 mL of water has a mass of 375 g.
Find the specific heat capacity of water from the Table 3.3.1.	The specific heat capacity of water is 4.18 J g^{-1} $°C^{-1}$.
To calculate the quantity of heat energy in joules, use the formula: $q = mc\Delta T$	$q = 375 \times 4.18 \times 45.0$ $= 7.05 \times 10^4$ J
Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10^{-3}.	$q = 7.05 \times 10^4 \times 10^{-3}$ $= 70.5$ kJ

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Worked example: Try yourself 3.3.2

CALCULATING THE HEAT OF COMBUSTION OF A PURE ORGANIC LIQUID FUEL FROM EXPERIMENTAL DATA

0.295 g of ethanol (C_2H_5OH) undergoes complete combustion in a spirit burner. The heat energy released is used to heat 100 g of water. The temperature of the water rose from 19.56°C to 38.85°C. Calculate the heat of combustion of ethanol in kJ mol^{-1} and write the thermochemical equation for the reaction.

Thinking	**Working**
Calculate the temperature change of the water.	$\Delta T = 38.85 - 19.56$ $= 19.29°\text{C}$
Use the specific heat capacity of water to determine the energy used to heat the water. Use the formula: $q = mc\Delta T$ (m in this formula is the mass of water.)	$q = 100 \times 4.18 \times 19.29$ $= 8063$ J
Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10^{-3}.	$q = 8063 \times 10^{-3}$ $= 8.063$ kJ
Calculate the amount, in moles, of methanol using the formula: $n = \frac{m}{M}$	$n = \frac{0.295}{46.0}$ $= 0.006\,41$ mol
Determine the heat of combustion of methanol, in kJ mol^{-1}. Heat of combustion $= \frac{\text{heat released by sample}}{\text{amount of sample (in mol)}}$ or Heat of combustion $= \frac{q}{n}$	Heat of combustion $= \frac{8.063}{0.006\,41}$ $= 1.26 \times 10^3$ kJ mol^{-1}
The thermochemical equation for this reaction is a balanced equation, including the enthalpy of combustion, ΔH, which has a negative sign.	$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O;$ $\Delta H = -1.26 \times 10^3$ kJ

Worked example: Try yourself 3.3.3

ESTIMATING THE ENERGY CONTENT OF A SAMPLE OF FOOD

A 2.500 g sample of a corn chip was burned under a steel can containing 200 g of water. After the flame went out, the mass of the corn chip sample was 1.160 g and the temperature of the water had risen by 35.0°C. Calculate the energy content of the corn chip in kJ g^{-1}.

Thinking	**Working**
Calculate the heat energy absorbed by the water in joules, using the formula: $q = mc\Delta T$	$q = mc\Delta T$ $= 200 \times 4.18 \times 35.0$ $= 29\,260$ J
Express the quantity of energy in kJ. Remember that to convert from joules to kilojoules, you divide by 10^3 or multiply by 10^{-3}.	$q\text{(in kJ)} = \frac{29\,260}{1000}$ $= 29.260$ kJ
Calculate the mass of the food that was burned by subtracting the final mass from the initial mass: $\Delta m = \Delta m_{\text{initial}} - \Delta m_{\text{final}}$	$\Delta m = \Delta m_{\text{initial}} - \Delta m_{\text{final}}$ $= 2.500 - 1.160$ $= 1.340$ g
Calculate the energy content of the food by dividing the energy transferred to the water by the change in mass during combustion: Energy content $= \frac{q}{\Delta m}$	Energy content $= \frac{q}{\Delta m}$ $= \frac{29.260}{1.340}$ $= 21.8$ kJ g^{-1} (3 significant figures)

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CASE STUDY: ANALYSIS

The energy of candlelight

1 $C_{20}H_{42}(s) + \frac{61}{2}O_2(g) \longrightarrow 20CO_2(g) + 21H_2O(l)$ or $2C_{20}H_{42}(s) + 61O_2(g) \longrightarrow 40CO_2(g) + 42H_2O(l)$

2 The liquid oil is heated by the burning wick, and changes state from liquid to gas. The gas is then ignited and burns. During the combustion reaction, carbon–carbon and carbon–hydrogen bonds in the oil, and oxygen–oxygen double bonds break, and new bonds are formed between hydrogen and oxygen in the water, and double bonds between carbon and oxygen in carbon dioxide. The energy required to break the bonds of the reactants (energy absorbed) is less than that released by the formation of bonds in the products, so more energy is released than is used, and the reaction is exothermic.

3 Heat of combustion of eicosane = 47.1 $kJ g^{-1}$

$q = mc\Delta T$

$= 100 \times 4.18 \times (100.0 - 18.0)$

$= 34\,276$ J

$= 34.3$ kJ

m(eicosane) that provides 34.3 kJ energy $= \frac{34.3}{47.1} = 0.728$ g

KEY QUESTIONS

Knowledge and understanding

1 **a** $q = mc\Delta T$

$= 100 \times 4.18 \times 25.1$

$= 10\,491.8$ J

$= 10.5$ kJ

b $q = mc\Delta T$

$= 500 \times 4.18 \times (80.0 - 17.0)$

$= 131\,670$ J

$= 132$ kJ

c $q = mc\Delta T$

$= (1.50 \times 10^3) \times 4.18 \times (30.0 - 20.0)$

$= 62\,700$ J

$= 62.7$ kJ

2 $q = mc\Delta T$. Therefore, $\Delta T = \frac{q}{c \times m}$

$= \frac{10.0 \times 10^3}{4.18 \times 200}$

$= 12.0$°C

The increase in temperature was 12.0°C, so the temperature reached by the water was 21.0 + 12.0 = 33.0°C

Analysis

3 $q = mc\Delta T$

$= 300 \times 4.18 \times 1.78$

$= 2232.12$ J

$= 2.23$ kJ

Heat of combustion $= \frac{q}{n}$

$= \frac{2.23}{1.00 \times 10^{-3}}$

$= 2.23 \times 10^3$ kJ mol^{-1}

4 $q = mc\Delta T$

$= 500 \times 4.18 \times 11.5$

$= 24\,035$ J

$= 24.0$ kJ

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$$\text{Heat of combustion} = \frac{q}{n} = \frac{24.035}{0.500} = 48.1\ \text{kJ g}^{-1}$$

5 $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890\ \text{kJ mol}^{-1}$

$$q = mc\Delta T = 500 \times 4.18 \times (100.0 - 20.0) = 167\,200\ \text{J} = 167.2\ \text{kJ}$$

$$\text{Heat of combustion} = \frac{q}{n}$$

$$890 = \frac{167.2}{n}$$

$$n(CH_4) = \frac{167.2}{890} = 0.1879\ \text{mol}$$

$$m(CH_4) = n \times M = 0.1879 \times 16.0 = 3.01\ \text{g}$$

6 $m(\text{coal}) = \dfrac{\text{energy released}}{\text{heat of combustion}} = \dfrac{62.7}{20.7} = 3.03\ \text{g}$

3.4 Solution calorimetry

Worked example: Try yourself 3.4.1

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY ELECTRICAL CALIBRATION

A solution calorimeter was calibrated by passing 1.05 A through the electric heater for 120 s at a potential difference of 5.90 V. The temperature of the water in the calorimeter was initially 15.20°C and rose to 17.50°C during the calibration. Determine the calibration factor of the calorimeter.

Thinking	Working
Calculate the thermal energy released by the heater in the calorimeter when the electric current was passed through it. Use the equation: $E = VIt$	$E = VIt$ $= 5.90 \times 1.05 \times 120$ $= 743.4$ J
Calculate the temperature change during the calibration. Use the equation: $\Delta T = \Delta T_{final} - \Delta T_{initial}$	$\Delta T = \Delta T_{final} - \Delta T_{initial}$ $= 17.50 - 15.20$ $= 2.30$°C
Calculate the calibration factor by dividing the energy by the change in temperature. Use the equation: $CF = \dfrac{E}{\Delta T} = \dfrac{VIt}{\Delta T}$	$CF = \dfrac{E}{\Delta T}$ $= \dfrac{743.4}{2.30}$ $= 323$ J °C^{-1}

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Worked example: Try yourself 3.4.2

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY CHEMICAL CALIBRATION

A solution calorimeter was calibrated by completely dissolving 8.20 g of potassium nitrate in 200 mL of water in a calorimeter. ($M(KNO_3) = 101.3$ g mol^{-1}; $\Delta H = +34.9$ kJ mol^{-1}). The temperature of the water in the calorimeter decreased from 20.0°C to 13.5°C during the calibration. Determine the calibration factor of the calorimeter.

Thinking	**Working**
Determine the amount, in mol, of potassium nitrate that dissolves. Use the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{8.20}{101.3}$ $= 0.0809$ mol
Calculate the thermal energy absorbed from the water when the potassium nitrate dissolves in the calorimeter. Use the equation $E = n \times \Delta H$, noting that the energy will be in kJ.	$E = n \times \Delta H$ $= 0.0809 \times 34.9$ $= 2.83$ kJ
Calculate the temperature change during the calibration. Use the equation: $\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$	$\Delta T = \Delta T_{\text{final}} - \Delta T_{\text{initial}}$ $= 20.0 - 13.5$ $= 6.5$°C
Calculate the calibration factor, *CF*, by dividing the energy by the change in temperature. Use the equation: $CF = \frac{E}{\Delta T}$	$CF = \frac{E}{\Delta T}$ $= \frac{2.83}{6.5}$ $= 0.435$ kJ °C^{-1} $= 435$ J °C^{-1}

Worked example: Try yourself 3.4.3

CALCULATING THE ENTHALPY OF SOLUTION USING A SOLUTION CALORIMETER

A solution calorimeter has a calibration factor of 396.4 J °C^{-1}. If the temperature decreases by 1.65°C when 41.587 g of sucrose, $C_{12}H_{22}O_{11}$, (M = 342.0 g mol^{-1}) is dissolved in water in the calibrated calorimeter, calculate the enthalpy of solution of sucrose.

Thinking	**Working**
Calculate the amount of reactant in moles, using the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{41.587}{342.0}$ $= 0.1216$ mol
Calculate the heat energy released or absorbed, in kJ, using the equation: $E = CF \times \Delta T$	$E = CF \times \Delta T$ $= 396.4 \times 1.65$ $= 654$ J $= 0.654$ kJ
Calculate the energy released or absorbed per mole, using the equation: $\Delta H = \frac{E}{n}$	$\Delta H = \frac{E}{n}$ $= \frac{0.654}{0.1216}$ $= 5.38$ kJ mol^{-1}
State the enthalpy of solution with the correct sign, remembering that a temperature increase indicates an exothermic process and a temperature decrease indicates an endothermic process.	$\Delta H = +5.38$ kJ mol^{-1} (3 significant figures)

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KEY QUESTIONS

Knowledge and understanding

1 Insulating a calorimeter improves the **accuracy** of measurement of the amount of energy **released** or absorbed by a chemical reaction.

Heat energy can be **lost** from a calorimeter, so a **lid** is a useful form of insulation.

If the reaction occurring in a calorimeter is exothermic, the temperature of the water **increases**. If the reaction occurring is **endothermic** the temperature of the water in a calorimeter decreases.

2 $n(NH_4Cl) = \dfrac{6.52}{53.5} = 0.122\text{ mol}$

$E = \Delta H \times n = 14.8 \times 0.122 = 1.806\text{ kJ}$

$\Delta T = 19.5 - 14.3 = 5.2°C$

$CF = \dfrac{E}{\Delta T} = \dfrac{1.806}{5.2} = 0.347\text{ kJ °C}^{-1} = 347\text{ J °C}^{-1}$

3 $n(\text{citric acid}) = \dfrac{9.60}{192.0} = 0.0500\text{ mol}$

$\Delta T = 2.34°C$

$CF = 389\text{ J °C}^{-1}$

$E = CF \times \Delta T = 389 \times 2.34 = 910\text{ J}$

$\Delta H = \dfrac{E}{n} = \dfrac{910}{0.0500} = 18205\text{ J mol}^{-1} = 18.2\text{ kJ mol}^{-1}$

4 $n(NaHCO_3) = \dfrac{15.00}{84.0} = 0.1786\text{ mol}$

$\Delta T = 4.20°C$

$CF = 674.3\text{ J °C}^{-1}$

$E = CF \times \Delta T = 674.3 \times 4.20 = 2832\text{ J} = 2.832\text{ kJ}$

$\Delta H = \dfrac{E}{n} = \dfrac{2.832}{0.1786} = 15.86\text{ kJ mol}^{-1}$

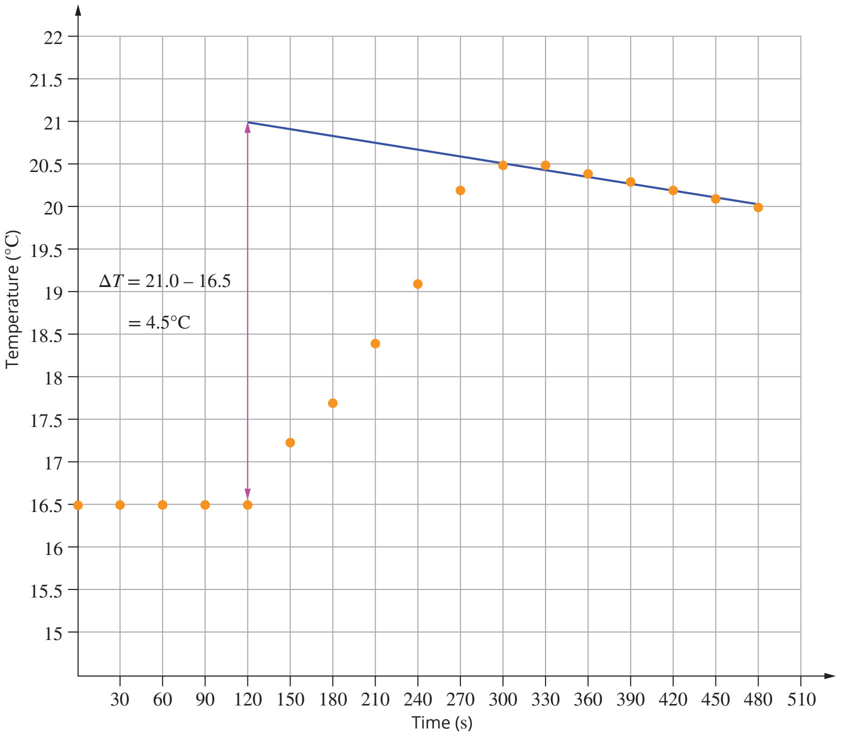
The enthalpy of solution = $+15.86\text{ kJ mol}^{-1}$

Analysis

5 **a** $CF = \dfrac{VIt}{\Delta T} = \dfrac{6.0 \times 3.8 \times (5.0 \times 60)}{9.5} = 720 = 7.2 \times 10^2\text{ J °C}^{-1}$

b If 50 g of water was used instead of 100 g, the calibration factor would be halved, since the same amount of energy was being added to half the volume of water, and the temperature increase would double. Dividing the same value for *VIt* by a value that is double the previous one will produce a calibration factor that is half the previous one.

6



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From the graph $\Delta T = 21.0 - 16.5 = 4.5$°C

$$CF = \frac{VIt}{\Delta T}$$

$$= \frac{5.75 \times 4.10 \times 150}{4.5}$$

$$= 786 = 7.9 \times 10^2\ \text{J °C}^{-1}$$

7

Mistake or error	Calibration factor is too small	Calibration factor would be correct	Calibration factor is too large	Explanation for answer
The lid is left off during calibration.			✓	Heat escapes during the calibration, so the temperature change recorded is smaller than is correct. The CF is divided by a number that is too small, so it will be too large.
During electrical calibration, the voltmeter had a systematic error making it read too low.	✓			The calculation of energy entering the calorimeter will be too small, so the numerator will be smaller than it should be, and the calibration factor will be too small.
During chemical calibration, not all of the solid KNO_3 dissolved in the water of the calorimeter.			✓	The energy absorbed from the water will be recorded as a larger figure than actually occurs. The actual temperature change will be smaller than it should be, so the calibration factor will be larger than it should be.

3.5 Energy from fuels and food

Worked example: Try yourself 3.5.1

CALCULATING THE ENERGY TRANSFORMATION EFFICIENCY OF AN EXPERIMENT

A pair of students carried out an experiment to measure the enthalpy of combustion of ethanol. They burned ethanol in a spirit burner under a can of water and measured the temperature change of the water and the mass change of the spirit burner. From this experiment they determined the enthalpy of combustion of ethanol to be –820 kJ mol^{-1}.

The theoretical enthalpy of combustion of ethanol was recorded in their data book as –1360 kJ mol^{-1}. Calculate the percentage efficiency of the energy transformation from chemical energy (of the ethanol) to thermal energy (in the water).

Thinking	Working
Identify which energy best matches the description of useful energy and which is the energy input.	The 'useful energy' quantity is the energy that heated the water and enabled the calculation of the experimental value, –820 kJ mol^{-1}. The energy input quantity is the theoretical enthalpy of combustion: –1360 kJ mol^{-1}
Use the formula: $\%\ \text{energy efficiency} = \frac{\text{useful energy}}{\text{energy input}} \times \frac{100}{1}$ to calculate the percentage energy transformation efficiency.	$\%\ \text{energy efficiency} = \frac{\text{useful energy}}{\text{energy input}} \times \frac{100}{1}$ $= \frac{-820}{-1360} \times \frac{100}{1}$ $= 60.3\%$

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Worked example: Try yourself 3.5.2

ALLOWING FOR % EFFICIENCY IN ENERGY TRANSFORMATIONS

The % efficiency of octane (petrol) in a particular car model is 42.0%. Calculate the energy released from the complete combustion of 22.0 g of octane. The heat of combustion of octane is 5460 kJ mol^{-1}.

Thinking	Working
Calculate the amount, in mol, of the fuel.	$n(C_8H_{18}) = \frac{m}{M} = \frac{22.0}{114} = 0.193$ mol
Calculate the quantity of energy released (the energy input) by the combustion of the fuel.	energy released = $n \times \Delta H$ $= 0.193 \times 5460 = 1053$ kJ
Rearrange the formula $\%\text{ energy efficiency} = \frac{\text{useful energy}}{\text{energy input}} \times \frac{100}{1}$ to useful energy = energy input × % energy efficiency so that the energy available to heat the water can be determined.	useful energy = energy input × % energy efficiency $= 1053 \times \frac{42}{100}$ $= 443$ kJ

Worked example: Try yourself 3.5.3

CALCULATING HEAT OF COMBUSTION USING % EFFICIENCY IN ENERGY TRANSFORMATIONS

A student burnt 0.0105 mol of butan-1-ol in a spirit burner to heat 200 g of water in a can. The % efficiency of this process was 57.0%. During the combustion experiment, the temperature of the water in the can increased by 19.2°C. Calculate the heat of combustion of butan-1-ol. (Remember that the specific heat capacity of water is 4.18 J °C^{-1} g^{-1}.)

Thinking	Working
Calculate the quantity of energy that heated the water—this is the useful energy. Use the formula $q = mc\Delta T$ to calculate the useful energy, because the can does not have a calibration factor.	$q = mc\Delta T$ $= 200 \times 4.18 \times 19.2$ $= 16051$ J $= 16.051$ kJ
Convert the % energy efficiency to a decimal to assist with calculations Divide % energy efficiency by 100.	$\frac{\%\text{ energy efficiency}}{100}$ $= \frac{57.0}{100}$ $= 0.570$
Rearrange the formula: $\%\text{ energy efficiency} = \frac{\text{useful energy}}{\text{energy input}} \times \frac{100}{1}$ to $\text{energy input} = \frac{\text{useful energy}}{\%\text{ energy efficiency (as a decimal)}}$ so that the energy released by the fuel can be determined.	$\text{energy input} = \frac{16.051}{0.570}$ $= 28.16$ kJ
Remembering that the energy released is represented by the energy input, rearrange the formula: energy released = $n \times \Delta H$ to $\Delta H = \frac{\text{energy released}}{n}$	$\Delta H = \frac{28.16}{0.0105}$ $= 2682$ $= 2.68 \times 10^3$ kJ mol^{-1} The heat of combustion of butan-1-ol is 2.68×10^3 kJ mol^{-1}.

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Worked example: Try yourself 3.5.4

CALCULATING THE ENERGY VALUE OF FOODS

The labelling on a sample of white bread indicates it contains 53.0% carbohydrates, 8.0% protein and 4.0% fat. The remaining 35.0% is water, which does not supply energy.

Calculate the energy value of the bread, in kJ g^{-1}.

Thinking	**Working**
Use the information on page 142 determine the available energy for each nutrient type.	carbohydrate: 16 kJ g^{-1} protein: 17 kJ g^{-1} fat: 37 kJ g^{-1}
Assuming that there is 100 g of the sample, multiply each percentage of nutrient by the available energy per gram for the nutrient type.	carbohydrate: 53.0 g × 16 kJ g^{-1} = 848 kJ protein: 8.0 g × 17 kJ g^{-1} = 136 kJ fat: 4.0 g × 37 kJ g^{-1} = 148 kJ
Find the sum of the energies for the three nutrient types and divide by 100 to find the energy value in kJ g^{-1}.	energy value $= \frac{848+136+148}{100}$ $= 11$ kJ g^{-1} (2 significant figures)

KEY QUESTIONS

Knowledge and understanding

1 carbohydrate: 16 kJ g^{-1}

10.0 g × 16 kJ g^{-1} = 160 kJ

a protein: 17 kJ g^{-1}

$$\frac{160}{17} = 9.41 \text{ g}$$

b fat: 37 kJ g^{-1}

$$\frac{160}{37} = 4.32 \text{ g}$$

2 **a** An energy transformation is when energy is converted from one form, such as chemical energy, to another form, such as heat energy.

b With each energy transformation, some energy is lost to the environment, so as the number of energy transformations increases, the percentage of energy lost increases. This means that the usefulness of the fuel decreases.

3 An 18.0 g chocolate frog contains 5.3 g fat, 11.0 g of carbohydrates and 1.4 g protein.

a $E = (5.3 \times 37) + (11.0 \times 16) + (1.4 \times 17) = 196.1 + 176 + 23.8 = 395.9$ kJ

b $\frac{196}{395.9} \times 100\% = 49.5\%$

Analysis

4 **a** $M(C_4H_9OH) = 74$

Heat of combustion of butanol $= \frac{2670}{74} = 36.08$ kJ g^{-1} = 36.08 MJ kg^{-1}

m(butanol) required to produce 200 MJ energy $= \frac{200}{36.08} = 5.54$ kg

b % energy efficiency $= \frac{\text{useful energy}}{\text{energy input}} \times \frac{100}{1}$

energy input = energy content × mass = 36.08 × 375 = 13 530 kJ

Energy transferred to water is 'useful energy'.

useful energy = energy input × % energy efficiency

= 13 630 × 0.380

= 5141 kJ

5141 kJ of energy is transferred to the water.

5 Available energy from page 81:

carbohydrates	16 kJ g^{-1}
proteins	17 kJ g^{-1}
fats	37 kJ g^{-1}

Energy per nutrient in 100 g of pesto:

carbohydrates	$3.3 \times 16 = 52.8$ kJ
proteins	$3.9 \times 17 = 66.3$ kJ
fats	$21.4 \times 37 = 791.8$ kJ

$$\text{Total energy per gram of pesto} = \frac{52.8+66.3+791.8}{100}$$
$$= 9.1 \text{ kJ g}^{-1}$$

6 energy content of fat = 37 kJ g^{-1}

$$\text{mass of fat} = \frac{425}{37} = 11.49 \text{ g}$$

$$\text{percentage of fat in butter} = \frac{11.49}{15.0} \times 100\% = 76.6\% \text{ fat}$$

7 **a** $q = mc\Delta T$

$$= 100 \times 4.18 \times (30.8 - 18.6)$$
$$= 5099.6 \text{ J}$$
$$= 5.10 \text{ kJ}$$

b $m(\text{propan-1-ol}) = 3.565 - 3.284 = 0.281$ g

$$n(\text{propan-1-ol}) = \frac{0.281}{60.0} = 4.683 \times 10^{-3} \text{ mol}$$

$$\text{heat of combustion} = \frac{E}{n} = \frac{5.10}{4.683 \times 10^{-3}} = 1.09 \times 10^{3} \text{ kJ mol}^{-1}$$

c $$\% \text{ energy efficiency} = \frac{\text{useful energy}}{\text{energy input}} \times \frac{100}{1}$$

$$= \frac{1089}{2021} \times \frac{100}{1} = 53.9\%$$

d Some suggestions as to how the student could improve the accuracy of the result:

- Insulate the can that holds the water and add a lid to the can.
- Try to prevent heat loss, by setting up some sort of insulation around the whole apparatus, while still allowing enough oxygen to reach the flame.
- Minimise the distance between the flame and the can that is being heated.

8 $q = mc\Delta T$

$$= 250 \times 4.18 \times 16.9$$
$$= 17660.5 \text{ J}$$
$$= 17.6605 \text{ kJ}$$

% energy efficiency as a decimal = 0.750%

$$\text{energy input} = \frac{\text{useful energy}}{\%\text{ energy efficiency (as a decimal)}}$$

$$= \frac{17.6605}{0.750}$$
$$= 23.547 \text{ kJ}$$

$$\Delta H = \frac{\text{energy released}}{n}$$

$$= \frac{23.547}{0.0325}$$
$$= 724.5 \text{ kJ mol}^{-1}$$

The heat of combustion of methanol is 725 kJ mol^{-1}

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Chapter 3 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 D. The calculations for each alternative are shown below:

A 15 g protein × 17 kJ = 255 kJ

B 8 g fat × 37 kJ = 296 kJ

C 20 g carbohydrate × 16kJ = 320 kJ

D 5 g fat × 37 kJ + 10 g protein × 17 kJ = 185 + 170 = 355 kJ

2 D.

$$\begin{aligned}\%\text{ energy efficiency} &= \frac{\text{useful energy}}{\text{energy input}} \times \frac{100}{1} \\ &= \frac{1800}{2018} \times \frac{100}{1} \\ &= 89.2\%\end{aligned}$$

3 The balanced equation shows that 1 mol of propane produces 3 mol of carbon dioxide. The number of moles of each is found using $n = \frac{m}{M}$, where m is the mass in grams and M is the molar mass in g mol^{-1}. Use a periodic table to calculate the molar masses. $M(C_3H_8) = 44.0$ g mol^{-1}, $M(CO_2) = 44.0$ g mol^{-1}, $M(H_2O) = 18.0$ g mol^{-1} and $M(O_2) = 32.0$ g mol^{-1}.

$$\begin{aligned}n(C_3H_8) &= \frac{6.70}{44.0} \\ &= 0.152 \text{ mol}\end{aligned}$$

a

$$\begin{aligned}\frac{n(CO_2)}{n(C_3H_8)} &= \frac{3}{1} \\ n(CO_2)\text{ produced} &= \frac{3}{1} \times 0.152 \\ &= 0.457 \text{ mol} \\ m(CO_2)\text{ produced} &= 0.457 \times 44.0 \\ &= 20.1 \text{ g}\end{aligned}$$

b

$$\begin{aligned}\frac{n(O_2)}{n(C_3H_8)} &= \frac{5}{1} \\ n(O_2)\text{ consumed} &= \frac{5}{1} \times 0.152 \\ &= 0.761 \text{ mol} \\ m(O_2)\text{ consumed} &= 0.761 \times 32.0 \\ &= 24.4 \text{ g}\end{aligned}$$

c

$$\begin{aligned}\frac{n(H_2O)}{n(C_3H_8)} &= \frac{4}{1} \\ n(H_2O)\text{ produced} &= \frac{4}{1} \times 0.152 \\ &= 0.609 \text{ mol} \\ \therefore\ m(H_2O)\text{ produced} &= 0.609 \times 18.0 \\ &= 11.0 \text{ g}\end{aligned}$$

4

$$\begin{aligned}n(Mg) &= \frac{m}{M} \\ &= \frac{5.0}{24.3} \\ &= 0.206 \text{ mol}\end{aligned}$$

$$\begin{aligned}n(O_2)\text{ reacted} &= \frac{1}{2} \times 0.206 \\ &= 0.103 \text{ mol} \\ m(O_2)\text{ reacted} &= n \times M \\ &= 0.103 \times 32.0 \\ &= 3.29 \text{ g} \\ m(O_2)\text{ in excess} &= 20.0 - 3.29 \\ &= 16.7 \text{ g}\end{aligned}$$

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5 The balanced equation shows that 1 mol carbon produces 1 mol of carbon dioxide. The number of moles of each is found using $n = \frac{m}{M}$ where m is the mass in grams and M is the molar mass in g mol^{-1}. Use a periodic table to calculate the molar masses. M(carbon) = 12.0 g mol^{-1} and $M(CO_2)$ = 44.0 g mol^{-1}.

$$n(\text{C}) = \frac{1000000}{12.0}$$
$$= 8.3 \times 10^4 \text{ mol}$$
$$\frac{n(\text{CO}_2)}{n(\text{C})} = \frac{1}{1}$$
$$n(\text{CO}_2) = \frac{1}{1} \times n(\text{C}) = 8.3 \times 10^4 \text{ mol}$$
$$\therefore m(\text{CO}_2) = 8.3 \times 10^4 \times 44.0$$
$$= 3.7 \times 10^6 \text{ g}$$
$$= 3.7 \text{ tonnes}$$

6 All of the species in the equation are in the gaseous state, so the mole ratio is also a volume ratio at constant temperature and pressure.

$$\frac{V(\text{C}_8\text{H}_{18})}{V(\text{CO}_2)} = \frac{2}{16}$$
$$V(\text{C}_8\text{H}_{18}) = \frac{2}{16} \times V(\text{CO}_2)$$
$$= \frac{2}{16} \times 50$$
$$= 6.25 \text{ L}$$

7 $q = m \times c \times \Delta T$
$$= 50.0 \times 4.18 \times (29.8 - 18.5)$$
$$= 2361.7 \text{ J}$$
$$= 2.36 \text{ kJ}$$

8 $n(\text{C}_4\text{H}_9\text{OH}) = \frac{m}{M}$
$$= \frac{806}{74.0}$$
$$= 10.9 \text{ mol}$$

From the equation, 1 mol of C_4H_9OH yields 2677 kJ.

10.9 mol of C_4H_9OH yields x kJ

By proportion: $\frac{10.9}{1} = \frac{x}{2677}$
$$x = \frac{10.9}{1} \times 2677$$
$$= 2.92 \times 10^4 \text{ kJ}$$

The energy released by the combustion reaction is 2.92 × 10^4 kJ = 29.2 MJ.

9 **a** $n(\text{C}_3\text{H}_8) = \frac{300}{44.0}$
$$= 6.82 \text{ mol}$$
$$n(\text{O}_2) = \frac{2000}{32.0}$$
$$= 62.5 \text{ mol}$$

For 6.82 of propane to completely react, it will require $\frac{5}{1} \times 6.82 = 34.1$ mol of oxygen. There is 62.5 mol of oxygen present, so oxygen is in excess and ethanol is the limiting reactant.

$n(O_2)$ in excess = $n(O_2)$ added – $n(O_2)$ that reacts
$$= 62.5 - 34.1$$
$$= 28.4 \text{ mol}$$
$$m(\text{O}_2) = n \times M$$
$$= 28.4 \times 32.0$$
$$= 909 \text{ g}$$

b $\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1}$

$n(CO_2)$ produced $= \frac{3}{1} \times 6.82$

$= 20.5$ mol

$V(CO_2) = n \times V_m$

$= 20.5 \times 24.8$

$= 507$ L

c $n(CO_2)$ produced $= \frac{3}{1} \times 6.82$

$= 20.5$ mol

$V(CO_2) = \frac{nRT}{p}$

$= \frac{20.5 \times 8.31 \times 288}{150}$

$= 326$ L

10 B. The mass, *m*, represents the mass of the material that is being heated. Alternative A is incorrect as the specific heat capacity, *c*, depends on the material that is absorbing the energy, not generating it. Alternative C is incorrect as *q* is measured in J or kJ, not kJ °C^{-1}. Alternative D is incorrect as ΔT refers to the change in temperature of the material absorbing the energy, not the fuel generating the heat.

11 A. $\Delta T = \frac{q}{m \times C} = \frac{2.10 \times 10^3}{100.0 \times 4.18}$

$= 5.02°C$

However, there is no insulation and no lid on the beaker of water, so heat will be lost from the water and the value of ΔT will be lower than expected. 3.20°C is a possible temperature change. The other alternatives are all too high.

12 Energy in pressed peat, $q = 12.8 \times 17.0$

$= 217.6$ kJ

$\Delta T = T_{initial} - T_{final}$

$= 60.0 - 20.0$

$= 40.0°C$

$q = m \times c \times \Delta T$

$m = \frac{q}{c \times \Delta T}$

$= \frac{217.6 \times 1000}{4.18 \times 40.0}$

$= 1301$ g

$= 1.30$ kg

13 **a** $KNO_3(s) \xrightarrow{H_2O(l)} K^+(aq) + NO_3^-(aq)$

b Calculate the energy input:

$E = VIt$

$E = 5.90 \times 1.50 \times 60.0$

$= 531$ J

Calculate the calibration factor:

$CF = \frac{\text{energy}}{\text{temperature rise}}$

$= \frac{531}{0.456}$

$= 1164.5$ J °C^{-1}

$= 1.16$ kJ °C^{-1}

c $E = CF \times \Delta T$

$= 1.1645 \times 0.672$

$= 0.7825$ kJ

$= 783$ J

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d Calculate the amount of KNO_3:

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

$n(KNO_3) = \frac{1.01\ \text{g}}{101\ \text{g mol}^{-1}}$

Calculate ΔH for the equation, using stoichiometry:

0.01 mol absorbed 783 J

1 mol will absorb $\frac{783}{0.01}$ J.

So $\Delta H = +78\,300\ \text{J mol}^{-1}$

$= +78.3\ \text{kJ mol}^{-1}$

14 Assuming 100 g of stuffed pepper:

$E = (16 \times 16) + (13 \times 17) + (6 \times 37) = 256 + 221 + 222 = 699$ kJ

$\frac{699}{100} = 7.0\ \text{kJ g}^{-1}$

Application and analysis

15 The calibration factor would be measured as being smaller than it should be. As $CF = \frac{VIT}{\Delta T}$, increasing the current, I, will increase the quantity of energy entering the calorimeter. However, it is not known that the quantity of current is greater, so VIT will not be a larger number, yet the change in temperature which is measure, ΔT, will be greater than it should be, thus decreasing the value of the calibration factor.

16 **a** Energy $= (4.0 \times 37) + (44.0 \times 16) + (10.0 \times 17.0)$

$= 148 + 704 + 170$

$= 1022$ kJ

b $\frac{2400}{1022} \times 1.5 = 2.34$ bars

The runner should consume 3 energy bars.

17 All of the species in the equation are in the gaseous state, so the mole ratio is also a volume ratio at constant temperature and pressure.

a $\frac{V(CH_4)}{V(CO_2)} = \frac{1}{1}$

$V(CH_4) = \frac{1}{1} \times V(CO_2)$

$= 5.0$ L

b $\frac{V(O_2)}{V(CO_2)} = \frac{2}{1}$

$V(O_2) = \frac{2}{1} \times V(CO_2)$

$= 10$ L

c $n(CO_2) = \frac{V}{V_m}$

$= \frac{5.0}{24.8}$

$= 0.2016$ mol

$m(CO_2) = n \times M$

$= 0.2016 \times 44.0$

$= 8.87$ g

$\frac{n(H_2O)}{n(CO_2)} = \frac{2}{1}$

$n(H_2O) = \frac{2}{1} \times 0.2016$

$= 0.4032$ mol

$m(H_2O) = 0.4032 \times 18.0$

$= 7.26$ g

Total mass of greenhouse gases produced $= 8.87 + 7.26 = 16.13 = 16$ g

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18 a From the equation:

2 moles of octane release 10 900 kJ.

Let x moles of octane release 100 kJ.

By proportion: $\frac{x}{2} = \frac{100}{10900}$

$$x = \frac{100}{10900} \times 2$$

$$= 0.0182 \text{ mol}$$

$$m(C_8H_{18}) = n \times M$$

$$= 0.0182 \times 114.0$$

$$= 2.09 \text{ g}$$

b Mass (g) = density (g mL^{-1}) × volume (mL)

$$m(C_8H_{18}) = 0.698 \times (50.0 \times 10^3)$$

$$= 3.49 \times 10^4 \text{ g}$$

$$n(C_8H_{18}) = \frac{m}{M}$$

$$= \frac{3.49 \times 10^4}{114.0}$$

$$= 306 \text{ mol}$$

From the equation, 2 mol of C_8H_{18} releases 10 900 kJ.

∴ 306 mol of C_8H_{18} releases x kJ.

By proportion: $\frac{x}{10900} = \frac{306}{2}$

$$x = \frac{306}{2} \times 10900$$

$$= 1.67 \times 10^6 \text{ kJ}$$

Energy released = 1.67×10^3 MJ

19 Write a balanced equation:

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

For each minute of operation:

$$n(C_3H_8) = \frac{12.7}{44.0}$$

$$= 0.289 \text{ mol}$$

$$\frac{n(O_2)}{n(C_3H_8)} = \frac{5}{1}$$

$$n(O_2) \text{ required} = \frac{5}{1} \times 0.289$$

$$= 1.44 \text{ mol}$$

$$m(O_2) \text{ required per minute} = 1.44 \times 32.0$$

$$= 46.2 \text{ g}$$

20 a The reactants and products are all in the gaseous state, so the mole ratio is also a volume ratio at constant temperature and pressure.

For 80 mL of propane to react, it will require $\frac{5}{1} \times 80 = 400$ mL of oxygen. There is 500 mL of oxygen present, so oxygen is in excess and propane is the limiting reactant.

$$V(O_2) \text{ in excess} = V(O_2) \text{ initially} - V(O_2) \text{ that reacted}$$

$$= 500 - 400$$

$$= 100 \text{ mL}$$

b 1 L of propane produces 3 L of CO_2 and 4 L of H_2O. CO_2 and H_2O are both greenhouse gases, so 1 L of propane produces 7 L of greenhouse gases.

80 mL of propane will produce $\frac{7}{1} \times 80 = 560$ mL greenhouse gases.

c Initial volume of gases = 80 + 500 = 580 mL

Final volume of gases = 560 mL + volume of O_2 in excess.

Final volume of gases = 560 + 100 = 660 mL

Change in volume of gases = 660 – 580 = increase of 80 mL

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d 1 tonne = 10^6 g

$$n(CO_2) = \frac{m}{M}$$
$$= \frac{10^6}{44.0}$$
$$= 2.27 \times 10^4 \text{ mol}$$

When 2.27×10^4 mol of CO_2 is produced, the energy released is 1.68×10^4 MJ

For the thermochemical equation, when 3 mol of CO_2 is produced *x* amount of energy is released.

By proportion: $\frac{3}{2.27 \times 10^4} = \frac{x}{1.68 \times 10^4}$

$$x = \frac{3}{2.27 \times 10^4} \times 1.68 \times 10^4$$
$$= 2.22 \text{ MJ}$$
$$\Delta H = -2.22 \times 10^3 \text{ kJ mol}^{-1}$$

21 $n(CO_2) = \frac{V}{V_m}$

$$= \frac{80.0}{24.8}$$
$$= 3.23 \text{ L}$$

Using the starting mass of ethanol, we can predict the theoretical volume of carbon dioxide produce if all of the ethanol reacted.

$$n(C_2H_5OH) = \frac{m}{M}$$
$$= \frac{10.0}{46.0}$$
$$= 0.217 \text{ mol}$$
$$\frac{n(CO_2)}{n(C_2H_5OH)} = \frac{2}{1}$$

So

$$n(CO_2) = \frac{2}{1} \times 0.217 = 0.435$$
$$V(CO_2) = n \times V_m$$
$$= 0.435 \times 24.8$$
$$= 10.8 \text{ L}$$

Only 3.23 L of CO_2 was produced, so the ethanol must have be in excess. It was not the limiting reactant as it did not limit the amount of carbon dioxide produced.

22 $q = mc\Delta T = 200 \times 4.18 \times 17.3$

$$= 14\,462.8 \text{ J}$$
$$= 14.46 \text{ kJ}$$
$$E(\text{peanut}) = \frac{q}{m} = \frac{14.46}{1.340 - 0.640}$$
$$= 20.7 \text{ kJ g}^{-1}$$

23 $q = m \times c \times \Delta T$

$$= 300 \times 4.18 \times (24.92 - 18.25)$$
$$= 8364.2 \text{ J}$$
$$= 8.36 \text{ kJ}$$
$$\text{heat of combustion} = \frac{E}{m}$$
$$= \frac{8.36}{0.254}$$
$$= 32.9 \text{ kJ g}^{-1}$$

24 $q = m \times c \times \Delta T$

$$= 100 \times 4.18 \times 5.52$$
$$= 2307.4 \text{ J}$$
$$= 2.307 \text{ kJ}$$
$$n(C_2H_6) = \frac{m}{M} = \frac{0.0450}{(2 \times 12) + (6 \times 1)} = 0.0015 \text{ mol}$$

energy released per mole $\frac{E}{n} = \frac{2.307}{0.0015} =$ 1538 kJ mol^{-1}

$C_2H_6(g)\ \frac{7}{2} + O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);\quad \Delta H = -1538 \text{ kJ mol}^{-1}$

25 **a** $q = m \times c \times \Delta T$

$= 500 \times 4.18 \times 22.9$

$= 47\,861$ J

$= 47.9$ kJ

Energy content $= \frac{E}{m}$

$= \frac{47.9}{3.00}$

$= 16.0$ kJ g^{-1}

b The calculated heat of combustion is likely to be lower than the actual heat of combustion of the wood. It is likely that all the energy from the burning wood was not transferred to the water. Parts of the wood may not be completely combusted, thus reducing the energy output of burning it. If the wood was not completely dry, this would also decrease the heat of combustion as energy is required to remove the water before it is able to combust.

26 $CF = \frac{VIt}{\Delta T}$

$= \frac{9.80 \times 3.60 \times 270}{3.49}$

$= 2729$ J °C^{-1}

$= 2.729$ kJ °C^{-1}

Energy transferred $= CF \times \Delta T$

$= 2.729 \times 18.14$

$= 49.50$ kJ

n(sucrose) $= \frac{m}{M} = \frac{3.00}{342}$

$= 8.77 \times 10^{-3}$ mol

ΔH_c(sucrose) $= \frac{q}{\text{n}}$

$= \frac{49.51}{0.00877}$

$= 5643$ kJ mol^{-1}

27 **a** If heat loss is not taken into account, ΔT will be too small.

b The calibration factor calculated for the calorimeter will be too large.

c The value of the enthalpy change will increase because the enthalpy change is found using $CF \times \Delta T$.

28 1 The student has multiplied VIt(energy) by the change in temperature instead of dividing by the temperature change when calculating the calibration factor.

2 The student has then multiplied the calibration factor by ΔT, which is correct, but the value is too large due to the earlier mistake.

3 The mass has been divided by the energy instead of the energy divided by the mass to calculate the energy content. This results in a significantly lower energy content of the jelly crystals than expected.

4 The student has stated that energy is given out when the jelly crystals are dissolved. The temperature has decreased, so energy has been absorbed. This agrees with the student's statement that the reaction is endothermic.

The student's calculations should be as follows:

$CF = \frac{6.30 \times 2.40 \times 210}{2.8}$

$= 1134$ J

Heat energy per gram to dissolve the jelly crystals:

$E = CF \times \Delta T$

$= 1134 \times 0.5$

$= 567$ J

Energy per gram $= \frac{567}{85.0}$

$= 6.67$ J g^{-1}

6.67 J of energy is taken in when 1 g of jelly crystals dissolves. This is an endothermic reaction.

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Chapter 4 Redox reactions

4.1 Oxidation and reduction

KEY QUESTIONS

Knowledge and understanding

1 When a reducing agent, such as Zn, reacts with an oxidising agent, such as **Cl_2**, an ionic compound is formed. The reducing agent, Zn, **loses** electrons (is **oxidised**) and at the same time the oxidising agent, Cl_2, **gains** electrons (is **reduced**). In this case, the products are Zn^{2+} and **Cl^-**, which form $ZnCl_2$.

2 Oxidation reactions involve the loss of electrons, so the electrons will be on the right-hand side of the arrow, while in reduction reactions, the electrons are gained, so will be on the left-hand side of the arrow.

- **a** oxidation
- **b** reduction
- **c** reduction
- **d** oxidation
- **e** reduction
- **f** reduction

3 $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

Because the nickel metal changes from solid metal to a positive ion it must be losing electrons, therefore it must be the species that is being oxidised.

Analysis

4 $Al(s) \rightarrow Al^{3+}(s) + 3e^-$: oxidation

$S(l) + 2e^- \rightarrow S^{2-}(s)$: reduction

5 **a** oxidation half-equation: $Zn(s) \rightarrow Zn^{2+}(s) + 2e^-$
reduction half-equation: $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$
oxidising agent: $O_2(g)$, reducing agent: Zn(s)

b oxidation half-equation: $Ca(s) \rightarrow Ca^{2+}(s) + 2e^-$
reduction half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$
oxidising agent: $Cl_2(g)$, reducing agent: Ca(s)

c oxidation half-equation: $Al(s) \rightarrow Al^{3+}(s) + 3e^-$
reduction half-equation: $Br_2(l) + 2e^- \rightarrow 2Br^-(s)$
oxidising agent: $Br_2(l)$, reducing agent: Al(s)

6 Because metal *M* forms a compound with formula *M*O with oxygen, the ion of metal *M* must be M^{2+}.

a $Ag^+(aq) + e^- \rightarrow Ag(s)$
$M(s) \rightarrow M^{2+}(aq) + 2e^-$
$M(s) + 2Ag^+(aq) \rightarrow M^{2+}(aq) + 2Ag(s)$

b The silver half-equation is reduction, the unknown metal half-equation is oxidation.

c *M*(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent.

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4.2 Oxidation numbers

Worked example: Try yourself 4.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 4.2.1 to determine the oxidation number of each element in $NaNO_3$.

Thinking	Working
Identify an element that has a set value.	Na is a main group metal in group 1. According to rule 3a, the oxidation number of Na is +1.
Identify any other elements that have set values.	According to rule 3c, oxygen will have an oxidation number of –2, unless attached to fluorine or in a peroxide.
Use algebra to work out the oxidation number of other the element.	Let the oxidation of nitrogen in $NaNO_3$ be x. $+1 + x + (3 \times -2) = 0$ $+1 + x - 6 = 0$ $x - 5 = 0$ $x = +5$
Write oxidation numbers above the elements in the formula.	$\overset{+1}{Na}\overset{+5}{N}\overset{-2}{O}_3$

Worked example: Try yourself 4.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation:

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l)$$

Thinking	Working
Determine the oxidation numbers of one of the elements on each side of the equation.	Choose copper as the first element. As copper can have a variable oxidation state, let the oxidation number = x. $x + -2 = 0$ $x = +2$ $\overset{+2}{Cu}O(s) + H_2(g) \rightarrow \overset{0}{Cu}(s) + H_2O(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of copper decreased from +2 to 0, so the copper in CuO has been reduced.
Determine the oxidation numbers of a second element on each side of the equation.	Choose hydrogen as the second element. $CuO(s) + \overset{0}{H_2}(g) \rightarrow Cu(s) + \overset{+1}{H_2}O(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of hydrogen has increased from 0 to +1, so H_2 has been oxidised.
Continue this process until the oxidation numbers of all elements have been determined.	Determine the oxidation numbers of oxygen. $Cu\overset{-2}{O}(s) + H_2(g) \rightarrow Cu(s) + H_2\overset{-2}{O}(l)$ The oxidation number of oxygen has not changed.

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KEY QUESTIONS

Knowledge and understanding

1 **a** +2
b +4
c –4
d 0
e +4

2 D. K_2MnO_4: the oxidation state of K is +1 and of O is –2
(2 × +1) + x + (4 × –2) = 0; hence x = +6
The other answers are incorrect as follows:
A. $MnCl_2$: the oxidation state of Cl is –1
x + –2 = 0; hence x = +2
B. $KMnO_4$: the oxidation state of K is +1, O is –2
+1 + x + (4 × –2) = 0; hence x = +7
C. MnO_2: the oxidation state of O is –2
x + –4 = 0; hence x = +4

3 **a** Ca: +2; O: –2
b Ca: +2; Cl: –1
c H: +1; S: +6; O: –2
d Mn: +7; O: –2
e F: 0
f S: +4; O: –2
g Na: +1; N: +5; O: –2
h K: +1; Cr: +6; O: –2

Analysis

4 **a** **i** $\overset{0}{Mg}(s) + \overset{0}{Cl_2}(g) \longrightarrow \overset{+2}{Mg}\overset{-1}{Cl_2}(s)$
ii Oxidising agent Cl_2; reducing agent Mg
b **i** $2\overset{+4}{S_2}\overset{-2}{O_2}(g) + \overset{0}{O_2}(g) \longrightarrow \overset{+6}{S}\overset{-2}{O_3}(g)$
ii Oxidising agent O_2; reducing agent SO_2
c **i** $\overset{+3}{Fe_2}\overset{-2}{O_3}(s) + 3\overset{+2}{C}\overset{-2}{O}(g) \longrightarrow 2\overset{+4}{Fe}(s) + 3\overset{+4}{S}\overset{-2}{O_2}(g)$
ii Oxidising agent Fe_2O_3; reducing agent CO
d **i** $2\overset{+2}{Fe^{2+}}(aq) + \overset{+1}{H_2}\overset{-1}{O_2}(aq) + 2\overset{+1}{H^+}(aq) \longrightarrow 2\overset{+3}{Fe^{3+}}(aq) + 2\overset{+1}{H_2}\overset{-2}{O}(l)$
ii Oxidising agent H_2O_2; reducing agent Fe^{2+}

5

Redox reaction with oxidation numbers	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$\overset{0}{Na}(s) + \overset{+1}{Ag^+}(aq) \longrightarrow \overset{+1}{Na^+}(aq) + \overset{0}{Ag}(s)$	$Na(s)/Na^+(aq)$	$Ag^+(aq)/Ag(s)$
$\overset{0}{Zn}(s) + \overset{+2}{Cu^{2+}}(aq) \longrightarrow \overset{+2}{Zn^{2+}}(aq) + \overset{0}{Cu}(s)$	$Zn(s)/Zn^{2+}(aq)$	$Cu^{2+}(aq)/Cu(s)$
$2\overset{0}{K}(s) + \overset{0}{Cl_2}(g) \longrightarrow 2\overset{+1}{K}\overset{-1}{Cl}(s)$	$K(s)/K^+(s)$	$Cl_2(g)/Cl^-(s)$

6 **a** In the reaction:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Sodium, Na, has an oxidation number of 0 and Na^+ (in NaOH) has an oxidation number of +1, so sodium is oxidised (an increase in oxidation number indicates oxidation).

While hydrogen has an oxidation number = + 1 in H_2O and OH^-, it has an oxidation number = 0 in H_2.

This means the statement is false and should read:

'In the following reaction sodium is **oxidised** and the oxidation number of hydrogen **changes from +1 to 0** in the equation.'

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

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b When the dichromate ion, $Cr_2O_7^{2-}$, reacts to form Cr^{3+}, the chromium is reduced.

The oxidation number of Cr in $Cr_2O_7^{2-}$ = +6 and the oxidation number of Cr in Cr^{3+} is +3. There is a decrease in oxidation number, so this is reduction.

This means the statement is false and should read:

'When the dichromate ion, $Cr_2O_7^{2-}$, reacts to form Cr^{3+}, the chromium is **reduced**.'

c $2\overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O}_4(aq) + 5\overset{+1}{H}_2\overset{-2}{S}(aq) + 6\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow 2\overset{+4}{Mn}\overset{-1}{Cl}_2(aq) + 5\overset{0}{S}(s) + 2\overset{+1}{K}\overset{-1}{Cl}(aq) + 8\overset{+1}{H}_2\overset{-2}{O}(l)$

The oxidation numbers of the elements are written above the elements in the equation above.

The oxidation number of hydrogen does not change (+1 throughout), nor does that of chlorine (–1 in HCl and KCl), so HCl is neither oxidised nor reduced. The MnO_4^- ion is reduced (the oxidation number of Mn decreases from +7 to +2), and H_2S is oxidised (the oxidation number of S increases from –2 to 0), so the oxidising agent is MnO_4^-.

This means the statement is false and should read:

'In the following reaction the oxidising agent is $\mathbf{MnO_4^-}$ and $\mathbf{H_2S}$ is oxidised.'

$2KMnO_4(aq) + 5H_2S(aq) + 6HCl(aq) \rightarrow 2MnCl_2(aq) + 5S(s) + 2KCl(aq) + 8H_2O(l)$

4.3 Writing complex redox equations

Worked example: Try yourself 4.3.1

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half–equation for the reduction of an acidified solution of MnO_4^- to solid MnO_2.

Thinking	Working
Balance all elements except hydrogen and oxygen in the half-equation.	There is 1 Mn in MnO_4^- and 1 Mn in MnO_2, so the Mn atoms are balanced. $MnO_4^- \rightarrow MnO_2$
Balance the oxygen atoms by adding water.	There are 4 O atoms in MnO_4^- and only 2 O atoms in MnO_2, so 2 H_2O must be added to the right-hand side. $MnO_4^- \rightarrow MnO_2 + 2H_2O$
Balance the hydrogen atoms by adding H^+ ions. Acids provide a source of H^+ ions.	There are now 4 H atoms on the right-hand side and none on the left-hand side, so $4H^+$ ions are added to the left-hand side. $MnO_4^- + 4H^+ \rightarrow MnO_2 + 2H_2O$
Balance the charge in the equation by adding electrons.	The charge on the left-hand side is (–1) + (4 × +1) = +3 and on the right-hand side is 0, so 3 electrons are added to the left-hand side to make the charges equal. $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$
Add states to complete the half-equation.	$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$

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Worked example: Try yourself 4.3.2

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

Write balanced oxidation and reduction half-equations for the reaction in which $SO_3^{2-}(aq)$ and $ClO^-(aq)$ react to form $H_2S(g)$ and $ClO_3^-(aq)$. Then write the overall equation for the reaction.

Thinking	**Working**
Identify one reactant and the product it forms, and write the balanced half-equation.	$SO_3^{2-}(aq) + 8H^+(aq) + 6e^- \rightarrow H_2S(g) + 3H_2O(l)$
Identify the second reactant and the product it forms, and write the balanced half-equation.	$ClO^-(aq) + 2H_2O(l) \rightarrow ClO_3^-(aq) + 4H^+(aq) + 4e^-$
Multiply one or both equations by a suitable factor to ensure that the number of electrons on both sides of the arrow is equal.	The lowest common multiple is 12, so multiply the reduction half-equation by 2 and the oxidation half-equation by 3. $2 \times [SO_3^{2-}(aq) + 8H^+(aq) + 6e^- \rightarrow H_2S(g) + 3H_2O(l)]$ $3 \times [ClO^-(aq) + 2H_2O(l) \rightarrow ClO_3^-(aq) + 4H^+(aq) + 4e^-]$ $2SO_3^{2-}(aq) + 16H^+(aq) + 12e^- \rightarrow 2H_2S(g) + 6H_2O(l)$ $3ClO^-(aq) + 6H_2O(l) \rightarrow 3ClO_3^-(aq) + 12H^+(aq) + 12e^-$
Add the oxidation and the reduction half-equations together, cancelling electrons so that none appear in the final equation. Also cancel H_2O and H^+ if these occur on both sides of the arrow.	$2SO_3^{2-}(aq) + \overset{4}{\cancel{16}}H^+(aq) + 12e^- \rightarrow 2H_2S(g) + \cancel{6H_2O(l)}$ $3ClO^-(aq) + \cancel{6H_2O(l)} \rightarrow 3ClO^{3-}(aq) + \cancel{12H^+(aq)} + 12e^-$
Write the overall redox equation for the reaction.	$2SO_3^{2-}(aq) + 4H^+(aq) + 3ClO^-(aq) \rightarrow 2H_2S(g) + 3ClO_3^-(aq)$

Worked example: Try yourself 4.3.3

BALANCING A HALF-EQUATION IN A BASIC SOLUTION BY DIRECT ADDITION OF HYDROXIDE IONS

Write the half-equation for the oxidation of copper, Cu(s), to copper hydroxide, $Cu(OH)_2(s)$ in a basic (alkaline) solution.

Thinking	**Working**
Note that there are hydroxide ions, OH^-, in the product formula, so the equation can be balanced by the direct addition of hydroxide ions.	$Cu \rightarrow Cu(OH)_2$
Balance all elements except hydrogen and oxygen in the half-equation.	$Cu \rightarrow Cu(OH)_2$
Balance the hydroxide ions by adding $OH^-(aq)$.	$Cu + 2OH^- \rightarrow Cu(OH)_2$
Balance the charge by adding electrons.	$Cu + 2OH^- \rightarrow Cu(OH)_2 + 2e^-$
Add states to complete the half-equation.	$Cu(s) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) + 2e^-$

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Worked example: Try yourself 4.3.4

BALANCING A HALF-EQUATION IN A BASIC SOLUTION WHEN OH⁻ IS NOT PRESENT IN A REACTANT OR PRODUCT

Write the half-equation for the oxidation of hydroxide ions, $OH^-(aq)$, to form oxygen gas, $O_2(g)$, in a basic solution.

Thinking	Working
Balance all elements except hydrogen and oxygen in the half-equation.	No other elements are present in this case. $OH^- \rightarrow O_2$
Balance the oxygen atoms by adding water.	$OH^- + H_2O \rightarrow O_2$
Balance the hydrogen atoms by adding H^+.	$OH^- + H_2O \rightarrow O_2 + 3H^+$
Balance the charge by adding electrons.	$OH^- + H_2O \rightarrow O_2 + 3H^+ + 4e^-$
Add enough hydroxide ions to both sides of the equation to neutralise the H^+.	$OH^- + H_2O + 3OH^- \rightarrow O_2 + 3H^+ + 3OH^- + 4e^-$
The neutralisation reaction between $H^+(aq)$ and $OH^-(aq)$ produces water, so cancel out the water molecules on the side where there are fewer water molecules and reduce the water molecules on the other side by the same number.	$4OH^- + \cancel{H_2O} \rightarrow O2 + \overset{2}{\cancel{3}}H_2O + 4e^-$ $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
Add state symbols.	$4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$

Worked example: Try yourself 4.3.5

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER BASIC CONDITIONS

Combine the following half-equations for the reaction between sulfite ions, $SO_3^{2-}(aq)$, and permanganate, $MnO_4^-(aq)$, ions in a basic solution to give the overall redox equation:

$$SO_3^{2-}(aq) + 2OH^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l) + 2e^-$$
$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$$

Thinking	Working
Multiply one or both equations by a suitable factor to ensure that the number of electrons on both sides of the arrow is equal.	The lowest common multiple is 6, so multiply the reduction half-equation by 3 and the oxidation half-equation by 2. $3 \times [SO_3^{2-}(aq) + 2OH^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l) + 2e^-]$ $2 \times [MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)]$ $3SO_3^{2-}(aq) + 6OH^-(aq) \rightarrow 3SO_4^{2-}(aq) + 3H_2O(l) + 6e^-$ $2MnO_4^-(aq) + 4H_2O(l) + 6e^- \rightarrow 2MnO_2(s) + 8OH^-(aq)$
Add the oxidation and the reduction half-equations together, cancelling electrons so that none appear in the final equation. Also cancel H_2O and OH^- if these occur on both sides of the arrow.	$3SO_3^{2-}(aq) + \cancel{6OH^-}(aq) \rightarrow 3SO_4^{2-}(aq) + \cancel{3H_2O}(l) + \cancel{6e^-}$ $2MnO_4^-(aq) + \cancel{4}H_2O(l) + \cancel{6e^-} \rightarrow 2MnO_2(s) + \overset{2}{\cancel{8}}OH^-(aq)$
Write the overall redox equation for the reaction.	$3SO_3^{2-}(aq) + 2MnO_4^-(aq) + H_2O(l) \rightarrow 3SO_4^{2-}(aq) + 2MnO_2(s) + 2OH^-(aq)$

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CASE STUDY: ANALYSIS

Alcohol and lives lost on the road

Analysis

1 a $C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
  b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
  c The lowest common multiple is 12.
  $3[C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-]$
  $\underline{2[Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)]}$
  $3C_2H_5OH(aq) + \cancel{3H_2O}(l) \rightarrow 3CH_3COOH(aq) + \cancel{12H^+}(aq) + \cancel{12e^-}$
  $2Cr_2O_7^{2-}(aq) + \overset{16}{\cancel{28}}H^+(aq) + \cancel{12e^-} \rightarrow 4Cr^{3}+(aq) + \overset{11}{\cancel{14}}H_2O(l)$
  $3C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

2 This colour change is shown in Figure 4.3.3. The colour change was from orange to green. The dichromate ions, $Cr_2O_7^{2-}$ were orange and the chromium(III), Cr^{3+}, ions were green.

3 0.075% = 0.075 g ethanol in 100 mL blood.
  5.5 L = 5.5×10^3 mL blood

$$\frac{5.5 \times 10^3}{100} = \frac{m(\text{ethanol})}{0.075}$$

$$m(\text{ethanol}) = \frac{5.5 \times 10^3 \times 0.075}{100} = 4.125 \text{ g}$$

KEY QUESTIONS

Knowledge and understanding

1 a $VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$
  b $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$
  c $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$
  d $S2O_3^{2-}(aq) + H_2O(l) \rightarrow 2SO_2(g) + 2H^+(aq) + 4e^-$
  e $NH_4^+(aq) + 3H_2O(l) \rightarrow NO_3^-(aq) + 10H^+(aq) + 8e^-$
  f $SO_4^{2-}(aq) + 10H^+(aq) + 8e^- \rightarrow H_2S(g) + 4H_2O(l)$

2 a Working: $VO_2^+(aq) + 2H^+(aq) + 2OH^-(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l) + 2OH^-(aq)$
  $VO_2^+(aq) + 2H_2O(l) + e^- \rightarrow VO^{2+}(aq) + H_2O(l) + 2OH^-(aq)$
  Final half-equation: $VO_2^+(aq) + H_2O(l) + e^- \rightarrow VO^{2+}(aq) + 2OH^-(aq)$
  b Working: $MnO_4^-(aq) + 4H^+(aq) + 4OH^-(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l) + 4OH^-(aq)$
  $MnO_4^-(aq) + 4H_2O(l) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l) + 4OH^-(aq)$
  Final half-equation: $MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$
  c Working: $SO_3^{2-}(aq) + H_2O(l) + 2OH^-(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2OH^-(aq) + 2e^-$
  $SO_3^{2-}(aq) + H_2O(l) + 2OH^-(aq) \rightarrow SO_4^{2-}(aq) + 2H_2O(l) + 2e^-$
  Final half-equation: $SO_3^{2-}(aq) + 2OH^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l) + 2e^-$

3 a $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
  b $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$
  c $3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$

Analysis

4 a $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
  $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
  $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$
  b $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$
  $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
  $5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$
  c $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
  $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
  $MnO2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$

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5 **a** **i** Ce^{4+} has been reduced to Ce^{3+} and H_2S has been oxidised to S.

ii $Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$

$H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2e^-$

iii $2Ce^{4+}(aq) + H_2S(aq) \rightarrow 2Ce^{3+}(aq) + S(s) + 2H^+(aq)$

b **i** NO_3^- has been reduced to NO and Fe^{2+} has been oxidised to Fe^{3+}.

ii $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$

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

iii $NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \rightarrow NO(g) + 2H_2O(l) + 3Fe^{3+}(aq)$

c **i** H_2O_2 has been reduced to H_2O and Br^- has been oxidised to Br_2.

ii $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$

iii $H_2O_2(aq) + 2H^+(aq) + 2Br^-(aq) \rightarrow 2H_2O(l) + Br_2(l)$

d **i** MnO_2 is reduced to Mn^{2+} and S is oxidised to SO_2.

ii $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$

$S(s) + 2H_2O(l) \rightarrow SO_2(g) + 4H^+(aq) + 4e^-$

iii $2MnO_2(s) + 4H^+(aq) + S(s) \rightarrow 2Mn^{2+} + 2H_2O(l) + SO_2(g)$

6 **a** **i** MnO_4^- has been reduced to MnO_2 and Br^- has been oxidised to $BrO_3^-(aq)$

ii $Br^-(aq) + 6OH^-(aq) \rightarrow BrO_3^-(aq) + 3H_2O(l) + 6e^-$

$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$

iii $Br^-(aq) + 2MnO_4^-(aq) + H_2O(l) \rightarrow BrO_3^-(aq) + 2MnO_2(s) + 2OH^-(aq)$

b **i** $NO_3^-(aq)$ has been reduced to $NH_3(aq)$ and Al(s) has been oxidised to $Al(OH)_4^-(aq)$

ii $Al(s) + 4OH^-(aq) \rightarrow Al(OH)_4^-(aq) + 3e^-$

$NO_3^-(aq) + 6H_2O(l) + 8e^- \rightarrow NH_3(aq) + 9OH^-(aq)$

iii $8Al(s) + 5OH^-(aq) + 3NO_3^-(aq) + 18H_2O(l) \rightarrow 8Al(OH)_4^-(aq) + 3NH_3(aq)$

7 oxidation: $Fe(OH)_2(aq) + OH^-(aq) \rightarrow Fe(OH)_3(aq) + e^-$

reduction: $H_2O_2(aq) + 2e^- \rightarrow 2OH^-(aq)$

overall: $2Fe(OH)_2(aq) + H_2O_2(aq) \rightarrow 2Fe(OH)_3(aq)$

Chapter 4 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 **a** False. Group 1 and 2 metal ions can only gain electrons, so they are oxidising agents.

b True. Reducing agents cause the other reactant to gain electrons, so they must lose electrons. Negative ions can lose electrons to form the neutral atom/molecule.

c False. Metal atoms cannot gain electrons, because they have 1, 2 or 3 electrons in their valence shell and so must lose electrons. Therefore, they are reducing agents, not oxidising agents.

2 D. All of the ions have the correct charge, and the atoms and the charge are both balanced.

A has the wrong charge on the silver ions, which should be Ag^+. B does not show the reaction between lead metal and silver ions; it shows lead ions and silver metal. In C, the charge is not balanced.

3 C. The oxidation number of H is +1 and there are two H atoms, so the oxidation number of S is –2 (the total must be 0).

In A, the oxidation number of S is +6 ($(2 \times +1) + x + (4 \times -2) = 0$, so $x = +6$).

In B, the oxidation number of S is +4 ($x + (2 \times -2) = 0$, so $x = +4$).

In D, the oxidation number of S is +2 ($(2 \times +1) + 2x + (3 \times -2) = 0$, so $2x = +4$ and $x = +2$).

4 The reducing agent will increase in oxidation number during each reaction.

a Ag(s) – Oxidation number increases from 0 in Ag(s) to +1 in $Ag_2O(s)$

b Mg(s) – Oxidation number increases from 0 in Mg(s) to +2 in $MgCl_2(s)$

c Zn(s) – Oxidation number increases from 0 in Zn(s) to +2 in $Zn^{2+}(aq)$

d Al(s) – Oxidation number increases from 0 in Al(s) to +3 in $Al^{3+}(aq)$

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5 A. The charges are balanced and the atoms are balanced.

B is incorrect because the charges are not balanced (negative on the left-hand side and positive on the right-hand side).

C is incorrect because the atoms are not balanced (2 iodine atoms on the left-hand side and only 1 on the right-hand side).

D is incorrect because chemical equations, by convention, only involve addition, never subtraction.

6 C. The correctly balanced equation is $Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-$

All other alternatives result in the charge not being balanced for this half-equation.

7 $Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

The oxidation number of copper **increases** from **0** to +**2** and the oxidation number of nitrogen **decreases** from +**5** to +**4**.

This means that the copper is the **reducing** agent because the nitrogen is **reduced** and the nitrogen (in NO_3^-) is the **oxidising** agent because the copper is **oxidised**.

8

Compound	Element	Oxidation number
$CaCO_3$	Ca	+2
HNO_3	O	–2
H_2O_2	O	–1
HCO_3^-	C	+4
HNO_2	N	+3
$KMnO_4^-$	Mn	+7
H_2S	S	–2
Cr_2O_3	Cr	+3
N_2O_4	N	+4

9 The order of increasing oxidation states of nitrogen is: K_3N, N_2, N_2O, NO, N_2O_3, N_2O_4, $Ca(NO_3)_2$

The oxidation states for nitrogen are as follows:

K_3N: –3
N_2: 0
N_2O: +1
NO: +2
N_2O_3: +3
N_2O_4: +4
$Ca(NO_3)_2$: +5

10

Step	Task	How it's done	Half–equation
1	Balance the nitrogen.	The nitrogen is already balanced.	$NO_3^- \rightarrow NO_2$
2	Balance the oxygen by adding **H_2O**.	Add **one** H_2O molecule(s) to the right-hand side of the equation.	**$NO_3^- \rightarrow NO_2 + H_2O$**
3	Balance the hydrogen by adding **H^+**.	Add **2** H^+ ion(s) to the **left-hand side** of the equation.	**$NO_3^- + 2H+ \rightarrow NO_2 + H_2O$**
4	Balance the charge by adding **electrons**.	Charge on left-hand side = **(–1)** + **(+2)** = +1 Charge on right-hand side = **0** Add e^- to the **left-hand side** of the equation.	**$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$**
5	Add state symbols to give the final half-equation.	Give the appropriate states for each reactant and product in the equation.	**$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$**

11

Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Sn(s) + Br_2(aq) \rightarrow SnBr_2(aq)$	$Sn(s)/Sn^{2+}(aq)$	$Br_2(aq)/Br^-(aq)$
$Zn(s) + CuCl_2(aq) \rightarrow ZnCl_2(aq) + Cu(s)$	$Zn(s)/Zn^{2+}(aq)$	$Cu^{2+}(aq)/Cu(s)$
$Br^-(aq) + 3F_2(g) + 3H_2O(l) \rightarrow 6F^-(aq) + 6H^+ + BrO_3^-(aq)$	$Br^-(aq)/BrO_3^-(aq)$	$F_2(g)/F^-(aq)$
$3Cu(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$	$Cu(s)/Cu^{2+}(aq)$	$Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$

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Application and analysis

12 **b**, **c**, **e**, **f** and **h** are redox reactions because the elements in the reactions undergo changes in oxidation number during the course of the reaction.

The changes in oxidation number that occur are:

b Ag from 0 to +1; Cl from 0 to –1
c Fe from +3 to +2; Sn from +2 to +4
e P from +3 to +5; I from 0 to –1
f Cu from +1 to +2; Cu from +1 to 0
h P from 0 to –3; H from 0 to +1

13 **a** **i** 0
ii +2
b **i** +5
ii +4
c Oxidising agent HNO_3; reducing agent Cu

14 $2IO_3^-(aq) + \mathbf{12}H^+(aq) + \mathbf{10}e^- \rightarrow I_2(aq) + \mathbf{6}H_2O(l)$
$x = 12$, $y = 10$ and $z = 6$

15 oxidation half-equation: $SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H+(aq) + 2e^-$
reduction half-equation: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
overall equation: $5SO_2(g) + 2MnO_4^-(aq) + 2H_2O(l) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 4H^+(aq)$

The lowest common multiple is 10, so you will need to multiply the oxidation half-equation by 5 and the reduction equation by 2 to cancel electrons.

$5SO_2(g) + 10H_2O(l) + 2MnO_4^-(aq) + 16H^+(aq) +10e^- \rightarrow 5SO_4^{2-}(aq) + 20H^+(aq) + 10e^- + 2Mn^{2+}(aq) + 8H_2O(l)$

Then cancel the electrons, H_2O and H^+:

$5SO_2(g) + 2MnO_4^-(aq) + 2H_2O(l) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 4H^+(aq)$

16 **a** **i** In $S_2O_4^{2-}$ oxidation number (ON) of sulfur = +3
$2x + (4 \times -2) = -2$
$2x = +6$
$x = +3$

ii In $S_2O_3^{2-}$ ON(sulfur) = +2
$2x + (3 - 2) = -2$
$2x = +4$
$x = +2$

iii In HSO_3^- ON(sulfur) = +4
$+1 + x + (3 - 2) = -1$
$x - 5 = -1$
$x = +4$

b $S_2O_4^{2-}(aq) + 2H_2O(l) \rightarrow 2HSO_3^-(aq) + 2H^+(aq) + 2e^-$
$S_2O_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow S_2O_3^{2-}(aq) + H_2O(l)$

17 **a** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

b $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

c $SO_2(aq) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
$SO_2(aq) + 2H_2O(l) + I_2(aq) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2I^-(aq)$

d $OCl^-(aq) + 2H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$
$2I^-(aq) \rightarrow I_2(aq) + 2e^-$
$OCl^-(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow Cl^-(aq) + H_2O(l) + I_2(aq)$

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18 a half-equations:
$C_6H_8O_6(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2e^-$
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
b oxidation reaction: $C_6H_8O_6(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2e^-$
reduction reaction: $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

19 a $2H_3AsO_4(aq) + 4H^+(aq) + 4e^- \rightarrow As_2O_3(s) + 5H_2O(l)$
$Br^-(aq) + 3H_2O(l) \rightarrow BrO_3^-(aq) + 6H^+(aq) + 6e^-$
b The lowest common multiple for electrons is 12, so the reduction equation needs to be multiplied by 3 and the oxidation equation needs to be multiplied by 2.
$6H_3AsO_4(aq) + 12H^+(aq) + 12e^- \rightarrow 3As_2O_3(s) + 15H_2O(l)$
$2Br^-(aq) + 6H_2O(l) \rightarrow 2BrO_3^-(aq) + 12H^+(aq) + 12e^-$
Then cancel the electrons, H_2O and H^+.
$6H_3AsO_4(aq) + 2Br^-(aq) \rightarrow 3As_2O_3(s) + 2BrO_3^-(aq) + 9H_2O(l)$

20 a i $2NH_4^+(s) \rightarrow N_2(g) + 8H^+(aq) + 6e^-$
ii $Cr_2O_7^{2-}(s) + 8H^+(aq) + 6e^- \rightarrow Cr_2O_3(s) + 4H_2O(g)$
b Reaction **i** is oxidation because the oxidation number of the nitrogen increases from –3 to 0; reaction **ii** is reduction because the oxidation number of chromium decreases from +6 to +3.
c $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$
d $NH_4^+(s)/N_2(g)$ and $Cr_2O_7^{2-}(aq)/Cr_2O_3(s)$

21 Half-equations:
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$
$H_2SO_3(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + 3H^+(aq) + 2e^-$
Overall equation: $H_2SO_3(aq) + Sn^{4+}(aq) + H_2O(l) \rightarrow Sn^{2+}(aq) + HSO_4^-(aq) + 3H^+(aq)$

22 a $Fe_2O_3(s) + 6e^- \rightarrow 2Fe(l) + 3O^{2-}(l)$
b It is reduction because electrons are gained by the Fe^{3+} in Fe_2O_3.
c $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s)$
d Write a balanced equation:
$Fe_2O_3(s) + 6e^- \rightarrow 2Fe(l) + 3O^{2-}(s)$
Calculate the amount of the given reactant, Fe.

$$n(\text{Fe}) = \frac{3.70\,\text{g}}{55.8\,\text{g}\,\text{mol}^{-1}} = 0.0663\ \text{mol}$$

From the equation, 1 mol Fe_2O_3 produces 2 mol Fe.

$$\frac{n(\text{Fe}_2\text{O}_3)}{n(\text{Fe})} = \frac{1}{2}$$

$$n(\text{Fe2O3}) = \frac{0.0663\ \text{mol}}{2} = 0.0332\ \text{mol}$$

Calculate the mass of Fe_2O_3.

$$m(\text{Fe}_2\text{O}_3) = 0.0332\ \text{mol} \times 159.6\ \text{g mol}^{-1}$$
$$= 5.29\ \text{g (to 3 significant figures)}$$

23 a i $Cr(OH)_3(s)$ is oxidised and $IO_3^-(aq)$ is reduced
ii $Cr(OH)_3(s) + 5OH^-(aq) \rightarrow CrO_4^{2-}(aq) + 4H_2O(l) + 3e^-$
$IO_3^-(aq) + 3H_2O(l) + 6e^- \rightarrow I^-(aq) + 6OH^-(aq)$
iii $2Cr(OH)_3(s) + IO_3^-(aq) + 4OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + I^-(aq) + 5H_2O(l)$
b i $Br^-(aq)$ is oxidised and $Al(OH)_4^-(aq)$ is reduced
ii $Br^-(aq) + 6OH^-(aq) \rightarrow BrO_3^-(aq) + 3H_2O(l) + 6e^-$
$Al(OH)_4^-(aq) + 3e^- \rightarrow Al(s) + 4OH^-(aq)$
iii $Br^-(aq) + 2Al(OH)_4^-(aq) \rightarrow BrO_3^-(aq) + 2Al(s) + 3H_2O(l) + 2OH^-(aq)$

24 half-equations:
$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$
$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$
overall equation:
$Zn(s) + 2MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$

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Chapter 5 Galvanic cells and fuel cells as sources of energy

5.1 Galvanic cells

CASE STUDY: ANALYSIS

A technological leap beginning with a frog's leg

Analysis

1 a $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
  b $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
  c $2Zn(s) + O_2(g) + 2H_2O(l) \rightarrow 2Zn^{2+}(aq) + 4OH^-(aq)$

2 O_2 is the oxidising agent; zinc is the reducing agent.

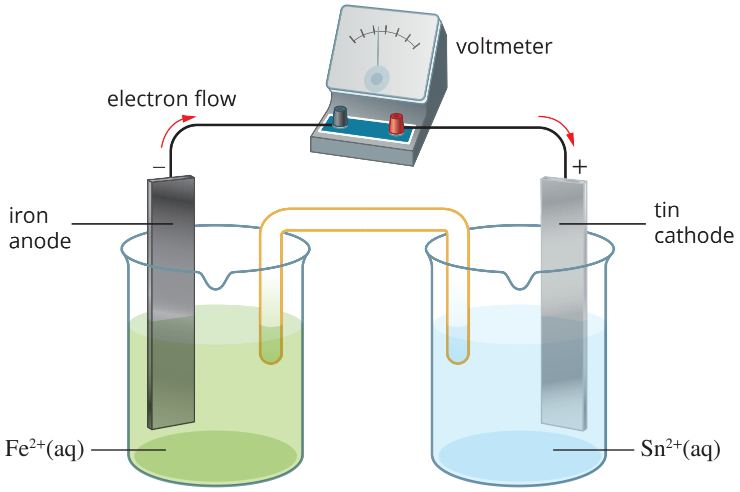
Worked example: Try yourself 5.1.1

DRAWING AND LABELLING A GALVANIC CELL

A cell has the cell reaction: $Sn^{2+}(aq) + Fe(s) \rightarrow Sn(s) + Fe^{2+}(aq)$

Write the two half-equations.

Draw a diagram of the cell, labelling the anode and cathode, electrode polarities (which electrode is positive and which is negative) and the direction of electron flow.

Thinking	Working
Identify the two relevant half-equations.	$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Identify the anode and the cathode in this cell. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.	The electrode in the $Fe^{2+}(aq)/Fe(s)$ half-cell is the anode and the electrode in the $Sn^{2+}(aq)/Sn(s)$ half-cell is the cathode.
Determine the polarities of the electrodes and the direction of electron flow in the cell. The anode is negative and the cathode is positive.	Electrons flow from the negative electrode (anode) to the positive electrode (cathode) as shown in the diagram of the cell below. 

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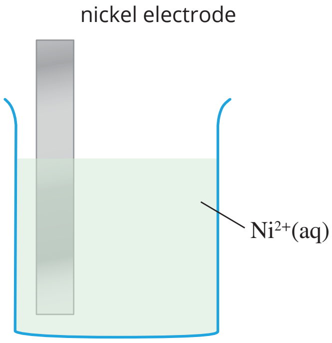
KEY QUESTIONS

Knowledge and understanding

1 **a** A galvanic cell is a type of electrochemical cell that converts chemical energy into electrical energy.
  b An electrochemical cell is a device that converts chemical energy into electrical energy, or vice versa.
  c A salt bridge is an electrical connection between two half-cells in a galvanic cell; it is usually made from a material saturated in electrolyte solution.
  d A battery is a combination of cells connected in series.
  e A primary cell is a galvanic cell that cannot be recharged.

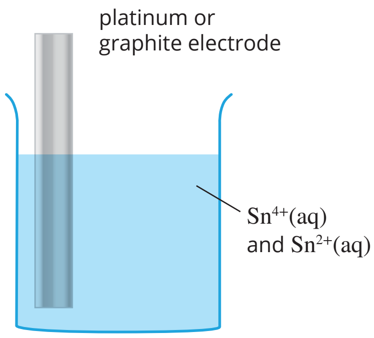
2 A galvanic cell is composed of two half-cells connected by a salt bridge. Each half-cell contains an electrode in contact with a solution. For example, one half-cell might contain Cu(s) and $Cu^{2+}(aq)$ and the other might contain Zn(s) and $Zn^{2+}(aq)$. The species present in each half-cell form a conjugate redox pair (an oxidising agent and its corresponding reduced form). The salt bridge is made from an absorbent material such as filter paper saturated in an electrolyte solution such as potassium nitrate solution.

3 **a**



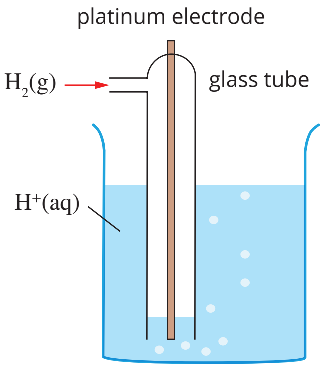
$Ni^{2+}(aq)/Ni(s)$ half-cell

b



$Sn^{4+}(aq)/Sn^{2+}(aq)$ half-cell

c



$H^+(aq)/H_2(g)$ half-cell

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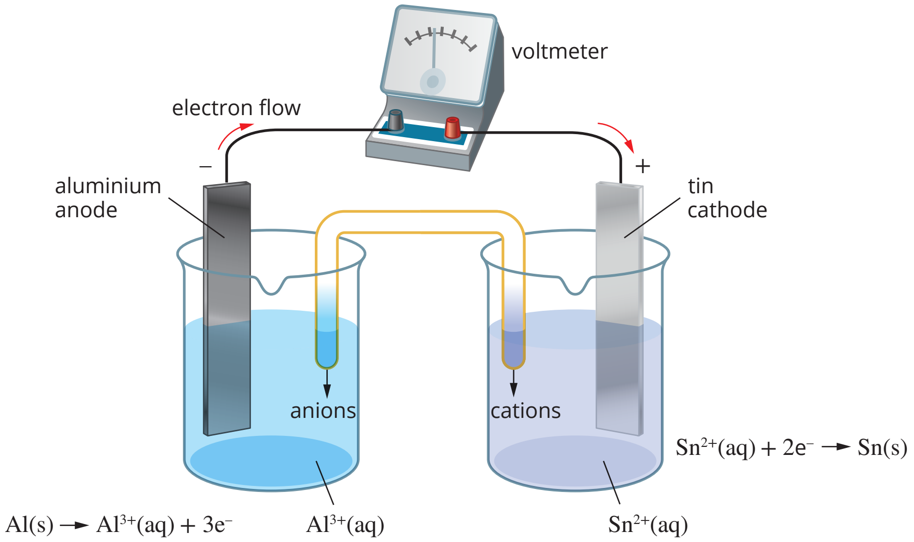
4 In a galvanic cell, electrons move through the external circuit from the **negative** terminal to the **positive** terminal. Cations in the salt bridge move towards the **cathode** and anions in the salt bridge move towards the **anode**.

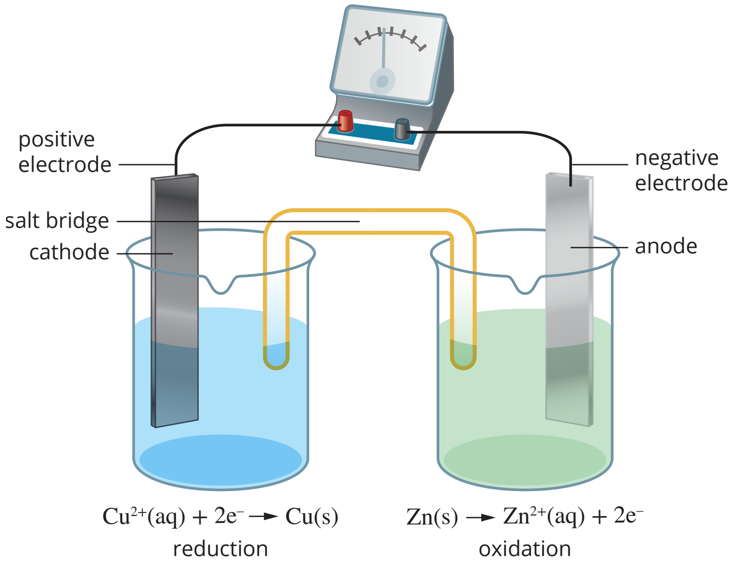
5 **a** Fe(s)—when one member of the conjugate pair in a half-cell is a metal, it is usually used as the electrode.
b Pt or graphite—an unreactive, solid conductive material should be used; Fe(s) is reactive and would be unsuitable.
c Pt or graphite—an unreactive, solid conductive material should be used.

Analysis

6 **a** Al(s) has lost electrons to form $Al^{3+}(aq)$ so it has been oxidised; $Sn^{2+}(aq)$ has gained electrons, so it has been reduced.
b **i** Reduction occurs at the cathode: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
ii Oxidation occurs at the anode: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
c



7 $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$



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5.2 The electrochemical series

Worked example: Try yourself 5.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $Sn^{2+}(aq)/Sn(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells under standard conditions at 25°C. Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Thinking	**Working**
Identify the two relevant half-equations in the electrochemical series.	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ $E° = -0.14$ V $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E° = -0.23$ V
Identify the strongest oxidising agent (the species on the left of the series with the most positive *E*° value) and the strongest reducing agent (the species on the bottom right).	Because Sn^{2+} is higher on the left side of the table than Ni^{2+}, it is the stronger oxidising agent. Ni is lower on the right side of the table than Sn, so it is the stronger reducing agent.
Write the two half-equations that will occur. The strongest oxidising agent will react with the strongest reducing agent. (Hint: The reduction equation has the most positive *E*° value and the oxidation equation has the most negative *E*° value.) Remember that the oxidation reaction should be written in reverse.	Reduction: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ Oxidation: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
Write the overall cell equation.	$Sn^{2+}(aq) + Ni(s) \rightarrow Sn(s) + Ni^{2+}(aq)$
Identify the anode and the cathode in this cell. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.	The nickel electrode is the anode and the tin electrode is the cathode.
Determine the polarities of the electrodes and the direction of electron flow in the cell. The anode is negative and the cathode is positive.	Electrons flow from the negative electrode (anode) to the positive electrode (cathode).

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Worked example: Try yourself 5.2.2

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series:

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)\ E^\circ = +1.36\ V$$

$$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)\ E^\circ = +0.54\ V$$

$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)\ E^\circ = -0.13\ V$$

Use the electrochemical series to predict the effect of mixing:

a $I_2(s)$ and $Pb^{2+}(aq)$

b $Cl^-(aq)$ and $I_2(s)$

c $Cl_2(g)$ and $Pb(s)$.

Thinking	Working
Identify the two relevant half-equations in the electrochemical series. Predict whether or not a reaction occurs. A chemical species on the left (an oxidising agent) of the electrochemical series reacts with a chemical species on the right (a reducing agent) that is lower in the series. If a reaction will occur, write the overall equation.	**a** $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)\ E^\circ = +0.54\ V$ $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)\ E^\circ = -0.13\ V$ No reaction occurs because both I_2 and Pb^{2+} are oxidising agents.
	b $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)\ E^\circ = +1.36\ V$ $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)\ E^\circ = +0.54\ V$ No reaction because the oxidising agent, I_2, is below the reducing agent, Cl^-, in the electrochemical series.
	c $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)\ E^\circ = +1.36\ V$ $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)\ E^\circ = -0.13\ V$ A reaction occurs because the oxidising agent, Cl_2, is above the reducing agent, Pb, in the electrochemical series. The higher half-equation occurs in the forward direction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ The lower half-equation occurs in the reverse direction: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$ The overall reaction equation is found by adding the half-equations: $Cl_2(g) + Pb(s) \rightarrow 2Cl^-(aq) + Pb^{2+}(aq)$

KEY QUESTIONS

Knowledge and understanding

1 **a** In the context of a galvanic cell, the potential difference measures the tendency to push electrons into the external circuit. It is the electromotive force between two points in a circuit.

b Standard conditions are reference conditions used to compare measurements. Gas pressure is 100 kPa and the concentration of dissolved species is 1 mol L^{-1}. Temperatures are usually measured at 25°C.

c The standard electrode potential is the voltage measured when a half-cell, at standard conditions, is connected to a standard hydrogen half-cell.

2 In a galvanic cell, the stronger reducing agent is in the half-cell with the **negative** electrode. This electrode is the **anode**. The stronger oxidising agent is in the half-cell with the **positive** electrode. This electrode is the **cathode**.

3 The half-cell should be constructed at standard conditions (gas pressures of 100 kPa, concentrations of 1 mol L^{-1}) and temperature of 25°C. The cell is connected to a standard hydrogen electrode to form a galvanic cell, and the potential difference of the cell is measured with a voltmeter. This value is the standard electrode potential (E°). If the electrode in the half-cell is negative, the E° is given a negative sign; if the electrode in the half-cell is positive the E° is given a positive sign.

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4 There are two possible reasons:

- When conditions are not standard, the order of half-reactions in the electrochemical series may be different.
- The rate of the reaction may be slow.

5 **a** Because the half-equation involving lithium in the electrochemical series has a more negative *E*° than the one involving sodium, lithium is a stronger reducing agent than sodium.

b Because the half-equation involving $Fe^{2+}(aq)$, an oxidising agent in the electrochemical series, has a more positive *E*° than the one involving $Ca^{2+}(aq)$, $Fe^{2+}(aq)$ is a stronger oxidising agent than $Ca^{2+}(aq)$.

c Because $Sn^{2+}(aq)$ appears in separate half-equations on both sides of the electrochemical series, it can act as either an oxidising agent or a reducing agent in different reactions.

As an oxidising agent, the half-equation is $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

As a reducing agent, the half-equation is $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

Analysis

6 –0.40 V

The *E*° of a half-cell is determined by connecting the half-cell to a standard hydrogen electrode to form a galvanic cell and measuring the potential difference of the cell.

In this case, the equation shows that a $Cr^{3+}(aq)/Cr^{2+}(aq)$ half-cell has been connected to a standard hydrogen electrode. Because oxidation is occurring in this half-cell (electrons are produced as $Cr^{2+}(aq)$ becomes $Cr^{3+}(aq)$), the electrode of the half-cell is negative and *E*° = –0.40 V.

7 **a** Because Pb^{2+} is higher on the left side of the table than Al^{3+}, it is the stronger oxidising agent and is reduced. Al is lower on the right side of the table than Pb, so it is a stronger reducing agent and is oxidised.

Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

b Multiply the Pb^{2+}/Pb half-equation by three and the Al^{3+}/Al half-equation by two so that the number of electrons in each half-equation is equal, and then add the two equations together:

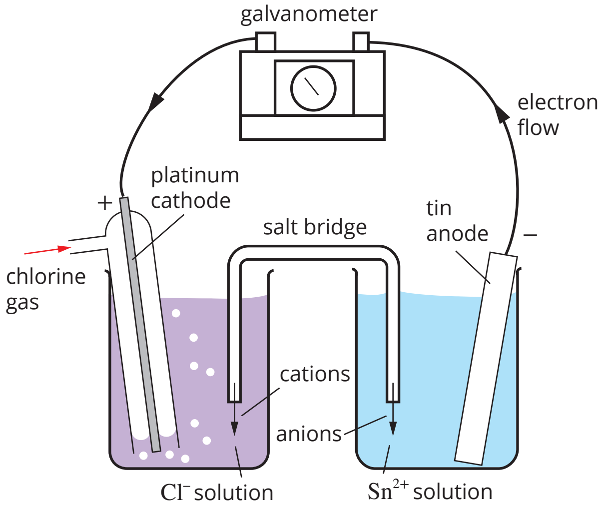
$[Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)] \times 3$

$[Al(s) \rightarrow Al^{3+}(aq) + 3e^-] \times 2$

$3Pb^{2+}(aq) + 2Al(s) \rightarrow 3Pb(s) + 2Al^{3+}(aq)$

c The lead electrode is the cathode and the aluminium electrode is the anode.

8



$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

Overall reaction: $Cl_2(g) + Sn(s) \longrightarrow 2Cl^-(aq) + Sn^{2+}(aq)$

9 Question **7** cell:

cell potential difference = higher half-cell *E*° – lower half-cell *E*°

$= E°(Pb^{2+}(aq)/Pb(s)) - E°(Al^{3+}(aq)/Al(s))$

$= -0.13 - (-1.67)$

$= 1.54$ V

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Question **8** cell:

cell potential difference = higher half-cell E° – lower half-cell E°

$= E^\circ(Cl_2(g)/Cl^-(aq)) - E^\circ(Sn^{2+}(aq)/Sn(s))$

$= 1.36 - (-0.14)$

$= 1.50$ V

10 **a** A reaction occurs because the oxidising agent, Cl_2, is above the reducing agent, Br^-, in the electrochemical series, i.e. Cl_2 is a stronger oxidising agent than Br_2.

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

b A reaction occurs because the oxidising agent, Cl_2, is above the reducing agent, I^-, in the electrochemical series, i.e. Cl_2 is a stronger oxidising agent than I_2.

$$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$$

c No reaction because the oxidising agent, Br_2, is below the reducing agent, Cl^-, in the electrochemical series, i.e. Br_2 is a weaker oxidising agent than Cl_2.

d A reaction occurs because the oxidising agent, Br_2, is above the reducing agent, I^-, in the electrochemical series, i.e. Br_2 is a stronger oxidising agent than I_2.

$$Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$$

5.3 Fuel cells

KEY QUESTIONS

Knowledge and understanding

1 A fuel cell is a type of galvanic cell that generates electricity from redox reactions quietly and efficiently, and with almost no pollution. Unlike primary cells, fuel cells do not run down. Electricity is available for as long as fuel is supplied to them from an external source.

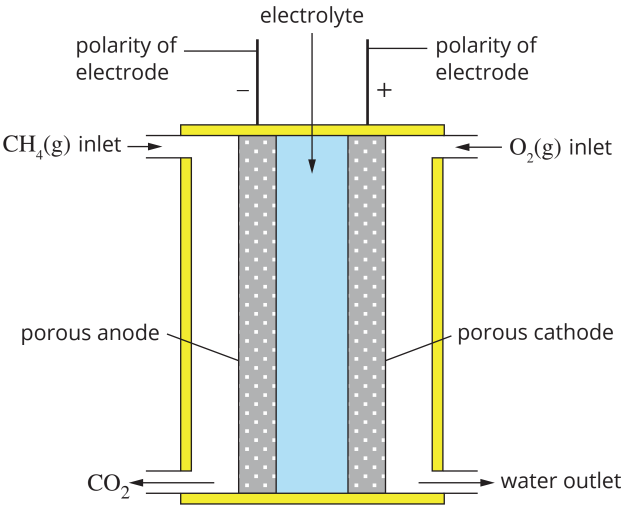
2 B. Cations in the electrolyte move towards the cathode, C. The anode is negative and G. Chemical energy is converted into electrical energy.

While A, D and F may be true for some primary cells, they are not true for all primary cells. Oxidation occurs at the anode in both types of cell.

3 The surface area of a porous material is the total of the surface area within all the pores. Therefore, the porosity of the electrodes creates a very large surface area. The increased surface area means that for the same flow rate of reactant gas there will be more molecules in contact with the catalyst. Therefore, the rate of half-cell reactions will increase. This will produce a greater current from the fuel cell.

Analysis

4



5 **a** anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

b $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

6 **a** $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

b reduction of $O_2(g)$

c KOH(aq) or NaOH(aq)

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- **d** Oxygen is reduced, forming OH^- ions at the cathode of the fuel cell, so an increase in pH occurs at this electrode initially. The OH^- ions migrate to the anode, where they are consumed. Once the rate of production of OH^- ions at the cathode becomes equal to the rate at which they depart, the pH near the electrode will be constant.
- **e** A fuel cell converts chemical energy into electrical energy directly, with relatively little energy being converted into thermal energy. If electrical energy were obtained by burning methanol (in a process like that used to obtain electrical energy from coal in coal-fired power stations), the energy 'losses' of the various energy transformations involved would be greater. Large losses occur when thermal energy is converted into mechanical energy.

5.4 Supplying energy sustainably

CASE STUDY: ANALYSIS

Redox flow batteries

Analysis

1 **a** $V^{2+}(aq) \rightarrow V^{3+}(aq) + e^-$

b $VO_2^+(aq) + 2H^+(aq) + V^{2+}(aq) \rightarrow VO^{2+}(aq) + H_2O(l) + V^{3+}(aq)$

c cell potential difference = higher half-cell $E°$ – lower half-cell $E°$

$$= 1.00 - (-0.26)$$
$$= 1.26\text{ V}$$

d Vanadium redox flow batteries can contribute to an energy supply based on sustainable sources (e.g. solar or wind) because they can balance fluctuations in supply that occur from these sources.

This question may be answered in terms of the green chemistry principles listed in Chapter 1 (page 15). These include:

- design for degradation—vanadium redox flow batteries have long lifetimes and vanadium is much safer for the environment and less toxic than other chemicals used in batteries, such as lead and cadmium
- design for energy efficiency—efficiencies of up to 85% have been achieved, and scientists continue to seek higher efficiencies by improving cell design
- prevention of waste—the reactants in the cell are regenerated almost indefinitely during the recharging cycles, so waste is minimal. There are almost no emissions of gases such as CO_2
- use of renewable feedstocks—the vanadium-based electrolyte is regenerated when the battery is recharged.

2 **a** $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$

b $Br_2(aq) + Zn(s) \rightarrow 2Br^-(aq) + Zn^{2+}(aq)$

c Zinc is plated on the cathode during the charging cycle, when the cell reaction above is reversed.

d The membrane between the compartments allows exchange of ions to balance charges formed in the compartments while preventing contact between the $Br_2(aq)$ and Zn(s), which would otherwise react directly.

KEY QUESTIONS

Knowledge and understanding

1 Fuel cells are about twice as efficient as coal-fired power stations. Consequently, fuel cells produce the same quantity of energy from about half as much fuel. Less fuel means less carbon dioxide gas is produced. As carbon dioxide is a major greenhouse gas, the use of fuel cells has the potential to reduce the greenhouse effect. The use of fuel cells operating on hydrogen obtained from sustainable sources is the ideal, but currently about 95% of hydrogen is produced from fossil fuels.

2 Fuel cells have a much higher efficiency than thermal power stations because chemical energy is directly converted into electrical energy. There are several energy conversions in a fossil fuel power stations (chemical energy → heat energy → mechanical energy → electrical energy), and each one involves a loss of energy.

3 Steam reforming of fossil fuels, decomposition of water using electricity (electrolysis) and steam reforming of biogas. Most hydrogen is produced from fossil fuels.

Analysis

4 Design for energy efficiency—efficiencies of up to 35% have been achieved, and scientists continue to seek higher efficiencies by improving cell design.

Use of renewable feedstocks—low-grade waste materials such as soils and sediments, wastewater and agricultural waste are used.

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5 **a** $CH_4(g) + 4O^{2-}(s) \rightarrow CO_2(g) + 2H_2O(g) + 8e^-$

b Catalysts are incorporated in electrodes to increase the rate of reaction and allow more current to be produced by the cell. Since reaction rate increases with temperature, the use of very high temperatures may mean that a catalyst is not required.

c Scientists may investigate different types of electrode materials, catalysts, electrolytes, fuels and cell operating conditions (e.g. different temperatures and pressures).

d SOFCs operate at much higher efficiencies than fossil fuel power stations, which are the traditional source of electricity. As a consequence, less fossil fuel is consumed (none at all if a sustainable source of fuel is used) and less CO_2 emissions are produced per quantity of electricity.

Chapter 5 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 **a** An oxidising agent is a substance that causes another substance to be oxidised and is reduced in the process. A reducing agent is a substance that causes another substance to be reduced and is oxidised in the process.

b An anode is the electrode at which oxidation occurs. A cathode is the electrode at which reduction occurs.

c An external circuit is a circuit where the electrons flow (e.g. through wires). An internal circuit is the part of cell where the current is due to the movement of ions (e.g. in the salt bridge).

d A battery consists of a number of cells connected together in series.

2 **a** the standard hydrogen electrode

b Standard conditions are gas pressures of 100 kPa (1 bar), and solution concentrations of 1 mol L^{-1}. A temperature of 25°C is usually used for measurements of electrode potentials.

3 cell potential difference = higher half-cell E° – lower half-cell E°

$$= E^\circ\,(Cu^{2+}(aq)/Cu(s)) - E^\circ\,(Zn^{2+}(aq)/Zn(s))$$
$$= 0.34 - (-0.76)$$
$$= 1.10\text{ V}$$

4 Oxidising agents are on the left-hand side of the table and reducing agents are on the right. The oxidising agents are listed in increasing order of strength, with the strongest oxidising agent, F_2, at the top left of the table. The reducing agents are listed in decreasing order of strength, with the strongest reducing agent, Li, at the bottom right of the table.

5 The electrochemical series is based on reactions occurring under standard conditions of 100 kPa pressure and 1 M concentration, and a temperature of 25°C (298 K), and can only be used to predict the possibility of reaction occurring under these conditions. The series gives no information about the rate of reactions, so even if a reaction is predicted it may be so slow that no reaction is apparent.

6 A spontaneous redox reaction will occur if an oxidising agent (on the **left** of the electrochemical series) reacts with a reducing agent (on the **right** of the series) that has a half-reaction with a **less** positive E° value. When the reactants are in direct contact, **heat** energy is released.

7 Although the cost of electrical energy purchased in the form of a dry cell or button cell is far higher than the cost of mains electricity, people are prepared to pay the higher price for the convenience and flexibility of the portable equipment powered by these cells. Furthermore, the price of individual cells is regarded as relatively low.

8 The redox reaction occurring in a galvanic cell takes place in two **half-cells**. The electrode at which oxidation occurs is called the **anode**, whereas the other electrode where reduction occurs is the **cathode**. The polarity of the anode is **negative** and the polarity of the cathode is **positive**.

Galvanic cells can be classified as either primary cells, which **cannot**, be recharged, or secondary cells, which **can** be recharged.

9 D. Reduction occurs at the cathode; the only substance in the list that can act as an oxidising agent (and be reduced) is O_2.

10 At the anode of a fuel cell the fuel (often **hydrogen**) undergoes **oxidation** that generates ions and electrons. The ions move through the **electrolyte**. At the same time, electrons flow from the **negative** electrode to the cathode, producing electricity. The cell converts the **chemical** energy of the fuel and an oxidising agent into **electrical** energy. The energy efficiencies of fuel cells are generally **higher** than if the fuel were burnt in a power station or internal combustion engine and they have **lower** levels of emissions.

11 **a** True. Currently, most hydrogen is produced from fossil fuels, particularly natural gas.

b False. Many scientists believe hydrogen will ultimately be regarded as being as safe as petrol as a fuel for vehicles.

c False. The energy available per litre of liquid or high pressure hydrogen is much less than for a liquid hydrocarbon fuel such as petrol.

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Application and analysis

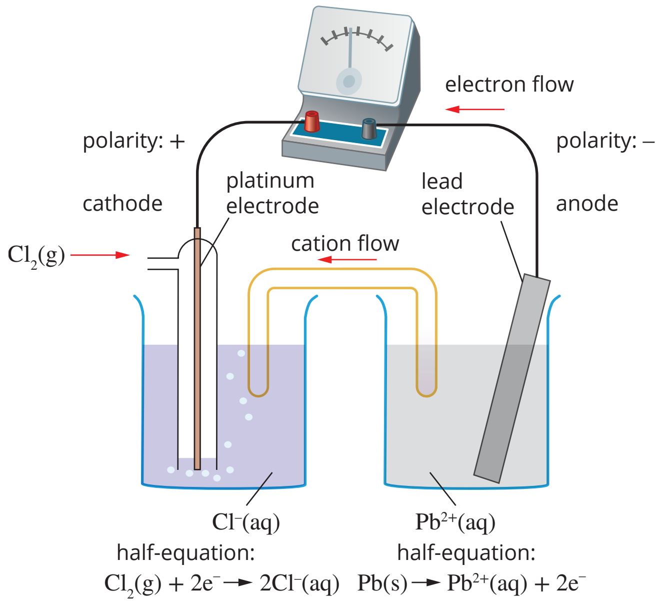
12 D. D is the only correct option—the electrode where oxidation occurs (i.e. the anode) has a negative polarity.

A is incorrect because in galvanic cells, the electrode in the half-cell in which oxidation occurs is called the anode.

B is incorrect because electrons flow from the anode to the cathode. The cathode is where reduction takes place.

C is incorrect because anions flow into the half-cell where oxidation, not reduction, occurs (towards the anode).

13



14 **a** Oxidising agent, since it can be reduced to form I^-.

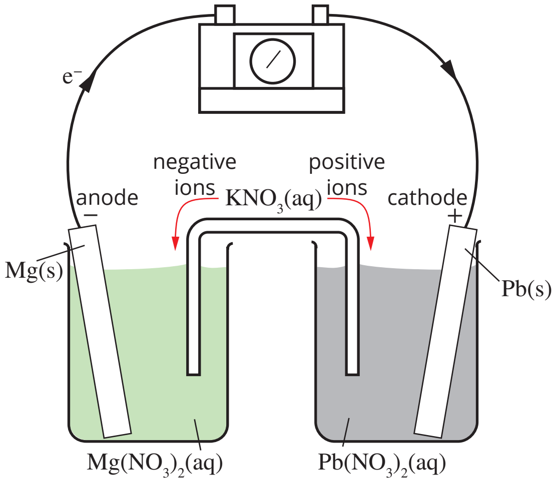
b Strong reducing agent, since it appears on the bottom right of the electrochemical series (E° $Ca^{2+}(aq)/Ca(s)$) = –2.87 V).

c True, since Ni is below Ag on the right-hand side of the electrochemical series.

d False, since Cu^{2+} is below Ag^+ on the left-hand side of the electrochemical series.

e True, since Fe^{2+} appears on both the left and right sides of the electrochemical series.

15 **a**



b $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

Overall: $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$

c The lead electrode is the cathode; the magnesium electrode is the anode.

d Anions will migrate to the $Mg^{2+}(aq)/Mg(s)$ half-cell, and cations will migrate to the $Pb^{2+}(aq)/Pb(s)$ half-cell.

16 D. CH_4 could be used as the fuel and O_2 is the oxidising agent in a fuel cell. The CH_4 would be oxidised in the anode compartment, forming CO_2. Reduction of oxygen would occur in the cathode compartment. None of the other reactions is a redox reaction.

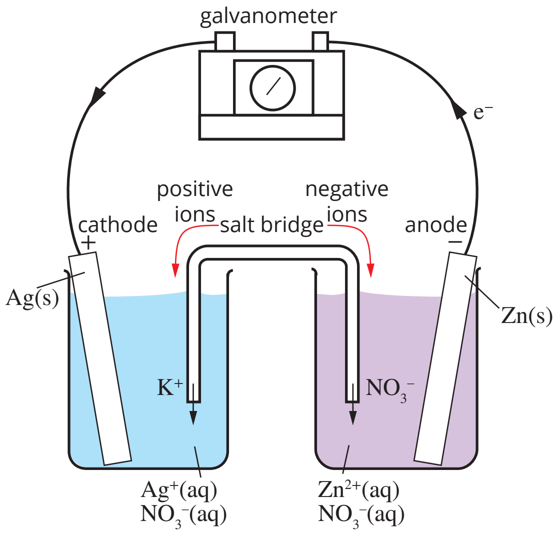
17 A reducing agent is oxidised. Oxidation occurs at the anode, which is the negative electrode.

In the first cell, the reducing agents are Sn^{2+} and Fe^{2+}. Because Sn^{2+} is contained in the half-cell with the anode, Sn^{2+} is the stronger reducing agent.

In the second cell, the reducing agents are Fe^{2+} and Br^-. Because Fe^{2+} is contained in the half-cell with the anode, Fe^{2+} is the stronger reducing agent.

Therefore, the order of reducing agent strength, from strongest to weakest, is $Sn^{2+} > Fe^{2+} > Br^-$.

18 i



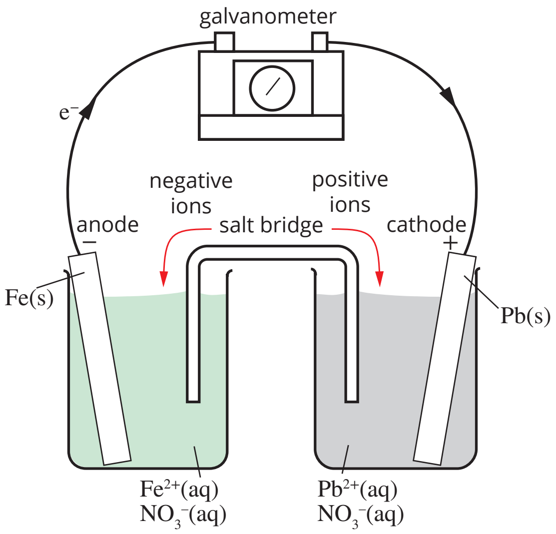
Cathode (+): $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Anode (−): $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Overall: $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

Standard cell potential difference = 1.56 V

ii



Cathode (+): $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$

Anode (−): $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Overall: $Fe(s) + Pb^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Pb(s)$

Standard cell potential difference = 0.31 V

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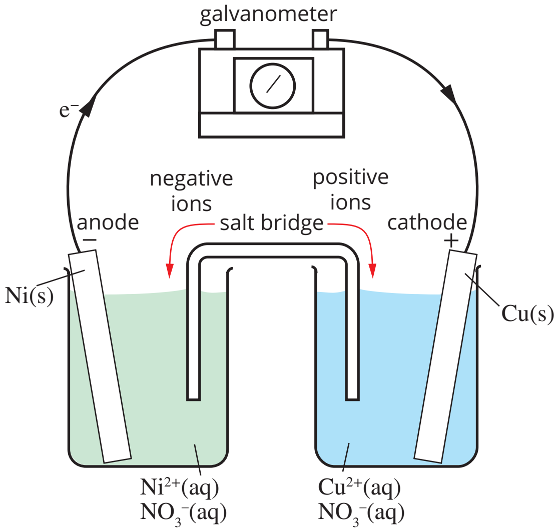
iii



Cathode (+): $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Anode (–): $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$

Overall: $Ni(s) + Cu^{2+}(aq) \longrightarrow Ni^{2+}(aq) + Cu(s)$

Standard cell potential difference = 0.57 V

19 Reduction occurs at the cathode, which is the positive electrode. The half-cell containing the cathode contains the stronger oxidising agent and, therefore, the higher reduction half-cell potential. Only the cations in solution can be reduced, so they are the oxidising agents in each half-cell.

In the first cell, the oxidising agents are A^{2+} and B^{2+}. Because B^{2+} is contained in the half-cell with the cathode, B^{2+} is the stronger oxidising agent.

In the second cell, the oxidising agents are A^{2+} and C^{2+}. Because A^{2+} is contained in the half-cell with the cathode, A^{2+} is the stronger oxidising agent.

In the third cell, the oxidising agents are C^{2+} and D^{2+}. Because C^{2+} is contained in the half-cell with the cathode, C^{2+} is the stronger oxidising agent.

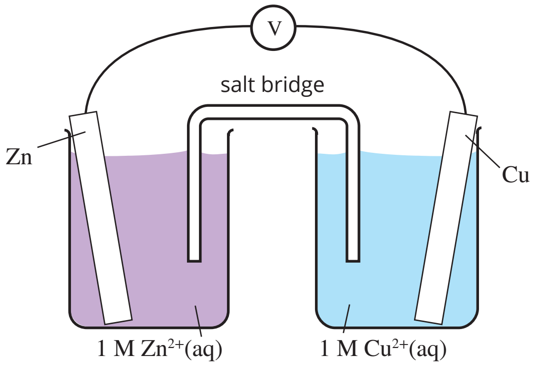
Therefore the order of half-cell potentials, from lowest standard electrode potential (most negative) to highest electrode potential, is $D^{2+}/D < C^{2+}/C < A^{2+}/A < B^{2+}/B$.

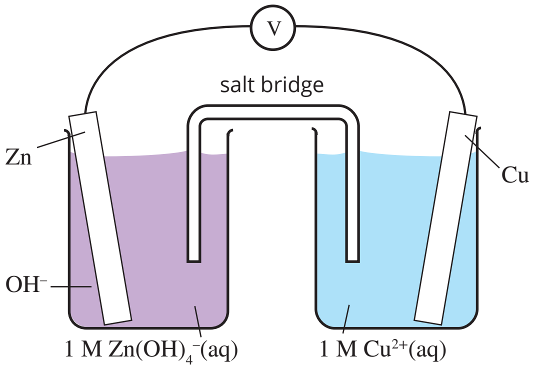
20 **a** $Zn(s) + 4OH^-(aq) + Cu^{2+}(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2Cu(s)$

b The student could make two electrochemical cells consisting of the following, and as shown in the diagrams below:

- Cu^{2+}/Cu half-cell and the Zn^{2+}/Zn half-cell.
- Cu^{2+}/Cu half-cell and the 'alkaline zinc half-cell'

The cell voltages could be measured and if they are identical then the two half-cells have the same *E*° values. (They would not be expected to have the same *E*° values.)





Alternatively, the student could construct a cell from the two different zinc half-cells. If a voltage is observed, they must have different *E*° values.

c The independent variable is the type of half-cell, $Zn^{2+}(aq)/Zn(s)$ or $Zn(OH)_4^{2-}(aq)/ Zn(s)$ (i.e. the reaction occurring in the half-cell with the zinc electrode). Another possible answer is that the independent variable is the electrolyte in the zinc half-cell ($Zn^{2+}(aq)$ or $Zn(OH)_4^{2-}(aq)$).

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d Any two of: the concentration of Zn^{2+} and $Zn(OH)_4^{2-}$ in the half-cells; the size of the zinc electrodes; the temperature of the solution.

e The dependent variable is the standard electrode potential (E°) of the half-cells, as measured by the cell voltages.

f For example: To determine whether the standard electrode potential (E°) of a $Zn^{2+}(aq)/Zn(s)$ half-cell is the same as that of a $Zn(OH)_4^{2-}(aq)/ Zn(s)$ half-cell.

21 a i Reaction would occur.

ii $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation)
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ (reduction)

iii $Zn(s) + Cl_2(g) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq)$

b i No reaction would occur.

c i Reaction would occur.

ii $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation)
$Ag^+(aq) + e^- \rightarrow Ag(s)$ (reduction)

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

d i No reaction would occur.

22 a strongest: $Ag^+(aq)$; weakest: $Mg^{2+}(aq)$

b strongest: $Mg(s)$; weakest: $Ag(s)$

c A coating of silver will form on the lead when it is placed in silver nitrate solution because Ag^+ ions are stronger oxidising agents than Pb^{2+} ions.

d zinc and magnesium

23 a $Fe^{2+}(aq)$ and $H^+(aq)$ will be formed, the half-equation with the oxidising agent $Fe^{3+}(aq)$ is higher on the electrochemical series than the half-equation with $H_2(g)$ acting as a reducing agent.

b $2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

c If significant reaction had occurred, the yellow solution containing Fe^{3+} ions would have become pale green as Fe^{2+} ions formed. Because no reaction was observed, the rate of the reaction may have been slow. It also must be remembered that the electrochemical series is only valid for certain conditions. It is possible that under the conditions in which the experiment was performed, little reaction would occur.

24 a $CH_3CH_2OH(g) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$

b $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

c Cations will move towards the cathode. Because H^+ ions are involved in the reduction reaction, positive charge is decreasing at the cathode. To maintain charge neutrality, cations from the electrolyte will move towards the cathode.

d Yes. The net cell reaction in the fuel cell is the oxidation of ethanol to form carbon dioxide and water. Like ethanol, methane in natural gas can be oxidised to carbon dioxide and water. Provided the electrode materials used in the cell act as effective catalysts for both reactions, it is likely that the use of natural gas would produce a voltage.

25 a $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$

b i negative

ii anode

c The technology promises a cleaner and more efficient way of converting coal to electrical energy than coal-fired power stations, which operate at about 40% efficiency. The CO_2 generated would be approximately half the volume of that produced by current systems for the same amount of electricity, and the cost to capture the carbon would be less. This technology could help to reduce the consumption of the world's declining coal reserves.

26 a $CH_4(g) + H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$. Oxidation occurs at the anode, which is the negative electrode in a fuel cell. CH_4 is the fuel that is oxidised.

b cell potential difference = higher half-cell E° – lower half-cell E°

$$= +1.23 - (+0.17)$$

$$= 1.06\ \text{V}$$

c There is evidence that some cobalt mining involves child labour and human rights violations and that some supply chains are controlled by militia.

27 a arrow A

b O_2 is the oxidising agent, entering the air space from outside.

c $4Al(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al^{3+}(aq) + 12OH^-(aq)$

d The cathode is the site of the reduction reaction involving oxygen/air, which must be in contact with the electrolyte. A porous electrode will allow a large surface area for this reaction, maximising the rate of reaction and therefore the current/power output of the cell.

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e From the electrochemical series:

cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $E° = +0.40$ V

anode reactions: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E° = –0.76$ V

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E° = + 0.80$ V

Because $E°(Zn^{2+}/Zn) < E°(O_2, H_2O/OH^-)$, a spontaneous cell reaction will occur. Because $E°(Ag^+/Ag) > E°(O_2, H_2O/OH^-)$ a spontaneous cell reaction will not occur.

f smaller, since $E°(Zn^{2+}/Zn) > E°(Al^{3+}/Al)$

$E°(O_2, H_2O/OH^-) – E°(Zn^{2+}/Zn) = (+0.40) – (–0.76) = 1.16$ V

$E°(O_2, H_2O/OH^-) – E°(Al^{3+}/Al) = (+0.40) – (–1.66) = 2.06$ V

g With an acidic electrolyte:

cathode reaction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E° = +1.23$ V

anode reactions: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E° = –0.76$ V

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E° = +0.80$ V

Because $E°(Zn^{2+}/Zn) < E°(O_2, H^+/H_2O)$, a spontaneous cell reaction will occur. Because $E°(Ag^+/Ag) < E°(O_2, H^+/H_2O)$, a spontaneous cell reaction will also occur.

Essentially, O_2 becomes a stronger oxidising agent in acidic conditions and is capable of spontaneous reaction with the relatively weak reducing agent, Ag.

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Unit 3 Area of Study 1

What are the current and future options for supplying energy?

Multiple-choice questions

1 C. Reactions involving fuels release energy to the surroundings, so the enthalpy stored in the products will always be lower (not higher) than that in the reactants. All combustion reactions (when energy is obtained from a fuel) are exothermic, with chemical energy being converted into heat and sometimes light energy. Exothermic reactions have a negative value for ΔH.

2 D. Carbon dioxide and water are the products of complete combustion of any carbon-based fuel and the equation in alternative D is correctly balanced. The equations in alternatives A and B are examples of incomplete combustion. While the equation in alternative C represents a combustion reaction, it is not correctly balanced.

3 A. The carbon released by combustion of biodiesel derives from carbon dioxide absorbed by plants during photosynthesis, so there is no net addition to existing levels from the combustion, whereas the carbon released by combustion of fossil fuels has come from underground deposits and adds to the existing levels of CO_2. There is no such thing as different strengths of carbon dioxide as a greenhouse gas. The combustion of biodiesel does not produce methane and does not produce significantly more energy than fossil fuels when it is burnt. Alternative D also does not state which fuel biodiesel produces more energy than, so is an alternative best avoided.

4 A. The oxidation numbers for nitrogen are as follows: $\overset{-3}{N}H_4^+$, $\overset{0}{N}_2$, $\overset{+2}{N}O$, $\overset{+5}{N}O_3^-$ Only alternative A has these in increasing order (most negative value to most positive value).

5 C. The anode is, by definition, the site of oxidation in any cell, so oxidation is the electrode reaction. In a galvanic cell, oxidation occurs when the best reducing agent loses electrons, which move into the external circuit, making this electrode the source of electrons, or the negative electrode.

6 D. $q = mc\Delta T$

$12.6 \times 10^3 = 250 \times 4.18 \times \Delta T$

$$\Delta T = \frac{12.6 \times 10^3}{250 \times 4.18}$$

$= 12.1°C$

The initial temperature of the water was 18.5°C, so with an increase of 12.1°C, the final temperature will be 30.6°C.

7 C. The negative ΔH value indicates a decrease in enthalpy overall, but bond breaking is necessary for initiation, so there will be an initial increase (i.e. an activation energy barrier). The definition of ΔH is H(products) – H(reactants), so the arrow with 2220 kJ should be between the enthalpy of the reactants and the enthalpy of the products.

8 B. $n(C_3H_8) = \frac{100}{44.0} = 2.27$ mol

energy released (exothermic) = $\frac{2220}{1} \times 2.27 = 5.05 \times 10^3$ kJ

9 B. 1 MJ = 1.00×10^3 kJ

$n(CO_2) = \frac{1.00 \times 10^3}{2200} \times 3 = 1.35$ mol

$V(CO_2) = n \times V_m = 1.35 \times 24.8 = 33.5$ L

10 C. The negative ΔH value indicates an exothermic reaction. Bond breaking absorbs energy and bond forming releases energy, and in an exothermic reaction there is a net release of energy because more energy is released by bond formation than is absorbed by bond breaking.

11 B. Because the amounts of both reactants are given, the limiting reactant must be identified. From the equation for the reaction, 1 mol of HCl reacts with 1 mol of NH_3. So, 0.0250 mol of HCl will react with 0.0250 mol of NH_3, and HCl is the limiting reactant.

Energy released = $0.0250 \times 52 = 1.30$ kJ

$E = CF \times \Delta T$

$1.30 \times 10^3 = 305 \times \Delta T$

$$\Delta T = \frac{1.30 \times 10^3}{305}$$

$= 4.26°C$

12 C. A spontaneous reaction will occur with the half-equations $Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$ and $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$. The products of the reaction include $H^+(aq)$, which will increase the acidity of the mixture (decrease the pH). Alternative B is not correct because there are no hydroxide (OH^-) ions made, so $Sn(OH)_4$ cannot form, and alternative D is incorrect because oxygen gas is not a product of either of the reactions that occur.

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13 A. The strongest oxidising agent will be the species gaining electrons (i.e. on the left-hand side) with the most positive (highest) *E*° value.

The equation involved here is:

$$VO_2^+(aq) + 2H^+(aq) + e^- \longrightarrow VO^{2+}(aq) + H_2O(l) \qquad E^\circ = +1.00\ V$$

So, $VO^{2+}(aq)$ is the strongest oxidising agent.

The strongest reducing agent will be the species losing electrons (i.e. on the right-hand side) with the most negative (lowest) *E*° value.

The equation involved here is:

$$V^{3+}(aq) + e^- \longrightarrow V^{2+}(aq) \qquad E^\circ = -0.25\ V$$

So, $V^{2+}(aq)$ is the strongest reducing agent.

It is important in this set of equations to note the difference between $VO_2^+(aq)$ and $VO^{2+}(aq)$, which are different ions.

14 D. The half-cell reactions will be as follows.

At the positive cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$. Hence, $Cu^{2+}(aq)$ is consumed and the blue colour of the solution will fade.

At the negative anode: $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$. Hence, Ni(s) is consumed and mass of the nickel electrode will decrease.

15 A and C. The correct answers need to use renewable fuel sources (feedstocks), so fossil fuels cannot be involved. Alternatives A and C both involve the use of waste materials, so the feedstocks are renewable, they can be replaced in a short period of time.

Alternatives B and C both use fossil fuels, even though the hydrogen used in B, is not a fossil fuel itself, it has been produced from a fossil fuel.

Short-answer questions

16 **a** Petrol is the only fossil fuel listed, although methanol and ethanol can be made from fossil fuels.

b Biodiesel is a renewable fuel, and ethanol can be a renewable fuel if it is made from the fermentation of glucose. Methanol can also be produced from biomass, so is renewable, but this has not been discussed in this book.

c **i** $C_6H_{12}O_6(aq) \longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$

ii The ethanol is produced during fermentation as an aqueous solution which is only about 10% (v/v) ethanol. The ethanol needs to be separated from the water for ethanol to be useful as a fuel. Distillation is used to separate the two liquids, by making use of their different boiling points.

d $C_2H_5OH(l) + 2O_2(g) \longrightarrow 2CO(g) + 3H_2O(l)$

17 **a**
$$\begin{aligned} n(C_2H_5OH) &= \frac{m}{M} \\ &= \frac{4.725}{46.0} \\ &= 0.103\ \text{mol} \end{aligned}$$

Calculate the volume of oxygen that would react with this amount of ethanol:

$$\frac{n(O_2)}{n(C_2H_5OH)} = \frac{7}{2}$$

$$\begin{aligned} \text{So } n(O_2) &= \frac{7}{2} \times 0.103 \\ &= 0.240\ \text{mol} \end{aligned}$$

$$\begin{aligned} V(O_2) &= n \times V_m \\ &= 0.240 \times 24.8 \\ &= 5.94\ \text{L} \end{aligned}$$

There is 10.0 L of O_2 present, so ethanol is the limiting reactant.

b
$$\frac{n(CO_2)}{n(C_2H_5OH)} = \frac{4}{2} = \frac{2}{1}$$

$$\begin{aligned} n(CO_2) &= 2 \times n(C_2H_5OH) \\ &= 2 \times \frac{4.725}{46.0} \text{ (from part } \mathbf{a}\text{)} \\ &= 0.205\ \text{mol} \end{aligned}$$

$$\begin{aligned} m(CO_2) &= 0.205 \times 44.0 \\ &= 9.04\ \text{g} \end{aligned}$$

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18 **a** **i** oxidation: $Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$

reduction: $Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$

ii overall: $2Al(s) + 3Br_2(aq) \longrightarrow 2Al^{3+}(aq) + 6Br^-(aq)$

b **i** oxidation: $S_2O_3^{2-}(aq) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8e^-$

reduction: $ClO^-(aq) + 2H^+(aq) + 2e^- \longrightarrow Cl^-(aq) + H_2O(l)$

ii overall: $4ClO^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 4Cl^-(aq) + 2H^+(aq)$

c **i** oxidation: $H_2O_2(aq) \longrightarrow O_2(aq) + 2H^+(aq) + 2e^-$

reduction: $MnO_4^-(aq) + 4H^+(aq) + 3e^- \longrightarrow MnO_2(s) + 2H_2O(l)$

ii overall: $3H_2O_2(aq) + 2MnO_4^-(aq) + 2H^+(aq) \longrightarrow 3O_2(aq) + 2MnO_2(s) + 4H_2O(l)$

19 **a** $E°(Sn^{2+}/Sn) = -0.14$ V and $E°(Fe^{2+}/Fe) = -0.44$ V

i cell voltage = (–0.14) – (–0.44) = 0.30 V

ii Fe^{2+}/Fe because it has the most negative (or lower) *E*° value.

iii $Sn^{2+}(aq) + Fe(s) \longrightarrow Sn(s) + Fe^{2+}(aq)$

b $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V and $E°(Al^{3+}/Al) = -1.66$ V

i cell voltage = (+0.77) – (–1.66) = 2.43 V

ii Al^{3+}/Al because it has the most negative (or lower) *E*° value.

iii $3Fe^{3+}(aq) + Al(s) \longrightarrow 3Fe^{2+}(s) + Al^{3+}(aq)$

c $E°(H^+/H_2) = 0$ V and $E°(I_2/I^-) = +0.54$ V

i cell voltage = (+0.54) – (0) = 0.54 V

ii H^+/H_2 because it has the most negative (or lower) *E*° value.

iii $I_2(aq) + H_2(g) \longrightarrow 2I^-(aq) + 2H^+(aq)$

20 **a** 75.6 × 9.82 = 742 MJ

b Heat losses occur in the boiler due to imperfect insulation. Heat is also lost through friction in moving parts within the turbines and generator.

c A non-renewable energy resource is one that cannot be replaced or regenerated as fast as it is consumed.

d Biogas is a renewable energy source, whereas existing coal supplies (which remain large) are non-renewable and would eventually be consumed. Because biogas carbon is derived from absorption of atmospheric CO_2 in photosynthesis, its use as a fuel has relatively little effect on net levels of atmospheric CO_2. Biogas can be produced from waste biomass that would otherwise require disposal.

21 **a** Oxidation number changes: I (+5 ⟶ –1) and S (+4 ⟶ +6), so this is a redox reaction.

The oxidising agent is HIO_3. The reducing agent is SO_2.

b Not redox because there is no change in oxidation numbers.

c Oxidation number changes: Fe (+2 ⟶ +3) and O (0 ⟶ –2), so this is a redox reaction.

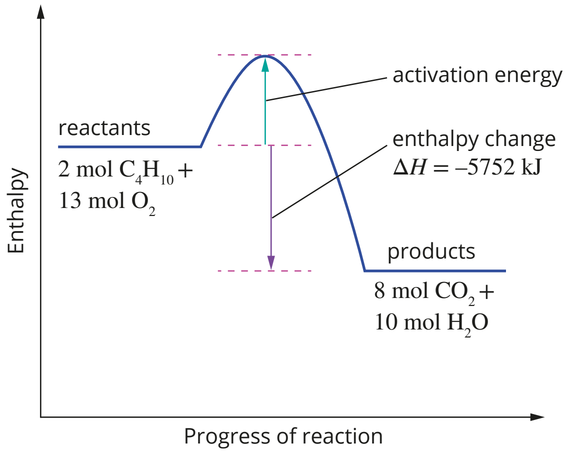
The oxidising agent is O_2. The reducing agent is $Fe(OH)_2$ (or Fe^{2+}).

d Oxidation number changes: H (–1 ⟶ 0) and H (+1 ⟶ 0), so this is a redox reaction.

The oxidising agent is H_2O. The reducing agent is NaH.

22 **a** The equation shows the combustion of 2 mol of butane, hence $\Delta H = 2 \times (-2876) = -5752$ kJ.

b



c Some initial input of energy is required to allow some reactants to overcome the activation energy barrier (associated with breaking bonds in reactants) to initiate the rapid reaction.

d Heat of combustion = $\frac{2876}{58.0} = 49.6\ kJ\ g^{-1}$

e i Energy released = 2.00 × 49.6 = 99.2 kJ

If 70% of heat energy generated by the lighter is lost to the surroundings, then only 30% of the heat energy will be heating the water.

So, energy absorbed by water $= \frac{30}{100} \times 99.2 = 29.76 \text{ kJ} = 2.976 \times 10^4 \text{ J}$

Using $q = mc\Delta T$

$$\Delta T = \frac{q}{mc} = \frac{2.976 \times 10^4}{150 \times 4.18} = 47.5°\text{C}$$

So, final temperature = 20.0 + 47.5 = 67.5°C

ii If the water is heated to 90.0 °C, then $\Delta T = 90.0 - 20.0 = 70.0°\text{C}$

$$\begin{aligned} q &= mc\Delta T \\ &= 150 \times 4.18 \times 70.0 \\ &= 43.89 \text{ kJ} \end{aligned}$$

$$\text{Energy transformation efficiency} = \frac{43.89}{99.2} \times \frac{100}{1} = 44.2\%$$

23 a Anode: $CH_3OH(g) + H_2O(l) \longrightarrow CO_2(g) + 6H^+(aq) + 6e^-$

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

b $n(CH_3OH) = \frac{m}{M} = \frac{1.00}{32.0}$ 0.0313 mol

$\Rightarrow$ maximum energy $= 0.0313 \times \frac{1453}{2} = 22.7$ kJ

c $V(CH_3OH)$ of 1.00 g of methanol $= \frac{1.00}{0.79} = 1.27$ mL

900 mL produces 1 kWh = 3600 kJ

$\Rightarrow$ energy obtained from fuel cell of 1.00 g of methanol $= \frac{1.27}{900} \times 3600 = 5.1$ kJ

d Percentage efficiency $= \frac{5.1}{22.7} \times \frac{100}{1} = 22\%$

e Incomplete reaction of the fuel (methanol) is likely. Some may be incompletely oxidised or pass into the electrolyte waste without reacting at all. Also, a significant amount of heat is generated in most fuel cells, further reducing efficiency.

24 a 100 s

b Exothermic (temperature increases)

c The temperature decreases due to loss of heat to the surroundings. Better insulation, such as aluminium foil, including a lid, around a beaker, or if possible a polystyrene surrounds with a lid, for the calorimeter would reduce this loss.

d 22.0 – 16.0 = 6.0°C

e Energy released $= 6.0 \times 486 = 2.92 \times 10^3 \text{ J} = 2.92 \text{ kJ}$

$n(Zn) = \frac{0.833}{65.4} = 0.0127$ mol

Heat released per mole of Zn $= \frac{2.92}{0.0127} = 230$ kJ

Hence $\Delta H = -230$ kJ

25 a

Trial number	Initial mass of corn chip (g)	Mass after corn chip was extinguished (g)	Mass loss (g)	Initial temperature of water in beaker (°C)	Final temperature of water in beaker (°C)	Temperature increase (ΔT) (°C)
1	2.510	0.627	1.883	16.0	63.5	47.5
2	2.452	0.613	1.839	16.5	65.0	48.5
3	2.425	0.606	1.819	16.0	64.0	48.0

$$\text{Average mass loss} = \frac{1.883 + 1.839 + 1.819}{3} = 1.847 \text{ g}$$

$$\text{Average temperature increase} = \frac{47.5 + 48.5 + 48.0}{3} = 48.0°\text{C}$$

b
$$\begin{aligned} q &= mc\Delta T \\ &= 100 \times 4.18 \times 48.0 \\ &= 20\,064 \text{ J} \\ &= 20.1 \text{ kJ} \end{aligned}$$

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c energy transferred $= \frac{50}{100} \times$ energy produced

So, energy produced $= \frac{100}{50} \times$ energy transferred

$$= \frac{100}{50} \times 20064$$
$$= 40128 \text{ J}$$
$$= 40.1 \text{ kJ}$$

d energy content $= \frac{40.128}{1.847} = 21.7 \text{ kJ g}^{-1}$

21.7 x 100 = 2172 kJ per 100 g

e In Table 2.3.1, energy value of carbohydrates = 16 kJ g^{-1} and energy value of fats and oils = 37 kJ g^{-1}

Energy due to fat = 26 × 37 = 962 kJ

Energy due to carbohydrates = 60 × 16 = 960 kJ

f The systematic error that had the greatest impact on the investigation was the loss of heat to the surroundings.

g The investigation is valid, as it is testing the quantity that was described in the aim of the experiment. 'A pair of students wanted to determine the energy content of 100 g of cheese-flavoured corn chips'.

The investigation is not very accurate, as a considerable quantity of heat (quoted as 50%) is lost to the surroundings.

The investigation has quite good precision, since the three trials had an average mass loss of 1.847 g, with the highest value being 0.036 g above that value and the lowest mass loss being 0.028 g below that value. The range of temperature increases for the water in the beaker was even smaller, being 0.5°C on either side of the average.

The repeatability is good because three trials were performed and the results were consistent within those three trials.

h To determine the reproducibility of the experimental design, other groups of students would need to be asked to perform the experiment following the same method and then their results could be compared to those of the original two students.

26 a Heat energy absorbed $= m \times c \times \Delta T = (224 \times 1000) \times 4.18 \times (70 - 14) = 5.24 \times 10^7 \text{ J} = 52.4 \text{ MJ}$

energy from fuel $= \frac{52.4}{1.25} = 41.9 \text{ MJ kg}^{-1}$

b Imperfect insulation may allow some heat losses; some of the energy released is absorbed by the container; incomplete combustion of the fuel will reduce energy released.

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Chapter 6 Rates of chemical reactions

6.1 Rate of reaction and collision theory

CASE STUDY: ANALYSIS

Saved by a very fast chemical reaction

Analysis

1 nitrogen, N_2, gas

2 Nitrogen is an inert gas, so it will not react with the sodium metal, even at high temperatures.

3 $pV = nRT$

$$n(N_2) = \frac{pV}{RT} = \frac{34.0 \times 67.0}{8.31 \times 298} = 0.91989 \text{ mol}$$

$$n(\text{NaN}_3) = n(\text{N}_2) \times \frac{5}{8} = 0.5749 \text{ mol}$$

$$\begin{aligned} m(\text{NaN}_3) &= n(\text{NaN}_3) \times M(\text{NaN}_3) \\ &= 0.5749 \times 65.0 \\ &= 37.4 \text{ g} \end{aligned}$$

KEY QUESTIONS

Knowledge and understanding

1 Particles must collide with each other; they must collide with sufficient energy to break the reactant bonds, and they must collide with the correct orientation to break the reactant bonds.

2 The activation energy is the minimum energy required to break the reactant bonds. If these are not broken, then new products cannot be formed and the reaction cannot proceed.

3 The larger the activation energy, the smaller the proportion of collisions that result in a reaction at a given temperature. A reaction with a larger activation energy will have a lower rate of reaction at a particular temperature than a reaction with a smaller activation energy.

Analysis

4 Note that the reaction is endothermic, so the activation energy of the reverse reaction will be less than the activation energy of the forward reaction.

$+167 - 28 = +139$ kJ mol^{-1}

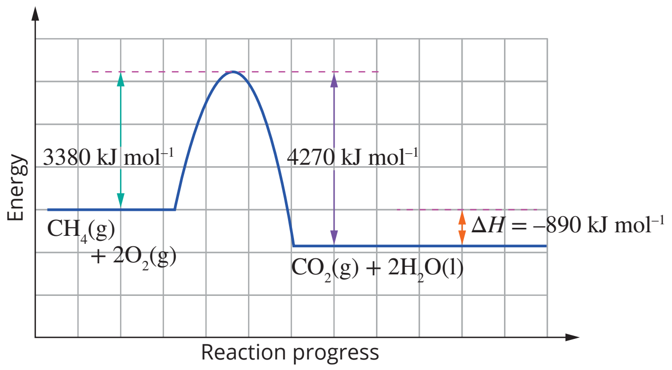
5 **a** $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

b ΔH = energy of bonds broken – energy of bonds formed

$= 3380 - 4270$

$= -890$ kJ mol^{-1}

c



6 The reaction flask could be placed on an electronic balance while the reaction proceeded, and the mass could be recorded at time intervals (e.g. initially every 15 s, then 30 s). Alternatively, the reaction flask could be connected to a gas syringe, as in Figure 6.1.3. The volume of gas could be measured either for a fixed amount of time or recorded at time intervals as for the mass measurements.

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6.2 Effect of changes of conditions on rate of reaction

Worked example: Try yourself 6.2.1

USING COLLISION THEORY TO EXPLAIN CHANGES IN RATES OF REACTIONS

Iron anchors recovered from shipwrecks deep in the sea, where the concentration of oxygen is low, can show little corrosion after years in the sea, whereas anchors recovered from shallow water are badly corroded. Explain this observation in terms of collision theory.

Thinking	Working
Consider the state of the reactants.	The iron anchor is a solid. The oxygen is a gas dissolved in the sea water.
Relate the state of the reactant to the factor that affects the reaction rate and explain in terms of collision theory.	The surface area of the iron anchor is relatively small. The concentration of oxygen at greater depths in the ocean is much lower than at sea level. The frequency of collisions with reacting particles that could cause corrosion would be low, so the rate of corrosion would also be low.
Return to the question to complete your answer.	The surface area of the iron anchor is relatively small, so the frequency of collisions with reacting particles would be low. The concentration of oxygen at greater depths is also low, so the frequency of collisions is further reduced. Therefore, the rate of corrosion is reduced.

KEY QUESTIONS

Knowledge and understanding

1 Increase in concentration of a solution; increase in surface area of a solid by making the particle size smaller; increase in gas pressure; increase in temperature.

2 As the temperature of a substance increases, the average kinetic energy of the substance increases. In other words, kinetic energy is proportional to temperature.

3 An increase in temperature increases the average kinetic energy of the particles. As a result, it increases the frequency of collisions between particles and, more importantly, it increases the energy with which the particles collide, thus increasing the proportion of collisions with an energy greater than or equal to the activation energy.

4 1 M HCl has a greater concentration than 0.1 M HCl, so the frequency of collisions between HCl and the magnesium will be greater for the 1 M HCl than for the 0.1 M HCl. Therefore the rate of reaction will be greater for the 1 M HCl.

Analysis

5 **a** Experiment A would have the greatest reaction rate, because the $CaCO_3$ has the greatest surface area (it is powdered) and the HCl has the greatest concentration (2 M), thus increasing the frequency of collisions. The temperature is also higher, at 40°C, than in the other experiments, increasing the proportion of collisions with an energy greater than or equal to the activation energy.

b Experiment C would have the smallest reaction rate because the surface area of $CaCO_3$ is the smallest (it is in large pieces) and the HCl has the lowest concentration (0.5 M), thus decreasing the frequency of collisions. The temperature is lower, at 15°C, than in the other experiments, reducing the proportion of collisions with an energy greater than the activation energy.

6 **a** At higher temperatures, the molecules that react to form fibreglass plastics have greater energy. They collide more frequently and are more likely to have a total energy greater than the activation energy of the reaction involved, increasing the rate of reaction.

b Fine particles have a large surface area, resulting in a high frequency of collisions—in this case, of aluminium particles with gas molecules (such as oxygen) in the air—and hence a rapid reaction rate. The aluminium can therefore burns vigorously and releases a large quantity of heat.

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6.3 Catalysts

CASE STUDY: ANALYSIS

Heterogeneous catalysts in industry

Analysis

1 The reaction between nitrogen and hydrogen has a very high activation energy, so only a small proportion of collisions have an energy greater than or equal to the activation energy.

2 The presence of a catalyst decreases the activation energy, the energy required to break the reactant bonds, but it does not change the enthalpy of the reactants or the enthalpy of the products. As a result, the change in enthalpy, ΔH, which is equal to $H_p - H_r$, does not change.

3 Sustainability concepts include the recycling of materials that are non-renewable. The metals used in catalytic converters, platinum, palladium and rhodium are expensive and their supply is limited, so they should be recycled wherever possible.

KEY QUESTIONS

Knowledge and understanding

1 A catalyst is not consumed during the reaction it speeds up and it does not appear as either a reactant or a product in the equation for the reaction.

A catalyst causes the rate of the reaction to increase because it provides an alternative reaction pathway with a lower activation energy, so a greater proportion of collisions have an energy greater than or equal to the activation energy.

2 The student has incorrectly stated that catalysts increase the frequency of collisions. Catalysts lower the activation energy for a reaction by providing an alternative reaction pathway, so they increase the proportion of collisions that are successful, i.e. that have an energy greater than or equal to the activation energy. The statement should read ‘A catalyst increases the rate of a reaction because all catalysts increase the proportion of collisions with energy greater than or equal to the activation energy’.

3 Porous pellets have a high surface area because of all the holes in the surface. This high surface area increases the frequency of collisions and so increases the rate of reaction.

Analysis

4 When salt is mixed with sugar, the salt acts as a catalyst and lowers the activation energy of the combustion reaction between the sugar and oxygen.

5 Both increase the reaction rate by increasing the proportion of collisions with energy greater than or equal to the activation energy. An increase in temperature increases the average kinetic energy of the collisions, but does not change the activation energy, so a greater proportion of collisions have $E \geq E_a$. Adding a catalyst does not change the energy of the reacting particles; instead it lowers the activation energy, so a greater proportion of collisions have $E \geq E_a$.

6 Independent variable: The type of catalyst used (yeast, potassium iodide, manganese dioxide).

Dependent variable: The volume of oxygen produced (and collected) in a given time, or the change in mass of the open reaction flask in a given time.

Controlled variables: Concentration of hydrogen peroxide, temperature of hydrogen peroxide, mass of catalyst used, method by which the catalyst is added (e.g. all at once, in the flask before, or after the hydrogen peroxide is added).

Chapter 6 Review

REVIEW QUESTIONS

Knowledge and understanding

1 B. When the temperature is decreased, the average kinetic energy of the particles decreases, and the energy and frequency of collisions decreases, thus decreasing the reaction rate. All of the other options will increase the reaction rate.

2 A. The rate of reaction is a measure of the change in concentration of a substance over time. Only option A has units that correspond to concentration (mol L^{-1}) per unit time (s^{-1}).

3 B. The powdered zinc has a larger surface area than the large zinc pieces. An increase in surface area increases the frequency of collisions between reactant particles. If the temperature does not change, then the energy of the collisions will not change, so options A and C are incorrect. Option D would have a lower frequency of collisions.

4 D. The collision must have enough energy to break the reactant bonds, i.e. an energy that is equal to or greater than the activation energy. The remaining alternatives do not meet this requirement.

5 C. A catalyst lowers the activation energy, so the proportion of successful collisions increases. Increasing the concentration increases the frequency of collisions because there are more reactant particles present in a given volume.

6 'Frequency of collisions' refers to how often collisions occur; for example, whether there are 100 collisions per second, or the greater frequency of 1000 collisions per second. In comparison 'proportion of collisions' refers to a share, or fraction of a total number. So, if the proportion of collisions with energy $\geq E_a$ increases, there is a greater share of the total collisions that have enough energy to react ($E \geq E_a$).

7 If a catalyst was used to increase the reaction rate, the activation energy barrier would be at a lower value, so quantities A (the activation energy of the forward reaction) and C (the activation energy of the backward reaction) would decrease. ΔH (B) would not change.

8 An increase in the concentration of a **solution**, the surface area of a **solid** or the pressure of a **gas**, will increase the **frequency** of collisions in a reaction, meaning that an increased number of **collisions** occur during a particular **time**. As a result, the frequency of **successful** collisions will also increase, and the **rate** of reaction will increase. Adding a catalyst to a reaction will increase the **proportion** of collisions which have energy that is **greater** than or equal to the **activation energy**. This means that out of the total number of collisions, **more** collisions have enough energy to overcome the **activation** energy. Increasing the temperature of a reaction will increase both the **frequency** of collisions and the **proportion** of collisions that have $E \geq E_a$.

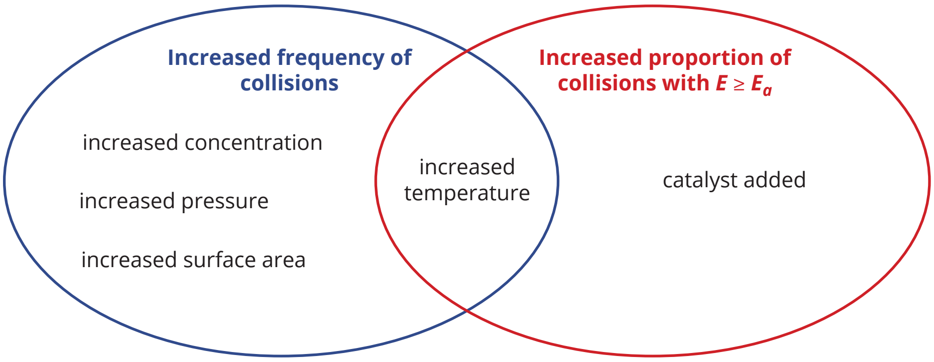
9 **a** The definition does include any sense of time. So, the mass of products in consideration could be made over a few seconds (a fast reaction) or could be made over several hours (a slow reaction). These two reactions would have very different rates.

b The rate of reaction is equal to the change in concentration of products or reactants divided by the change in time.

$$\text{rate} = \frac{\text{change of concentration}}{\text{time}}$$

10 **a** The surface area of a solid reactant, concentration of reactants in a solution, pressure of any gaseous reactants, temperature of the reaction and presence of a catalyst, all affect the rate of reaction.

b

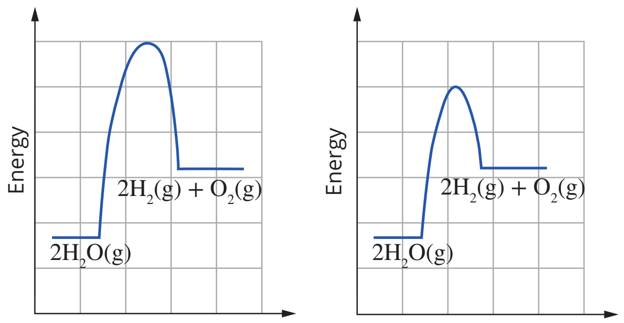


11 In the first experiment (0.5 M $CuSO_4$ and zinc powder at 40°C), the temperature is higher than in the second experiment (0.5 M $CuSO_4$ and zinc pieces at 25°C). When the temperature is increased, the average kinetic energy of the particles in solution (Cu^{2+}) will increase, and the proportion of collisions with an energy greater than or equal to the activation energy will increase. In addition, the frequency of collisions will increase because of the increased kinetic energy, and because of the increased surface area of the zinc in the first experiment.

12 **a** 1370 kJ mol^{-1}

b –572 kJ mol^{-1}

c


Without catalyst

With catalyst

d +572 kJ mol^{-1}

Application and analysis

13 Collision 1 has the correct collision orientation, because the hydroxide is in the correct position to substitute for the chlorine, allowing bonds to break within the reactants and bonds to form within the products.

14 To increase the rate at which the sugar dissolves without ruining the toffee, you could:

- grind up the sugar crystals or use caster sugar
- use a cup of hot water to dissolve the sugar
- gently heat the sugar and water mixture while the sugar is dissolving
- stir the sugar and water mixture while the sugar is dissolving, to ensure that all of the solid sugar is coming in contact with the water.

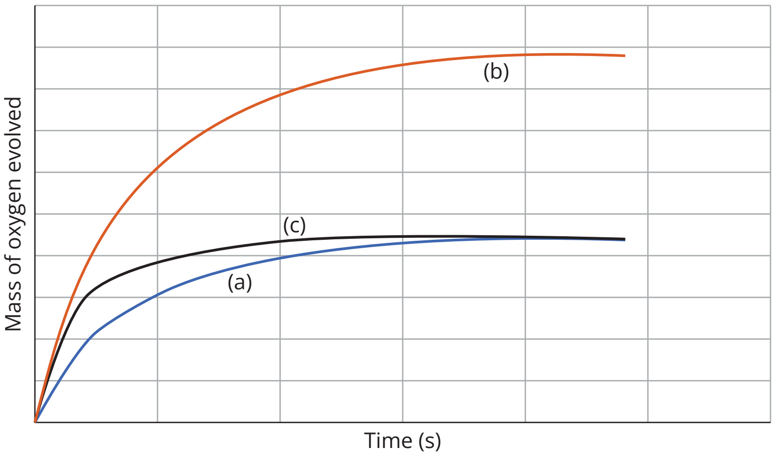
15 **a** $CaCO_3(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

b The rate of reaction is decreasing over time. This is shown in the graph as the gradient of the slope decreases as the time progresses.

16 **a** When salt is added to the water, the maximum temperature that the water can reach (its boiling temperature) increases. As a result, the pasta will cook more quickly because the rate of reaction (i.e. the process by which it cooks) increases.

b On top of Mt Everest the atmospheric pressure is very low due to the high altitude, so the temperature at which water boils decreases. The pasta cooks more slowly because the rate of reaction (i.e. the process by which it cooks) decreases due to its decreased temperature.

17



a This graph is labelled ‘a’ above.

b This graph is labelled ‘b’ and should have a much higher finishing mass, as the concentration of the hydrogen peroxide is double that which was used in part **a**. The rate of reaction, shown by the gradient of the graph is also greater than for part **a**.

c This graph is labelled ‘c’ and should finish at the same mass as the graph for part **a**, but it should have a steeper gradient due to the higher temperature. Generally, the rate of reaction doubles for every increase of 10°C.

18 **a** $CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

b $n(CaCO_3) = \frac{m}{M} = \frac{10.0}{100.1} = 0.0999$ mol

$n(HCl) = cV = 0.1 \times 0.1 = 0.01$ mol

$\therefore$ $CaCO_3$ is in excess

c The rate of reaction could be measured by:

- measuring the decrease in the mass of reaction mixture as $CO_2(g)$ escapes to the atmosphere
- measuring the increase in pH with a pH probe as the acid is consumed.

d The rate of reaction with the smaller lumps will be faster. The smaller lumps have a larger surface area, so more collisions can occur per second.

e The rate of the reaction can be altered by an increase in temperature or an increased concentration of hydrochloric acid.

For an increase in temperature, a greater proportion of collisions have $E \geq E_a$, and the particles collide with greater frequency, so the rate of reaction increases.

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For an increase in concentration of HCl, there are more HCl molecules in a given volume, so the frequency of collisions between the $CaCO_3$ and HCl increases.

19 **a** A gas is produced, so mass is lost from the mixture.

b $n(\text{Cu}) = \frac{m}{M}$

$= \frac{5.00}{63.5}$

$= 0.0787$ mol

$n(\text{HNO}_3) = cV$

$= 2.00 \times 0.500 = 1.00$ mol

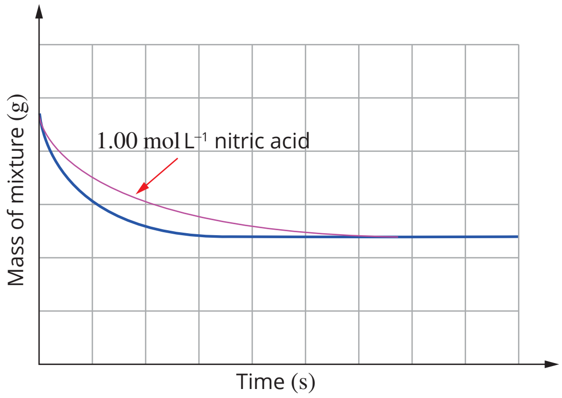
$n(\text{HNO}_3)$ reacts with Cu $= \frac{8}{3} \times n(\text{Cu})$

$= \frac{8}{3} \times 0.0787$

$= 0.210$ mol

$0.210 < 1.00$; therefore HNO_3 is in excess, so Cu is limiting.

c

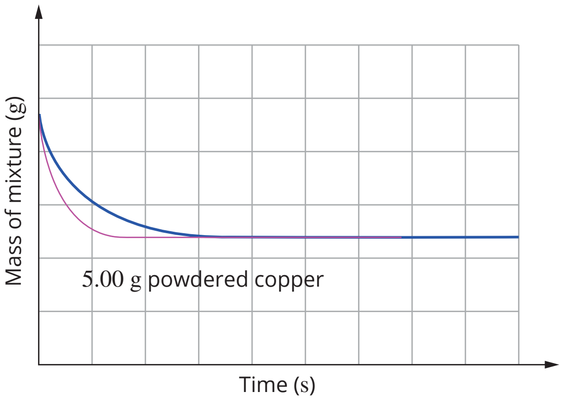


The decreased rate of mass loss is due to the lower nitric acid concentration.

$n(\text{HNO}_3) = cV = 1.00 \times 0.500 = 0.500$ mol

Copper is still limiting, so the final mass remains the same.

d



The increased rate of mass loss is due to the increased copper surface area.

Copper is still limiting, so the final mass remains the same.

20 **a** Any two of: the concentration of HCl in the mixture; the concentration of $Na_2S_2O_3$ in the mixture; the temperature of the solution.

b The dependent variable is the time taken for the cross to disappear (i.e. for so much sulfur to be present in the solution that the cross can no longer be seen).

c The dependent variable would be inversely proportional to the rate of reaction, because the less time it takes to make that quantity of sulfur, the greater the rate of reaction.

d Students' answers will vary. For example: To determine how the concentration of HCl in a mixture of HCl and $Na_2S_2O_3$ affects the time it takes for a cross underneath the reaction beaker to no longer be visible.

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21 **a** The graphs start at a high value and decrease as the reaction progress. If these graphs were of carbon dioxide produced over time, they would start out at zero and would increase. It is most likely that this is the overall mass of the open container plus reactants during the course of the reaction.

b Graph B is likely to represent the higher temperature reaction because it has a greater initial gradient, which corresponds to a greater initial rate.

c The results shown in graph B were obtained at a higher temperature than those in graph A. This means that the reactant particles have a greater average kinetic energy for graph B. The frequency of collisions is greater in graph B and the proportion of collisions with $E \geq E_a$ is greater in graph B, so the initial rate of reaction, and hence the gradient at the beginning of graph B is greater.

22 **a** The temperature of the new process (550°C) is much lower than the temperature of 1800°C in the blast furnace.

b $2Fe(s) + O_2(g) \longrightarrow 2FeO(s)$

$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

c No, a catalyst does not participate in the reaction. The reaction of iron with water is different to the reaction of iron with dry oxygen and proceeds at a different rate.

d exothermic

e The high surface area of the iron pellets and the high temperature caused by trapped heat that was unable to escape rapidly.

f Water would have caused the production of more hydrogen and increased the fire. Students' answers will vary, but the method used by the firefighters to extinguish the fire was to flood the hold with liquid nitrogen, which extinguished the surface fire, but did not stop the deeper burning. A crane and clamshell bucket were then used to unload the iron into piles less than 1 m deep so the heat could escape.

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Chapter 7 Extent of chemical reactions

7.1 Dynamic equilibrium

CASE STUDY: ANALYSIS

Investigating dynamic equilibrium

Analysis

1 Initially there are no Na^+ ions or I^- ions present in the water. Because NaI is very soluble, once the solid NaI is added to the pure water, the ions are released into solution. As the concentrations of Na^+ and I^- increase, they recombine to form solid NaI. The forward and reverse reactions continue to occur until the rate at which the ions come into solution is equal to the rate at which they recombine. Dynamic equilibrium is achieved.

2 $NaI(s) \rightleftharpoons Na^+(aq) + I^-(aq)$ or $NaI(s) \rightleftharpoons NaI(aq) \rightleftharpoons Na^+(aq) + I^-(aq)$

3 Dynamic equilibrium is achieved when the rate of the forward reaction is equal to the rate of the reverse reaction. This means that there is no change in the concentration of either the reactants or the products. Each are being constantly formed, but at equal rates.

4 Initially, when the radioactive NaI is added, the radiation detector records the radioactivity only in the solid on the bottom of the container, but after some time the radiation detector will show that the solution is also radioactive. The fact that the concentration remains constant indicates that as some radioactive iodide is dissolved, the same amount of non-radioactive or radioactive iodide must recombine and form solid NaI. Although we cannot see this reaction occurring, the radiation detector indicates the presence of radioactivity in both the solid and the solution.

KEY QUESTIONS

Knowledge and understanding

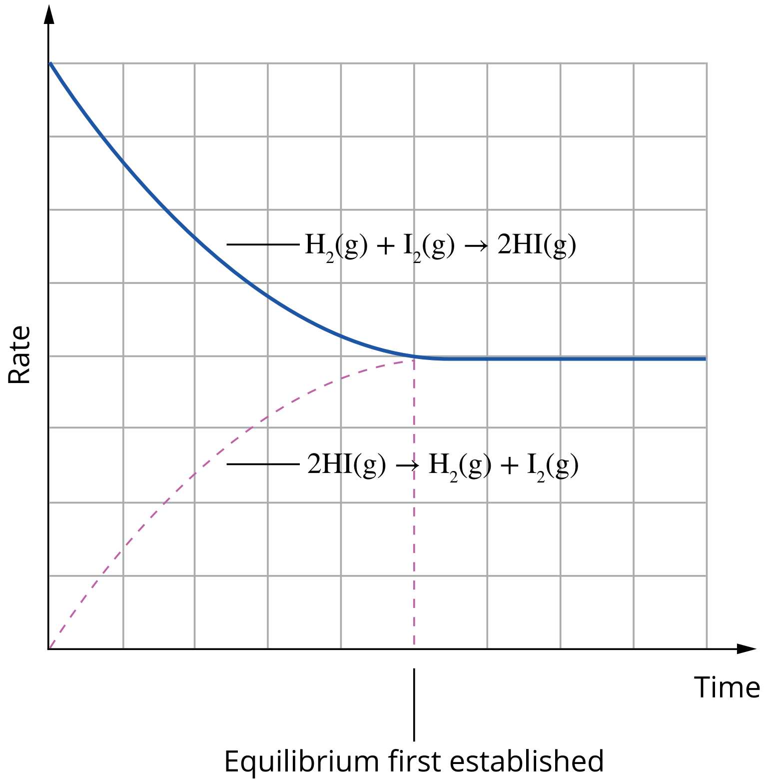
1 Option A: False, because the extent of reaction gives no indication of the rate of reaction

Option B: False, because the extent of reaction only indicates the relative amounts of reactants and products when equilibrium is achieved. It does not necessarily mean that there are equal amounts of reactants and products when equilibrium is achieved.

Option C: True – correct answer

Option D: False, because the extent of reaction gives no indication of the rate of reaction

2 a



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- **b** We are told that initially H_2 and I_2 are present in the sealed container and there is no product, HI. Therefore, the higher curve is the forward reaction where H_2 and I_2 are producing HI. As the reactants are being consumed, the rate of the forward reaction decreases. The lower curve is the reverse reaction, which occurs when some product has been formed and reconverts to the original reactants. The more products produced, the more the rate of the reverse reaction increases. When the rate of the forward reaction becomes equal to the rate of the reverse reaction, equilibrium has been achieved.

3 In a **closed** system, as the concentrations of the reactants **decrease**, the rate of the forward reaction also decreases. The collisions between these reactant molecules occur **less** frequently. Once some product starts to form, the **reverse** reaction occurs and the frequency of collisions between product molecules **increases** and between reactant molecules decreases. At equilibrium, the rates of the forward and backward reactions are **equal** and the **concentrations** of all species do not change.

4 For a reaction to be at equilibrium, the reaction must be reversible and have reached a state where the rate of the forward reaction is equal to the rate of the reverse reaction. There is no observable change in concentrations of the reactants or the products.

Analysis

5 For parts **a**, **b**, **c**, **d** reading from the graph and estimating the second significant figure:

- **a** 0.070 M
- **b** 0.00 M
- **c** 0.030 M
- **d** 0.080 M
- **e** From the graph, in a 1 litre container as given, $[N_2O_4]$ initially is 0.070 M and at equilibrium it becomes 0.030 M. So 0.070 – 0.030 = 0.040 mol has decomposed.
- **f** The horizontal regions of the graph indicate that there is no change in concentration of NO_2 or N_2O_4. This is when the system is at equilibrium and both the forward and reverse reactions are occurring at the same rate.
- **g** 6 s
- **h** As the reaction proceeds, the intensity of the brown colour will increase as the concentration of NO_2 increases until equilibrium is reached. Once equilibrium is reached, the colour of the reaction mixture will remain constant.

7.2 The equilibrium law

Worked example: Try yourself 7.2.1

DETERMINING THE UNITS FOR AN EQUILIBRIUM EXPRESSION

Write the equilibrium expression and determine the units for *K* for the reversible reaction:

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

Thinking	Working
Write the expression for *K*. $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$
Substitute the units of concentration into the expression for *K* to find the units of *K*.	$\frac{M^2}{M^2 \times M} = \frac{1}{M} = M^{-1}$ (or $L\,mol^{-1}$)

KEY QUESTIONS

Knowledge and understanding

1
- **a** A homogeneous system is a system in which all the species are in the same state.
- **b** The reaction quotient, *Q*, is the concentration ratio at any time during a reversible reaction, and is equal to *K* at equilibrium.

  $$Q = \frac{[\text{products}]^{\text{coefficient}}}{[\text{reactants}]^{\text{coefficient}}}$$

- **c** The equilibrium constant, *K*, is the ratio of the equilibrium concentrations of the products divided by the equilibrium concentrations of the reactants raised to the power of their coefficients. The value for the equilibrium constant changes with temperature.

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2 $Q = \frac{[HBr]^2}{[H_2][Br_2]}$

3 $K = \frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}]^2[Sn^{2+}]}$

Analysis

4 The reaction quotient $Q < K$. The reaction will shift to the right to establish equilibrium. This causes the concentration of the products to increase.

5 $Q = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

As $Q > K$, in order to reach equilibrium $[[Cu(NH_3)_4]^{2+}]$ must decrease and the concentration of the reactants must increase. This will occur if the reaction shifts to the left to produce more reactants.

7.3 Calculations involving equilibrium

Worked example: Try yourself 7.3.1

CALCULATING AN EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

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

Calculate the value of the equilibrium constant, K, for the reaction at that temperature.

Thinking	Working
Find the molar concentrations for all species at equilibrium. Convert mol to mol L⁻¹ using $c = \frac{n}{V}$.	$[N_2O_4] = \frac{n}{V}$ $= \frac{0.120}{3.00}$ $= 0.0400$ M $[NO_2] = \frac{n}{V}$ $= \frac{0.500}{3.00}$ $= 0.167$ M
Write the expression for K.	$K = \frac{[NO_2]^2}{[N_2O_4]}$
Substitute into the expression for K to determine the value of K.	$K = \frac{0.167^2}{0.0400}$ $= 0.694$
Determine the units of K.	$\frac{M^2}{M} = M$ $K = 0.694$ M (or 0.694 mol L^{-1}) Note that if you carried all values through in your calculator, you would get this value. If you round off along the way, you might get an answer of 0.697 M.

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Worked example: Try yourself 7.3.2

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium with an equilibrium constant of 0.72 M at 250°C.

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

An equilibrium mixture contains 0.040 M N_2O_4 at 250°C. Calculate the equilibrium concentration of NO_2 in this mixture.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Write the expression for <i>K</i>.</td><td>$K = \frac{[NO_2]^2}{[N_2O_4]}$</td></tr>
<tr><td>Substitute the known values into the expression for <i>K</i>.</td><td>$0.72 = \frac{[NO_2]^2}{0.040}$</td></tr>
<tr><td>Rearrange the expression to make the unknown the subject and calculate the concentration of this species.</td><td>$[NO_2] = \sqrt{0.72 \times 0.040}$
$= 0.17$ M (or mol L^{-1})</td></tr>
</table>

Worked example: Try yourself 7.3.3

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetroxide (N_2O_4) at 60°C:

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

0.350 mol of N_2O_4 was placed in a 2.0 L vessel. When equilibrium was achieved, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at this temperature.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Construct a reaction table using each species in the balanced equation as the headings for the columns. Insert three rows in the table labelled ‘I’ (Initial), ‘C’ (Change) and ‘E’ (Equilibrium):
<table>
<tr><th></th><th colspan="2">Reactants ⇌ Products</th></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
Enter the data provided in the table.
When a species is consumed, the change is negative; when a species is produced, the change is positive.</td><td>Initially, there is:

0.350 mol of $N_2O(g)$
0 mol of the product $NO_2(g)$.

If <i>x</i> mol of N_2O_4 reacts, 2<i>x</i> mol of NO_2 is produced.
At equilibrium, there is 0.120 mol of $NO_2(g)$.
<table>
<tr><th></th><th colspan="2">$N_2O_4(g) \rightleftharpoons 2NO_2(g)$</th></tr>
<tr><td>I</td><td>0.350 mol</td><td>0 mol</td></tr>
<tr><td>C</td><td>$-x$</td><td>$+2x$</td></tr>
<tr><td>E</td><td>$0.350 - x$</td><td>$2x = 0.120$ mol</td></tr>
</table></td></tr>
<tr><td>Using the coefficients from the equation, calculate the moles of all species at equilibrium.</td><td>Initially no NO_2 was present, so because 0.120 mol NO_2 has been produced at equilibrium:
$$2x = 0.120 \text{ mol}$$
$$x = 0.0600 \text{ mol}$$
Enter these values in the table:
<table>
<tr><th></th><th colspan="2">$N_2O_4(g) \rightleftharpoons 2NO_2(g)$</th></tr>
<tr><td>I</td><td>0.350</td><td>0</td></tr>
<tr><td>C</td><td>$-x = -0.0600$</td><td>$+2x = 0.120$</td></tr>
<tr><td>E</td><td>$0.350 - 0.0600 = 0.290$</td><td>$2x = 0.120$</td></tr>
</table></td></tr>
</table>

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Using the volume of the vessel, calculate the equilibrium concentrations for all species at equilibrium. Use the formula $c = \frac{n}{V}$.	The volume of the vessel is 2.00 L. $[N_2O_4] = \frac{n}{V} = \frac{0.290}{2.00} = 0.145\ M$ $[NO_2] = \frac{n}{V} = \frac{0.120}{2.00} = 0.0600\ M$
Write the expression for *K* and substitute the equilibrium concentrations. Calculate the equilibrium constant, *K*, and include the units for the equilibrium constant.	$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.0600^2}{0.145} = 0.0248\ M$ (or $0.0248\ mol\ L^{-1}$)

KEY QUESTIONS

Knowledge and understanding

1 B. From the equilibrium law, the larger the product concentration, the greater the extent of reaction and the more the reaction moves in the direction of products. The values of the equilibrium constants for reactions 1, 3 and 4 are all smaller values than the value of the equilibrium constant for Reaction 2 and so the correct answer is B. Reaction 2 has a large value of K ($>10^4$), indicating that at equilibrium, reaction 2 favours the products, i.e. it would have more products than reactants.

2 **a** No, very little (negligible) reaction would occur. $K = 10^{-10}$ is very small, indicating that the amount of product is minimal.

b For the reverse reaction, $K = 10^{10}$.

c For this reverse reaction, the equilibrium constant is the reciprocal of that for the forward reaction, so $K = 10^{10}$. Because K is very large, provided the rate is sufficiently fast there will be significant reaction in the forward direction—in fact, a virtually complete reaction will occur with a very high amount of product.

3 **a** $K = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

b **i** The coefficients of each species have been halved. $K = \frac{[Br_2]^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}}{[BrCl]} = \sqrt{32} = 5.7$

ii The reaction is the reverse of that in part **a**. $K = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \frac{1}{32} = 0.031$

iii Each of the coefficients has been doubled. $K = \frac{[Br_2]^2[Cl_2]^2}{[BrCl]^4} = 32^2 = 1.0 \times 10^3$

iv The reaction has been reversed and the coefficients have been halved. $K = \frac{[BrCl]}{[Br_2]^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}} = \frac{1}{\sqrt{32}} = 0.18$

4 **a** $K = \frac{[COCl_2]}{[CO][Cl_2]}$

b $K = \frac{0.28}{2.4 \times 10^{-2} \times 0.108} = 1.1 \times 10^2\ M^{-1}$

5 From the equation, write the expression for the equilibrium constant:

$K = \frac{[NO_2]^2}{[N_2O_4]}$

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Calculate the equilibrium concentrations of the reactants and products.

$$[NO_2] = \frac{n}{v}$$
$$= \frac{0.40}{2.0}$$
$$= 0.20\ M$$

$$[N_2O_4] = \frac{0.80}{2.0}$$
$$= 0.40\ M$$

Substitute the equilibrium concentrations into the equilibrium expression and calculate the value of the equilibrium constant.

$$K = \frac{0.20^2}{0.40}$$
$$= 0.10\ M$$

Analysis

6 $K = \frac{[NO_2]^2}{[NO]^2[O_2]}$

$$= \frac{15.5^2}{0.0542^2 \times [O_2]}$$
$$= 6.44 \times 10^5\ M^{-1}$$

$$[O_2] = \frac{15.5^2}{0.0542^2 \times (6.44 \times 10^5)}$$
$$= 0.127\ M$$

7

	PCl_3(g) +	**Cl_2(g) ⇌**	**PCl_5(g)**
I	3.45	4.50	0
C	$-x = -0.25$	$-x = -0.25$	$+x = 0.25$
E	$3.45 - x$ $= 3.45 - 0.25$ $= 3.20$	$4.50 - x$ $= 4.50 - 0.25$ $= 4.25$	$x = 0.25$

volume of vessel = 2.00 L

$$[PCl_3] = \frac{3.20}{2.00} = 1.60\ M$$

$$[Cl_2] = \frac{4.25}{2.00} = 2.13\ M$$

$$[PCl_5] = \frac{0.25}{2.00} = 0.13\ M$$

$$K = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.13}{(1.60 \times 2.13)} = 0.038\ M^{-1}$$

8

	N_2(g) +	**$3H_2$(g) ⇌**	**$2NH_3$(g)**
I	4.89	7.23	0
C	$-x = -0.14$	$-3x = -0.42$	$+2x = 0.28$
E	$4.89 - x$ $= 4.89 - 0.14$ $= 4.75$	$7.23 - 3x$ $= 7.23 - 0.42$ $= 6.81$	$2x = 0.28$

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volume of vessel = 5.00 L

$$[N_2] = \frac{4.75}{5.00} = 0.950\ \text{M}$$

$$[H_2] = \frac{6.81}{5.00} = 1.36\ \text{M}$$

$$[NH_3] = \frac{0.28}{5.00} = 0.056\ \text{M}$$

$$K = \frac{[NH_3]^2}{[N_2]\times[H_2]^3} = \frac{0.056^2}{(0.950\times1.36^3)} = 0.001305 = 1.3\times10^{-3}\ \text{M}^{-2}$$

7.4 Le Châtelier's principle

Worked example: Try yourself 7.4.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME INCREASE

Consider the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Predict the shift in equilibrium position and the effect on the amount of Cl_2 when the volume is doubled at constant temperature.

Thinking	**Working**
Determine the immediate effect of the change of volume on the pressure.	Doubling the volume will halve the pressure and therefore the concentration of all species at equilibrium.
The system will try to partially oppose the change in pressure by reducing or increasing the pressure in the system. For a volume decrease, the system will shift in the direction of the fewest particles; for a volume increase, the system will shift in the direction of the most particles. Decide how the equilibrium will respond.	There are 2 molecules of gas on the reactant side and 1 molecule of gas on the product side, so the system will shift to the left (the reactant side). This increases the amount of the reactants, including Cl_2. (Note that the PCl_3 and Cl_2 concentrations will still be lower than they were at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.)

CASE STUDY: ANALYSIS

Equilibria in a swimming pool

Analysis

1 $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

2 As pH increases, the concentration of $H_3O^+(aq)$ decreases because of the inverse relationship between pH and $[H_3O^+]$. From the equation in the case study, $OCl^-(aq) + H_3O^+(aq) \rightleftharpoons HOCl(aq) + H_2O(l)$, Le Châtelier's principle tells you that the position of equilibrium will move to the left, increasing the concentration of H_3O^+ ions and consuming some of the HOCl. More hydrochloric acid, H_3O^+, will need to be added to re-establish the appropriate [HOCl]. Adding the acid will shift the equilibrium to the right again.

3 To shift the equilibrium to the right, and therefore increase the pH and decrease the $[H_3O^+]$, pool chlorine must be added to restore the correct balance.

KEY QUESTIONS

Knowledge and understanding

1 **a** According to Le Châtelier's principle, adding a reactant will result in a net forward reaction.
  b Adding a product will result in a net reverse reaction.
  c Adding a reactant will result in a net forward reaction.

2 **a** According to Le Châtelier's principle, removing a product will result in a net forward reaction.
  b Doubling the pressure, the system will move to reduce the pressure. The equilibrium position will move in the direction of the lower number of particles. There are 4 moles of gas on the reactant side and 2 moles of gas on the product side, so the system will move in a forward direction.

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- **c** In this system there are equal moles of gas particles on each side, so increasing the pressure will have no effect.
- **d** Increasing the temperature of an endothermic reaction will result in a forward reaction. An endothermic reaction has a positive Δ*H*, indicating that the reaction needs heat in order to proceed. You can think of the increasing temperature resulting in more heat (on the reactant side) being added to the system. Hence, the system moves to oppose this increase by consuming the heat. Alternatively, you can also predict the effect of the change from the knowledge that when the temperature of an endothermic reaction is increased, the equilibrium constant will increase. This means that the amount of product increases and the reaction moves in a forward direction.

3 **a** A positive Δ*H* indicates the reaction is endothermic. An increase in temperature will increase the equilibrium constant, *K*, and the amount of product will increase, resulting in a net forward reaction.
- **b** A negative Δ*H* indicates the reaction is exothermic. An increase in temperature will decrease the equilibrium constant, *K*, and the amount of product will decrease, resulting in a net backward reaction.
- **c** A positive Δ*H* indicates it is an endothermic reaction. An increase in temperature will increase the equilibrium constant, *K*, and the amount of product increases, resulting in a net forward reaction.
- **d** A negative Δ*H* indicates the reaction is exothermic. An increase in temperature will decrease the equilibrium constant, *K*, and the amount of product decreases, resulting in a net backward reaction.

Analysis

4 **a** **i** Δ*H* is positive, so increasing the temperature causes *K* to increase and therefore results in a net forward reaction.
  - **ii** Δ*H* is positive, so increasing the temperature causes *K* to increase and therefore results in a net forward reaction.
  - **iii** Δ*H* is negative, so decreasing the temperature causes *K* to increase and therefore results in a net forward reaction.
- **b** **i** No. Volume is inversely proportional to pressure. The reaction has equal moles of gas on both sides, so changing the volume will not cause a forward reaction.
  - **ii** Yes. Increasing the volume will have the effect of decreasing the pressure. The system will try to oppose this decrease by increasing pressure and so move in the direction of the most particles.
  - **iii** No. Because the reaction has equal moles of gas on both sides, we cannot cause a forward reaction to occur.

5 Doubling the volume will halve the pressure. The equilibrium mixture will respond by favouring the direction that increases pressure, i.e. more NO_2 molecules will be formed in order to re-establish equilibrium.
- **a** As the volume is increased, the concentration of NO_2 will decrease. Although the reaction will favour the formation of NO_2 according to Le Châtelier's principle, the adjustment can only partially oppose the change, so the corresponding increase in concentration will not reach the initial NO_2 concentration level.
- **b** The mass of NO_2 will be higher. By favouring the forward reaction, the shift in equilibrium will result in a higher yield of NO_2

6 **a** Decreasing the temperature would favour the forward exothermic process, resulting in a net forward reaction.
- **b** There are 5 particles on the reactant side and 3 particles on the product side. A decrease in volume would increase the pressure of the system. This would cause the system to favour the forward reaction to reduce the overall number of particles, hence reducing the pressure.

Chapter 7 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 **a** Chemical equilibrium is 'dynamic' because both forward and reverse reactions occur at the same rate. An equilibrium develops between water vapour and water when wet clothes are in a sealed bag, with water evaporating as rapidly as water vapour condenses, so the clothes remain wet.
- **b** When the bag is opened, water vapour escapes and the rate of evaporation exceeds the rate of condensation. The system is not in equilibrium and the clothes dry.

2 The reaction quotient is the ratio of the concentrations of the products to the concentration of the reactants, with the index of each concentration the same as the coefficient of the substance in the reaction equation. It can be calculated at any time during the reaction. The equilibrium constant is the same concentration ratio of products to reactants, but occurs when the rate of the forward reaction is equal to the rate of the reverse reaction. This is when the system is at equilibrium. The value of the reaction quotient becomes equal to the equilibrium constant at equilibrium.

3 **a** $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$
- **b** $S_2(g) + 2H_2(g) \rightleftharpoons 2H_2S(g)$
- **c** $NO_2(g) \rightleftharpoons \frac{1}{2}N_2O_4(g)$

4 **a** If $K = 0.0001$ for a particular reaction, at equilibrium the concentrations of products will be **less than** the concentrations of reactants.

b For the reaction with the equation:

$$2H_2(g) + 2NO(g) \rightleftharpoons 2H_2O(g) + N_2(g)$$

the expression for the equilibrium constant, K, is written as $\frac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$.

c When the reaction quotient is smaller than K, the reaction moves to the **right** to establish equilibrium.

5 $K = \frac{\left[Fe^{2+}\right]^2\left[Sn^{4+}\right]}{\left[Fe^{3+}\right]^2\left[Sn^{2+}\right]} = \frac{\left(0.20^2 \times 0.40\right)}{\left(0.10^2 \times 0.30\right)} = 5.3$ (no units)

6 The container is 2.0 L, so calculate equilibrium concentrations of reactants and products as follows:

$$[H_2O] = \frac{0.040}{2} = 0.020 \text{ M}$$

$$[H_2] = \frac{0.050}{2} = 0.025 \text{ M}$$

$$[CO] = \frac{0.020}{2} = 0.010 \text{ M}$$

$$[CO_2] = \frac{0.030}{2} = 0.015 \text{ M}$$

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.020 \times 0.010)}{(0.025 \times 0.015)} = 0.53 \text{ (no units)}$$

7 Write the expression for the equilibrium constant:

$$K = \frac{[C_3H_6O][H_2]}{[C_3H_8O]}$$

Calculate the equilibrium concentrations of the reactants and products:

$$[C_3H_6O] = \frac{0.21}{20} = 0.011 \text{ M}$$

$$[H_2] = \frac{0.21}{20} = 0.011 \text{ M}$$

$$[C_3H_8O] = \frac{0.21}{20} = 0.011 \text{ M}$$

Substitute the equilibrium concentrations into the equilibrium expression and find the value of the equilibrium constant.

$$K = \frac{(0.011 \times 0.011)}{0.011} = 0.011 \text{ M}$$

8 **a** The concentration of hydrogen gas will increase, because when the temperature of an exothermic reaction increases, the equilibrium constant decreases, the reaction moves in a reverse direction and the reactant concentrations increase. If ΔH is negative, an increase in T means a decrease in K.

b The concentration of hydrogen gas will increase, because when the temperature of an endothermic reaction increases, the equilibrium constant increases, the reaction moves in a forward direction and the product concentrations increase. If ΔH is positive, an increase in T means an increase in K.

9 A volume increase means a pressure decrease. The system opposes this by increasing the pressure and therefore moving in the direction of the most particles.

a In this case, a forward reaction occurs and more $C_3H_6O(g)$ and $H_2(g)$ will be produced.

b In this case, a reverse reaction occurs and more CO(g) and $2H_2(g)$ will be produced.

c There will be no effect, because there are equal numbers of particles on each side. In this case, there will be no more $N_2(g)$, $O_2(g)$ or NO(g).

10 B. The position of equilibrium cannot shift to oppose a change in volume, and therefore in pressure, because there are equal numbers of particles on each side. In the other three cases, there are different number of reactant and product particles, so the system will move to oppose the change.

11 **a** $K = \frac{[HCl]^8[O_2]^2}{[H_2O]^4[Cl_2]^4}$

Because the coefficients are doubled those in the first equation, the equilibrium constant for this expression will be the square of the given K.

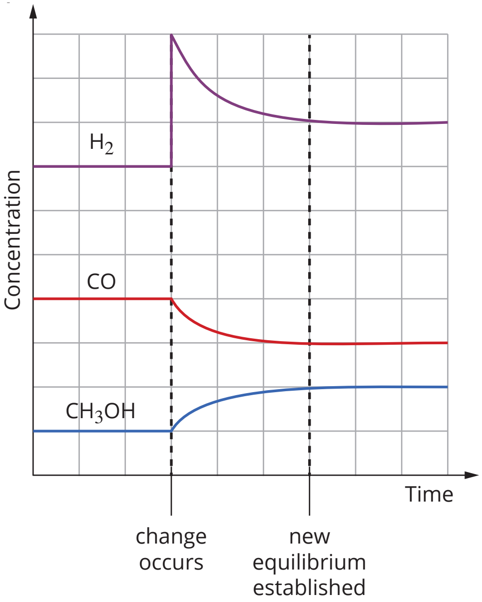
So, $K = (4.0 \times 10^{-4})^2 \text{ M}^2 = 1.6 \times 10^{-7} \text{ M}^2$

b This equation is the reverse of the first equation, so the expression for the equilibrium constant will be the inverse (reciprocal) of the given equilibrium constant.

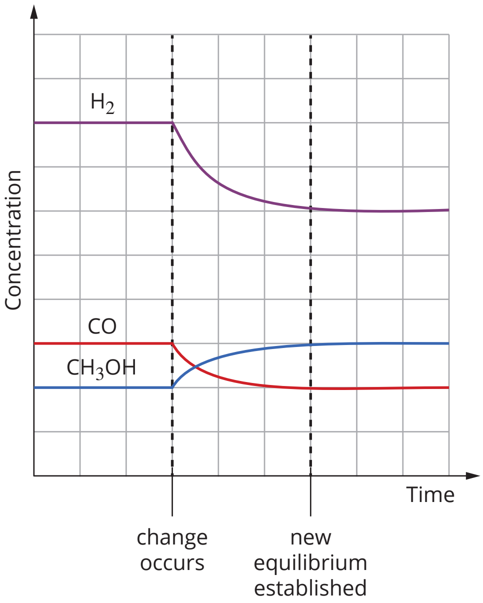
$$\text{So, } K = \frac{1}{4.0 \times 10^{-4}} = 2.5 \times 10^{3}\ \text{M}^{-1}$$

Application and analysis

12 a



b



13 As Q for the reaction is larger than K, the reaction must move to decrease Q. This will happen with a decrease in the concentration of the products. This will occur as the reverse reaction is favoured, decreasing the concentration of ethyl ethanoate as the mixture reaches equilibrium.

14 Because the volume is 1.0 L, the mole values are easily converted concentrations.

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.35^2}{(1.5 \times 1.5^3)} = 0.024\ \text{M}^{-2}$$

The reaction quotient $Q = 0.024$ is less than $K = 0.052$, so the reaction is not at equilibrium and will shift towards the right (in the forward direction), to increase Q and reach equilibrium.

15 a $K = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b Calculate equilibrium concentrations of reactants and products.

$$[PCl_5] = \frac{4.50}{3.00} = 1.50\ \text{M}$$

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$$[Cl_2] = \frac{0.900}{3.00} = 0.300\text{ M}$$

$$[PCl_2] = \frac{6.00}{3.00} = 2.00\text{ M}$$

Use the expression for the equilibrium constant from part **a**. Substitute equilibrium concentrations into the equilibrium expression.

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(2.00 \times 0.300)}{1.50} = 0.400\text{ M}$$

c Rearrange the expression to find $[Cl_2]$.

$$[Cl_2] = K \times \frac{[PCl_5]}{[PCl_3]}$$

Substitute equilibrium concentrations in the equilibrium constant expression and find the concentration of Cl_2.

$$[Cl_2] = 0.400 \times \frac{0.0020}{0.0010} = 0.80\text{ M}$$

d This equation is the reverse of the one given at the start of the question, and the temperature is constant. For the reverse reaction, the equilibrium constant is the reciprocal of the given reaction.

$$K = \frac{1}{0.400}\text{ M}^{-1} = 2.5\text{ M}^{-1}$$

16

	$N_2O_4(g)$	$2NO_2(g)$
I	0.540	0
C	$-x = -0.140$	$+2x = 0.280$
E	$0.540 - x$ $= 0.540 - 0.140$ $= 0.400$ $\frac{0.400}{2.0} = 0.20\text{ M}$	0.280 $\frac{0.280}{2.0} = 0.140\text{ M}$

Substitute the equilibrium concentrations into the equilibrium expression and find the value of the equilibrium constant.

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.140^2}{0.200} = 0.0980\text{ M}$$

17 a Write the expression for the equilibrium constant.

$$K = \frac{[C]^2[D]}{[A][B]^3}$$

Calculate the equilibrium concentrations of the reactants and products.

$$[A] = \frac{1.8}{2.0} = 0.90\text{ M}$$

$$[B] = \frac{0.54}{2.0} = 0.27\text{ M}$$

$$[D] = \frac{3.2}{2.0} = 1.6\text{ M}$$

b Substitute the equilibrium concentrations into the equilibrium expression and calculate the equilibrium concentration of C.

$$K = 0.024 = \frac{([C]^2 \times 1.6)}{(0.90 \times 0.27^3)}$$

Therefore $[C]^2 = \frac{(0.024 \times 0.90 \times 0.27^3)}{1.6} = 0.00027$

$$[C] = 0.016\text{ M}$$

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c Convert the equilibrium concentration of C into a mole value.

[C] = 0.016 M

$n(\text{C}) = 0.016 \text{ M} \times 2.0 \text{ L} = 0.032 \text{ mol}$

18 If Ca^{2+} ions are absorbed inefficiently from food, decreased concentrations of these ions could occur in body fluids. As a consequence, a net forward reaction of the given equation would occur, raising the concentration of dissolved Ca^{2+} ions in body fluids, but resulting in decreased amounts of calcium phosphate in bones.

19 a

	$2HI(g) \rightleftharpoons$	**$H_2(g)$ +**	**$I_2(g)$**
I	4.00	0	0
C	$-2x = -0.88$	$+x = 0.44$	$+x = 0.44$
E	$4.00 - 2x$ $= 4.00 - 0.88$ $= 3.12$ $\frac{3.12}{2.0} = 1.56$ M	$x = 0.44$ $\frac{0.44}{2.0} = 0.22$ M	$x = 0.44$ $\frac{0.44}{2.0} = 0.22$ M

$$K = \frac{[H_2][I_2]}{[HI]^2}$$

$$= \frac{0.22 \times 0.22}{1.56^2}$$

$$= 0.019\ 89$$

$$= 0.020 \text{ (no unit)}$$

b The reaction quotient for this reaction is: $Q = \frac{[H_2][I_2]}{[HI]^2}$

Calculate the value of Q in the second mixture.

$$[H_2] = \frac{0.240}{2.0} = 0.12 \text{ M}$$

$$[I_2] = \frac{0.320}{2.0} = 0.16 \text{ M}$$

$$[HI] = \frac{1.00}{2.0} = 0.50 \text{ M}$$

The value of the reaction quotient is: $Q = \frac{0.12 \times 0.16}{0.50^2} = 0.077$

The value of the reaction quotient is greater than the value of the equilibrium constant at the same temperature, as calculated in part **a**. Therefore, the system is not at equilibrium. A net reverse reaction will occur. As the reaction moves towards equilibrium, the concentrations of H_2 and I_2 will decrease and the concentration of HI will increase until the value of the reaction quotient is equal to the equilibrium constant.

20

	$2NO(g)$ +	**$2H_2(g) \rightleftharpoons$**	**$N_2(g)$ +**	**$2H_2O(g)$**
I	0.100	0.051	0	0.100
C	$-x = -(0.100 - 0.062)$ $= -0.038$	$-x = -0.038$	$+\frac{x}{2}$ $= +0.038/2$ $= +0.019$	$+x$ $= +0.038$
E	0.062	$0.051 - x$ $= 0.051 - 0.038$ $= 0.013$	$0 + \frac{x}{2}$ $= 0 + 0.019$ $= 0.019$	$0.100 + 0.038$ $= 0.138$

The volume of the vessel = 1.0 L, so using $c = \frac{n}{V}$, the amounts, in mol, are equivalent to the concentrations in M.

$$K = \frac{(0.138^2 \times 0.019)}{(0.013^2 \times 0.062^2)} = 5.6 \times 10^2 \text{ M}^{-1}$$

21 a The word ‘fuel’ indicates that the reaction will be exothermic (with a negative ΔH) and that the reaction will proceed extensively in the forward direction, so the equilibrium constant will be large.

b **i** It will move in the direction of the reactants, i.e. a net reverse reaction.

ii There will be no change in equilibrium position because a catalyst increases the rate of the forward and reverse reactions equally.

iii It will move in the direction of the products, i.e. a net forward reaction.

c **i** Decrease in value of *K* because as the temperature of an exothermic reaction increases, the value of K decreases.

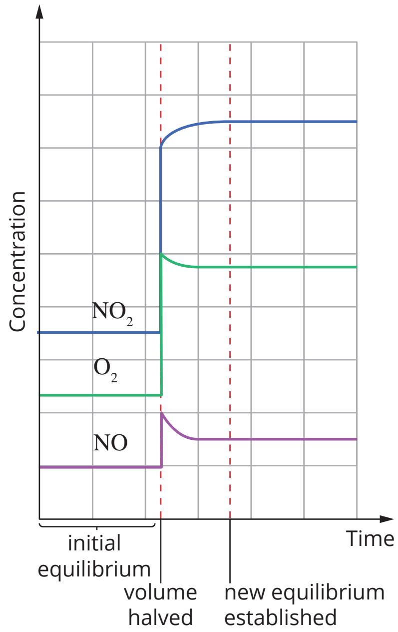
ii no change

iii No change because the value of *K* does not change unless there is a temperature change.

22 **a**

Change	Colour change (lighter or darker)	Explanation
i The temperature is decreased to 250°C at constant volume.	yes (darker)	This is an exothermic reaction, so *K* would increase as the temperature decreases and a net forward reaction would occur, producing more brown NO_2 gas.
ii The volume of the container is halved at constant temperature.	yes (darker)	The decrease in volume means an increase in pressure. The system would oppose this change by decreasing the pressure and moving in direction of least particles—i.e. a forward reaction would occur. The colour of the gas mixture would increase because more brown NO_2 will form.
iii A catalyst is added at constant volume and temperature.	no change	The addition of a catalyst would not change the colour because the rate of the forward and reverse reactions would be increased equally.

b



23 **a** For the initial mixture, $Q = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{0.300 \times 0.400}{0.100 \times 0.200^3} = 150\ M^{-2}$

Q = 150 is larger than *K* = 0.67. The reverse reaction will occur so that *Q* becomes equal to *K*. The [products] will decrease and [reactants] will increase.

i increase

ii increase

iii decrease

iv decrease

b The enthalpy change will be positive, indicating that the reaction is endothermic. An increased value of the equilibrium constant with an increased temperature indicates that the reaction has moved in the direction of the products. The extra heat has favoured the forward reaction, indicating it is an endothermic reaction, which consumes heat to occur.

24 **a** $2SO_3(g) + CO_2(g) \rightleftharpoons CS_2(g) + 4O_2(g)$

b $K = \frac{[CS_2][O_2]^4}{[SO_3]^2[CO_2]}$

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c **i** $n(O_2) = 4 \times n(CS_2) = 4 \times 0.028 = 0.112$ mol (according to the stoichiometry of the equation)

ii $[CS_2] = \frac{0.028}{20} = 0.0014$ M

$[O_2] = \frac{0.112}{20} = 0.0056$ M

$[SO_3] = \frac{0.022}{20} = 0.0011$ M

$[CO_2] = \frac{0.014}{20}$ 0.00070 M

$$K = \frac{0.0014 \times 0.0056^4}{0.0011^2 \times 0.00070} = 1.6 \times 10^{-3}\ \text{M}^{-2}$$

d **i** increase

ii increase

iii no effect

iv decrease

v no effect

25 **a** $K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

b 15–20 minutes, 25–30 minutes, 35–40 minutes

c $K = \frac{0.020^2}{(0.080^2 \times 0.040)} = 1.6\ \text{M}^{-1}$

d $K = \frac{0.044^2}{(0.106^2 \times 0.052)} = 3.3\ \text{M}^{-1}$

e $K = \frac{0.050^2}{(0.100^2 \times 0.078)} = 3.2\ \text{M}^{-1}$

f At 10 minutes; before 10 minutes the concentrations were changing slowly (shown in the graph by the very slight slope), but the addition of the catalyst at 10 minutes caused equilibrium to be reached more rapidly (shown by the steeper gradients of the graphs).

g The pressure was increased by reducing the volume. To oppose this pressure increase, the reaction moved forward, as shown by the graphs. (Also, because the value of K at 25–30 minutes is larger than at 15–20 minutes and this is an exothermic reaction, a decrease in temperature must have occurred.)

h O_2 gas was added, moving the reaction in the forward direction. (Also, because the equilibrium constant decreased and this is an exothermic reaction, there must have been an increase in temperature.)

i This is an exothermic reaction. Between 15 and 25 minutes the equilibrium constant increased, indicating that the temperature was decreased at 20 minutes. Between 25 and 35 minutes, the equilibrium constant decreased, indicating that the temperature was increased at 30 minutes.

Chapter 8 Production of chemicals by electrolysis

8.1 Electrolytic cells

CASE STUDY: ANALYSIS

Producing hydrogen for the hydrogen economy

Analysis

1 The electrolysis cells use electricity that is produced predominantly at power stations using coal or natural gas as their fuel source. The combustion of fossil fuels such as coal or natural gas produces CO_2, a key greenhouse gas.

2 Anode: $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$. OH^- is oxidised as it is the strongest reducing agent present.

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$. H_2O is reduced as it is the strongest oxidising agent present.

The advantage of using NaOH over NaCl is that when using NaCl there is the possibility of producing Cl_2. Cl_2 is a toxic gas, so it would need to be removed to prevent its release into the environment.

3 The steam reforming process involves a reaction where methane (CH_4) and steam react to produce carbon monoxide and hydrogen:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

Additional hydrogen can be obtained by reacting the carbon monoxide with steam:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

The steam reforming process has a negative environmental impact because the first reaction is energy-intensive, requiring temperatures of 700–1100°C (currently, the energy required for this process comes from the combustion of fossil fuels) and the second reaction produces CO_2, a key greenhouse gas. The release of greenhouse gases into the environment can be reduced through the use of carbon capture and storage technology.

Worked example: Try yourself 8.1.1

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the electrochemical series to predict the products of the electrolysis of 1 M zinc sulfate solution with copper electrodes at 25°C.

Thinking	Working
Identify which species are present in the solution.	$Zn^{2+}(aq)$, $SO_4^{2-}(aq)$ and $H_2O(l)$
Identify what the electrodes are made of.	copper
Refer to the electrochemical series and identify the possible reactions. Write these half-equations in the order they appear in the series.	By referring to the electrochemical series, you can see that a number of reactions need to be considered as the cell contains two oxidising agents, Zn^{2+}, and H_2O, and two reducing agents, Cu and H_2O. $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$ +1.77 V $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ +1.23 V $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ +0.34 V $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ −0.76 V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ −0.83 V The SO_4^{2-} ions are not involved in the reaction.
Determine the reactions that could occur at the anode.	At the anode (+), oxidation reactions that could occur are: $2H_2O(l) \rightarrow H_2O_2(aq) + 2H^+(aq) + 2e^-$ $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Determine the most likely reaction at the anode.	The strongest reducing agent, Cu(s), will be oxidised: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

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Determine the reactions that could occur at the cathode.	At the cathode (–), reduction reactions that could occur are: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
Determine the most likely reaction at the cathode.	The strongest oxidising agent, $Zn^{2+}(aq)$, will be reduced: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
Summarise your results to answer the question.	Nickel is produced at the cathode and Cu^{2+} is produced at the anode.

KEY QUESTIONS

Knowledge and understanding

1 In electrolytic cells:
  - **a** the reactions are **non-spontaneous**
  - **b** electrical energy is converted into **chemical** energy
  - **c** the anode is **positive** and the cathode is **negative**
  - **d** **oxidation** occurs at the anode and **reduction** occurs at the cathode.

2 Cu^{2+} ions move towards the cathode (–). Br^- ions move towards the anode (+).

3 The products are iodine, $I_2(g)$ and potassium, K(l).

This is because the only ions present are $K^+(l)$ and $I^-(l)$.

At the anode, the reaction is: $2I^-(l) \longrightarrow I_2(g) + 2e^-$

At the cathode, the reaction is: $K^+(l) + e^- \longrightarrow K(l)$

Analysis

4 **a** Silver rod. The silver rod is the negative electrode (cathode), which attracts positive Ag^+ ions in the solution towards it. Electrons from the power supply are 'pushed' towards the negative electrode. The Ag^+ ions are reduced to solid Ag.

b Carbon rod (anode, positive): $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Silver rod (cathode, negative): $Ag^+(aq) + e^- \longrightarrow Ag(s)$

c $4Ag^+(aq) + 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4Ag(s)$

5 **a** Possible reactions at the anode (positive electrode):

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23 V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34 V
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71 V

Possible reactions at the cathode (negative electrode):

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25 V
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83 V
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71 V

b Anode: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$. Cu(s) is oxidised because it is the strongest reducing agent present at the anode. Cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$. As water is a stronger oxidising agent than Na^+, water will be reduced in preference to Na^+. The electrode is made of nickel, but it is a reducing agent, not an oxidising agent, so it will not react.

c $Cu(s) + 2H_2O(l) \longrightarrow Cu^{2+}(aq) + 2OH^-(aq) + H_2(g)$

Note that if the $Cu^{2+}(aq)$ and $OH^-(aq)$ ions are allowed to meet, they will form a precipitate of $Cu(OH)_2(s)$.

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8.2 Commercial electrolytic cells

CASE STUDY: ANALYSIS

Electrorefining of copper

Analysis

1. The top 10 impurities are silver, gold, platinum, tin, antimony, lead, iron, nickel, cobalt, zinc—so any five of these is acceptable.
2. Tin, antimony, lead, iron, nickel, cobalt, zinc. These metals are all stronger reducing agents than copper, so they are oxidised.
3. Silver, gold and platinum. These metals are all weaker reducing agents than copper, so copper is oxidised instead.
4. Lead is oxidised to form lead(II) ions, which react with sulfate ions in the electrolyte to form a precipitate of lead(II) sulfate. The precipitate ends up in the 'anode mud'.

KEY QUESTIONS

Knowledge and understanding

1. The sodium metal produced is a very strong reducing agent and the chlorine gas produced is a very strong oxidising agent. If they came into contact with each other, they would spontaneously react to re-form sodium chloride.
2. The iron cathode is connected to the negative terminal of the power supply so it receives a continual supply of electrons, preventing it from being oxidised.

Analysis

3. **a** An inert electrode would be suitable. A reactive electrode would be oxidised at the anode, releasing cations into the solution, thus contaminating the electrolyte. The only reactive electrode that would be suitable is a zinc electrode.
   b Zinc ions are a stronger oxidising agent than water, so the zinc ions are preferentially reduced at the cathode. The use of an aqueous electrolyte is also cheaper than a molten electrolyte.
   c The strongest reducing agent present is water, so it is oxidised at the anode to produce oxygen gas:

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

4. **a** It is cheaper to obtain chlorine by electrolysis of concentrated sodium chloride solution than from molten sodium chloride because energy is required to melt sodium chloride.
   b Fluorine is the strongest oxidising agent known. Since a stronger oxidising agent than fluorine would be required to convert F^- ions into fluorine, the element cannot be made by direct reaction. However, it is generated at the anode during electrolysis of molten metal fluorides.
   c Na^+ ions are stronger oxidising agents than Ca^{2+} ions, so sodium metal is formed at the cathode in preference to calcium.
5. Changing to unreactive anodes from carbon anodes would avoid the production of carbon dioxide and reduce the cost of having to replace the electrodes.

8.3 Faraday's laws

Worked example: Try yourself 8.3.1

CALCULATING THE MASS OF A PRODUCT AT AN ELECTRODE

A copper-plating cell operates with a steady current of 20.0 A for 15.0 minutes. What mass of copper is plated on the object at the cathode? The equation for the reaction is:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Thinking	Working
Calculate the quantity of charge passing through a cell using the formula: $Q = I \times t$ Remember that time must be expressed in seconds.	$Q = I \times t$ $= 20.0 \times (15.0 \times 60)$ $= 1.80 \times 10^4$ C

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Calculate the amount of electrons, in mol, that passed through the cell using the formula: $n(e^-) = \frac{Q}{F}$	$n(e^-) = \frac{Q}{F}$ $= \frac{1.80 \times 10^4}{96\,500}$ $= 0.187$ mol
Use the mole ratio from the equation for the reaction, to determine the amount, in mol, of metal plated at the cathode.	The cathode reaction is: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ 2 moles of electrons will deposit 1 mole of copper metal. Mole ratio $\frac{n(Cu)}{n(e^-)} = \frac{1}{2}$ $n(Cu) = \frac{1}{2} \times n(e^-)$ $= 0.0933$ mol
Calculate the mass of metal plated at the cathode.	The molar mass of Cu is 63.5 g mol^{-1}. $m(Cu) = n \times M$ $= 0.0933 \times 63.5$ $= 5.92$ g

Worked example: Try yourself 8.3.2

CALCULATING THE TIME TAKEN TO PRODUCE A PRODUCT AT AN ELECTRODE

How long would it take, in hours, to deposit 20.0 g of silver at the cathode of a silver-plating cell operating at a current of 6.50 A? The half-equation for the reaction is: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Thinking	**Working**
Calculate the amount of substance, in mol, that was deposited or consumed at the electrode using the formula: $n = \frac{m}{M}$	$n(Ag) = \frac{m}{M}$ $= \frac{20.0}{107.9}$ $= 0.185$ mol
Calculate the amount of electrons, in mol, that passed through the cell using the mole ratio from the equation.	The cathode reaction is: $Ag^+(aq) + e^- \longrightarrow Ag(s)$ 1 mol of electrons will deposit 1 mol of silver metal. $\frac{n(e^-)}{n(Ag)} = \frac{1}{1}$ $n(e^-) = n(Ag)$ $= 0.185$ mol
Calculate the quantity of charge which passed through the cell using the formula: $Q = n(e^-) \times F$	$Q = n(e^-) \times F$ $= 0.185 \times 96\,500$ $= 1.79 \times 10^4$ C
Calculate the time required using the formula: $t = \frac{Q}{I}$	$t = \frac{Q}{I}$ $= \frac{1.79 \times 10^4}{6.50}$ $= 2.75 \times 10^3$ s
Convert seconds to hours by dividing by (60 × 60).	$t = \frac{2.75 \times 10^3}{60 \times 60}$ $= 0.764$ h

Worked example: Try yourself 8.3.3

CALCULATING THE TIME TAKEN TO USE A FIXED MASS OF FUEL IN A FUEL CELL

A fuel cell uses propanal (CH_3CH_2CHO) as its fuel source. How long would it take, in seconds, for 375 g of propanal to be used in the fuel cell operating at a current of 5.40 A? The half-equation for the reaction is:

$$CH_3CH_2CHO(l) + 5H_2O(l) \longrightarrow 3CO_2(g) + 16H^+(aq) + 16e^-$$

Thinking	**Working**
Calculate the amount of propanal, in mol, used in the fuel cell using the formula: $n(CH_3CH_2CHO) = \frac{m}{M}$	$n(CH_3CH_2CHO) = \frac{m}{M}$ $= \frac{375}{58.0}$ $= 6.47$ mol
Use the mole ratio from the equation for the reaction to determine the amount of electrons, in mol, produced in the reaction.	The reaction is: $CH_3CH_2CHO(l) + 5H_2O(l) \longrightarrow 3CO_2(g) + 16H^+(aq) + 16e^-$ 16 moles of electrons are produced for every 1 mole of propanal that reacts. Mole ratio: $\frac{n(e^-)}{n(CH_3CH_2CHO)} = \frac{16}{1}$ $n(e^-) = 16 \times n(CH_3CH_2CHO)$ $= 16 \times 6.47$ $= 103$ mol
Calculate the quantity of charge generated by the fuel cell using the formula: $Q = n(e^-) \times F$	$Q = n(e^-) \times F$ $= 103 \times 96\,500$ $= 9.98 \times 10^6$ C
Calculate the time taken to use the propanal using the formula: $Q = I \times t$	Rearrange to find t: $t = \frac{Q}{I}$ $= \frac{9.98 \times 10^6}{5.40}$ $= 1.85 \times 10^6$ s

KEY QUESTIONS

Knowledge and understanding

1 **a** $Ag^+(aq) + e^- \longrightarrow Ag(s)$

b $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$

c $2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

d $H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

2 **a** To produce 1 mole of silver requires 1 mole of electrons, which has a charge of 96 500 C.

b To produce 0.2 mole of zinc requires $2 \times 0.2 = 0.4$ mole of electrons, which has a charge of $0.4 \times 96\,500 = 38\,600$ C.

c To produce 25 mole of chlorine requires $2 \times 25 = 50$ mole of electrons, which has a charge of $50 \times 96\,500 = 4\,825\,000$ C.

d To produce 0.006 mole of hydrogen requires $2 \times 0.006 = 0.012$ mole of electrons, which has a charge of $0.012 \times 96\,500 = 1158$ C.

Analysis

3 $Q = I \times t$

$= 12.5 \times (75.0 \times 60)$

$= 5.63 \times 10^4$ C

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

$$n(e^-) = \frac{Q}{F}$$

$$= \frac{5.63 \times 10^4}{96\,500}$$

$= 0.583$ mol

$$n(\text{Cu}) = \frac{1}{2} \times n(\text{e}^-)$$
$$= \frac{1}{2} \times 0.583$$
$$= 0.291 \text{ mol}$$
$$m(\text{Cu}) = n \times M$$
$$= 0.583 \times 63.5$$
$$= 18.5 \text{ g}$$

4 $$n(\text{Pb}) = \frac{m}{M}$$
$$= \frac{52.9}{207.2}$$
$$= 0.255 \text{ mol}$$
$$n(\text{e}^-) = 2 \times n(\text{Pb})$$
$$= 2 \times 0.255$$
$$= 0.511 \text{ mol}$$
$$Q = n(\text{e}^-) \times F$$
$$= 0.511 \times 96\,500$$
$$= 4.93 \times 10^4 \text{ C}$$
$$t = \frac{Q}{I}$$
$$= \frac{4.93 \times 10^4}{9.0}$$
$$= 5.5 \times 10^3 \text{ s}$$
$$= \frac{5.5 \times 10^3}{(60 \times 60)}$$
$$= 1.5 \text{ h}$$

5 **a** $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$. In an electroplating cell, the negative terminal is the cathode where reduction occurs. $Zn^{2+}(aq)$ ions are reduced to Zn(s).

b $$n(\text{Zn}) = \frac{m}{M}$$
$$= \frac{0.085}{65.4}$$
$$= 1.3 \times 10^{-3} \text{ mol}$$

$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$

$$n(\text{e}^-) = 2 \times n(\text{Zn})$$
$$= 2 \times 1.3 \times 10^{-3}$$
$$= 2.6 \times 10^{-3} \text{ mol}$$
$$Q = n(\text{e}^-) \times F = I \times t$$
$$I = \frac{n(\text{e}^-) \times F}{t}$$
$$= \frac{2.6 \times 10^{-3} \times 96\,500}{21.0 \times 60}$$
$$= 0.20 \text{ A}$$

6 $$Q = I \times t$$
$$= 1.50 \times (25.0 \times 60)$$
$$= 2.25 \times 10^3 \text{ C}$$
$$n(\text{e}^-) = \frac{Q}{F}$$
$$= \frac{2.25 \times 10^3}{96\,500}$$
$$= 2.33 \times 10^{-2} \text{ mol}$$
$$n(\text{metal}) = \frac{m}{M}$$
$$= \frac{1.40}{118.7}$$
$$= 1.18 \times 10^{-2} \text{ mol}$$

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$$\begin{aligned}\frac{n(\mathrm{e}^-)}{n(\text{metal})} &= \frac{2.33\times10^{-2}}{1.18\times10^{-2}}\\ &= 1.98\\ &\approx 2\end{aligned}$$

2 mol of electrons are required to produce 1 mol of metal ∴ The metal ions have a 2+ charge.

7
$$\begin{aligned}Q &= I\times t\\ &= 3.3\times10^{3}\times(24\times60\times60)\\ &= 2.9\times10^{8}\ \mathrm{C}\end{aligned}$$

$$\begin{aligned}n(\mathrm{e}^-) &= \frac{Q}{F}\\ &= \frac{2.9\times10^{8}}{96500}\\ &= 3.0\times10^{3}\ \text{mol}\end{aligned}$$

$$\begin{aligned}n(\mathrm{CH_3OH}) &= \frac{1}{6}\times n(\mathrm{e}^-)\\ &= \frac{1}{6}\times3.0\times10^{3}\\ &= 4.9\times10^{2}\ \text{mol}\end{aligned}$$

$$\begin{aligned}m(\mathrm{CH_3OH}) &= n\times M\\ &= 4.9\times10^{2}\times32.0\\ &= 1.6\times10^{4}\ \mathrm{g}\\ &= 16\ \mathrm{kg}\end{aligned}$$

Chapter 8 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 **a** In galvanic cells, the anode is negative and the cathode is positive; in electrolytic cells, the anode is positive and the cathode is negative.

b In galvanic cells, the direction of electron flow is determined by the cell reaction; in electrolytic cells, the direction of electron flow is determined by the external power supply. Direction of electron flow is always from anode to cathode through the external circuit.

c In galvanic cells, chemical energy is converted into electrical energy; in electrolytic cells, electrical energy is converted into chemical energy.

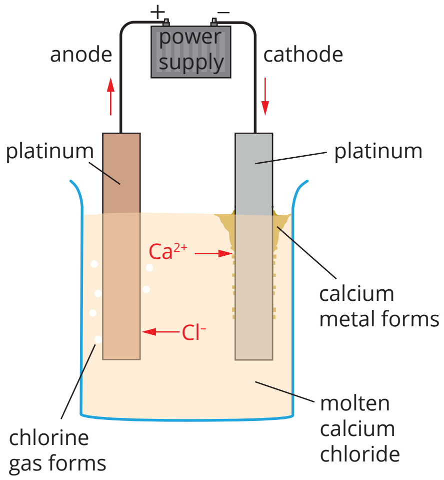
d Galvanic cell reactions occur spontaneously; electrolytic cell reactions are non-spontaneous.

2 anode: $2\mathrm{Cl^-(l)} \longrightarrow \mathrm{Cl_2(g)} + 2\mathrm{e^-}$

cathode: $\mathrm{Sn^{2+}(l)} + 2\mathrm{e^-} \longrightarrow \mathrm{Sn(l)}$

overall: $\mathrm{Sn^{2+}(l)} + 2\mathrm{Cl^-(l)} \longrightarrow \mathrm{Sn(l)} + \mathrm{Cl_2(g)}$

3



4 C. C is correct because $H^+(aq)$ is the strongest oxidising agent present, so is reduced to $H_2(g)$, H_2O is the strongest reducing agent present, so is oxidised to $O_2(g)$. A is incorrect because $Br^-(aq)$ is a stronger reducing agent than H_2O so $Br_2(l)$ is produced. B is incorrect because $Cl^-(aq)$ is preferentially oxidised instead of H_2O when very concentrated NaCl(aq) is used, $Cl_2(g)$ is produced. D is incorrect because $Co^{2+}(aq)$ is a stronger oxidising agent than H_2O so Co(s) is produced.

5 C. $Fe^{2+}(aq)$ is the strongest oxidising agent present, so is reduced to Fe(s) at the cathode. Cu(s) is also the strongest reducing agent present, so is oxidised to $Cu^{2+}(s)$ at the anode.

6 In the cell with lead electrodes, $Pb^{2+}(aq)$ is the strongest oxidising agent and Pb(s) is the strongest reducing agent.

anode: $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

cathode: $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$

In the cell with the platinum electrodes, $Pb^{2+}(aq)$ is the strongest oxidising agent and $H_2O(l)$ is the strongest reducing agent.

anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode: $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$

7 If an aqueous solution of sodium chloride was used instead of molten sodium chloride, water would be present. Water is a stronger oxidising agent and reducing agent than $Na^+(aq)$ and $Cl^-(aq)$ respectively. This means water is preferentially oxidised and reduced instead of $Cl^-(aq)$ and $Na^+(aq)$ respectively. Therefore, neither sodium nor chlorine would be produced.

8 **a** anode: $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

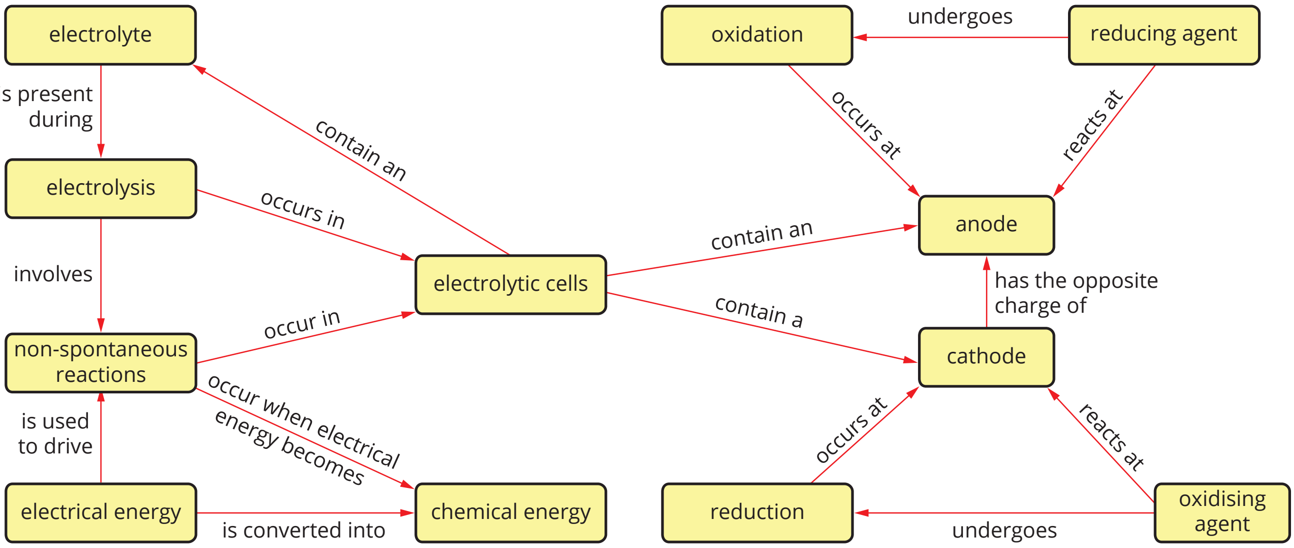
b The semipermeable membrane only allows Na^+ ions to move through from the anode compartment to the cathode compartment. This allows for a very pure sodium hydroxide product to be produced. The semipermeable membrane also prevents mixing between the reactive products.

Application and analysis

9 The reaction in a galvanic cell is spontaneous and if the reactants in the cell were in the one container and in contact with each other, the reaction between them could occur directly, releasing energy as heat rather than as electricity.

In electrolytic cells, the reaction is non-spontaneous, so that both the electrode reactions can occur within the same container. The products of the electrolysis reaction should not be allowed to come into contact with each other, however, or a reaction may occur.

10



11 The electrolyte solution contains water. As water is a stronger oxidising agent than Mn^{2+}, water will be reduced in preference to the Mn^{2+}. The reaction that occurred was:

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

12 **a** At the anode:

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons H_2O(l)$ +1.23 V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ +0.34 V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ −0.76 V

At the cathode:

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ +0.34 V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ −0.76 V
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ −0.83 V

The SO_4^{2-} ions are not involved in the reaction.

b Anode: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$. Because Cu(s) is a stronger reducing agent than water, Cu(s) will be oxidised in preference to water.

Cathode: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$. Because $Zn^{2+}(aq)$ is a stronger oxidising agent than water, $Zn^{2+}(aq)$ will be reduced in preference to water.

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

13

Experiment	Cathode reaction	Anode reaction
a	$K^+(l) + e^- \longrightarrow K(l)$	$2I^-(l) \longrightarrow I_2(l) + 2e^-$
b	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$
c	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
d	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$
e	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

14 The electrochemical series shows that the oxidising strength of H_2O is greater than that of Al^{3+}. If water is present in the electrolysis cell, it reacts preferentially at the cathode and electrolysis of aqueous aluminium salts does not yield aluminium metal.

15 C. Water is the strongest reducing agent present, so the half-equation for the reaction at the anode is:

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

Water is also the strongest oxidising agent present, so the half-equation for the reaction at the cathode is:

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

The overall equation is:

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

$$\begin{aligned} n(H_2) &= 2 \times n(O_2) \\ &= 2 \times 0.05 \\ &= 0.1 \text{ mol} \end{aligned}$$

16 A. $$\begin{aligned} n(Cr) &= \frac{m}{M} \\ &= \frac{0.50}{52.0} \\ &= 9.6 \times 10^{-3} \text{ mol} \end{aligned}$$

0.019 F of charge = 0.019 mol of e^-

$$\begin{aligned} \frac{n(e^-)}{n(Cr)} &= \frac{0.019}{9.6 \times 10^{-3}} \\ &= 1.976 \\ &\approx 2 \end{aligned}$$

The reaction occurring at the cathode must be: $Cr^{2+} + 2e^- \longrightarrow Cr$

So, the oxidation number of chromium in the compound is +2.

17 B. $$\begin{aligned} Q &= I \times t \\ &= 0.45 \times (1.2 \times 60 \times 60) \\ &= 1.9 \times 10^3 \text{ C} \end{aligned}$$

$$\begin{aligned} n(e^-) &= \frac{Q}{F} \\ &= \frac{1.9 \times 10^3}{96500} \\ &= 0.020 \text{ mol} \end{aligned}$$

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$$n(\text{Zn}) = \frac{1}{2} \times n(\text{e}^-) = \frac{1}{2} \times 0.020 = 0.010 \text{ mol}$$

$$m(\text{Zn}) = n \times M = 0.010 \times 65.4 = 0.66 \text{ g}$$

18 $n(\text{H}_2) = \frac{pV}{RT} = \frac{70.0 \times 10^3 \times 2.48 \times 10^{-3}}{8.31 \times 298.0} = 0.0701 \text{ mol}$

$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

$$n(\text{e}^-) = 2 \times n(\text{H}_2) = 2 \times 0.0701 = 0.140 \text{ mol}$$

$$Q = n(\text{e}^-) \times F = 0.140 \times 96500 = 1.35 \times 10^4 \text{ C}$$

$$I = \frac{Q}{t} = \frac{1.35 \times 10^4}{(45.0 \times 60)} = 5.01 \text{ A}$$

19 **a** anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

b $n(\text{e}^-) = \frac{Q}{F} = \frac{38600}{96500} = 0.400 \text{ mol}$

$$\frac{n(\text{Cu}^{2+})}{n(\text{e}^-)} = \frac{1}{2}$$

$$n(\text{Cu}^{2+}) = \frac{1}{2} \times n(\text{e}^-) = \frac{1}{2} \times 0.400 = 0.200 \text{ mol}$$

Calculate the amount of Cu^{2+} initially present.

$$n(\text{Cu}^{2+}) \text{ initial} = c \times V = 1.00 \times 1.00 = 1.00 \text{ mol}$$

Calculate the amount of Cu^{2+} remaining.

$$n(\text{Cu}^{2+}) \text{ remaining} = n(\text{Cu}^{2+}) \text{ initial} - n(\text{Cu}^{2+}) \text{ reduced} = 1.00 - 0.200 = 0.80 \text{ mol}$$

Calculate the concentration of Cu^{2+} remaining.

$$c(\text{Cu}^{2+}) = \frac{n}{V} = \frac{0.80}{1.00} = 0.80 \text{ M}$$

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20 $Q = I \times t$

$= 25\,000 \times (24 \times 60 \times 60)$

$= 2.16 \times 10^9$ C

$n(e^-) = \frac{Q}{F}$

$= \frac{2.16 \times 10^9}{96\,500}$

$= 2.24 \times 10^4$ mol

Write a balanced equation.

$M^{2+} + 2e^- \longrightarrow M$

$n(M) = \frac{1}{2} \times n(e^-)$

$= \frac{1}{2} \times 2.24 \times 10^4$

$= 1.12 \times 10^4$ mol

Mass of metal produced = 2.72×10^5 g

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

$= \frac{2.72 \times 10^5}{1.12 \times 10^4}$

$= 24.3$ g mol^{-1}

Therefore, this metal must be magnesium.

21 **a** $Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$; however, the reaction that occurs in practice is $Al(s) + 3OH^-(aq) \longrightarrow Al(OH)_3(s) + 3e^-$

b $n(Al) = \frac{m}{M}$

$= \frac{1.15}{27.0}$

$= 0.0426$ mol

$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$

$n(e^-) = 3 \times n(Al)$

$= 3 \times 0.0426$

$= 0.128$ mol

$Q = n(e^-) \times F = I \times t$

$t = \frac{n(e^-) \times F}{I}$

$= \frac{0.128 \times 96\,500}{105 \times 10^{-3}}$

$= 1.17 \times 10^5$ s

There are 60 seconds in 1 minute, and 60 minutes in 1 hour, so convert to hours by dividing by (60 × 60 = 3600).

$1.17 \times 10^5 \times \frac{1}{3600} = 32.6$ hours

22 **a** $C_6H_{12}O_6(aq) + 6H_2O(l) \longrightarrow 6CO_2(g) + 24H^+(aq) + 24e^-$

b $Q = I \times t = n(e^-) \times F$

$n(e^-) = \frac{I \times t}{F}$

$= \frac{5.00 \times 10^{-3} \times (60 \times 60)}{96\,500}$

$= 1.87 \times 10^{-4}$ mol per hour

$n(C_6H_{12}O_6) = \frac{n(e^-)}{24}$

$= \frac{1.87 \times 10^{-4}}{24}$

$= 7.77 \times 10^{-6}$ mol per hour

c $V(C_6H_{12}O_6) = \frac{n}{c}$

$= \frac{7.77 \times 10^{-6}}{1.18 \times 10^{-3}}$

$= 0.006\,59$ L per hour

$= 6.59$ mL per hour

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23 **a** $Au^+(aq) + e^- \longrightarrow Au(s)$

$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$

$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$

b $n(Au) = \frac{15.0}{197.0}$

$= 0.0761$ mol

$\frac{n(e^-)}{n(Au)} = \frac{1}{1}$

$n(e^-) = 0.0761$ mol

$\frac{n(Zn)}{n(e^-)} = \frac{1}{2}$

$n(Zn) = \frac{1}{2} \times 0.0761$

$= 0.0381$ mol

$m(Zn) = n \times M$

$= 0.0381 \times 65.4$

$= 2.49$ g

$\frac{n(Cr)}{n(e^-)} = \frac{1}{3}$

$n(Cr) = \frac{1}{3} \times 0.0761$

$= 0.0254$ mol

$m(Cr) = n \times M$

$= 0.0254 \times 52.0$

$= 1.32$ g

24 **a** cathode

b negative

c $A(Ag) = 0.0900\ m^2 = 900\ cm^2$

$V(Ag) =$ area × thickness

$= 900 \times 0.00500$

$= 4.5\ cm^3$

$m(Ag) =$ density × V

$= 10.5 \times 4.5$

$= 47.3$ g

$n(Ag) = \frac{m}{M}$

$= \frac{47.3}{107.9}$

$= 0.438$ mol

$\frac{n(e^-)}{n(Ag)} = \frac{1}{1}$

$n(e^-) = n(Ag) = 0.438$ mol

$Q = n(e^-) \times F$

$= 0.438 \times 96\ 500$

$= 4.23 \times 10^4$ C

$t = \frac{Q}{I}$

$= \frac{4.23 \times 10^4}{0.500}$

$= 8.45 \times 10^4$ s

25 **a** To investigate Faraday's first law of electrolysis by examining the effect of increasing current on the mass of copper deposited at the cathode of a copper-plating cell.

b Independent variable: current, in A. Dependent variable: mass of copper deposited on the nickel medallion (or the cathode), in g.

c **i** At cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

$Q = I \times t$

$= 10.0 \times (20.0 \times 60)$

$= 1.20 \times 10^4$ C

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$$n(e^-) = \frac{Q}{F}$$
$$= \frac{1.20 \times 10^4}{96500}$$
$$= 0.124 \text{ mol}$$
$$\frac{n(Cu)}{n(e^-)} = \frac{1}{2}$$
$$n(Cu) = \frac{1}{2} \times n(e^-)$$
$$= \frac{1}{2} \times 0.124$$
$$= 0.0622 \text{ mol}$$
$$m(Cu) = n \times M$$
$$= 0.0622 \times 63.5$$
$$= 3.95 \text{ g}$$

ii Systematic error. The experimental value is inaccurate as it is below the expected value.

iii Examples of systematic errors are: small pieces of copper flaking off the medallion in the cell; the actual current is lower than the recorded current, so less copper than expected is deposited on the medallion; small pieces of copper are washed off the medallion during the washing and drying stage before weighing.

iv cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
anode: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Because the reverse reaction is occurring at each electrode, the concentration of Cu^{2+} and therefore $CuSO_4$ will remain constant, 1.00 M.

d i cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$
Therefore, $O_2(g)$ is produced.

ii
$$Q = I \times t$$
$$= 10.0 \times (20.0 \times 60)$$
$$= 1.20 \times 10^4 \text{ C}$$
$$n(e^-) = \frac{Q}{F}$$
$$= \frac{1.20 \times 10^4}{96500}$$
$$= 0.124 \text{ mol}$$
$$\frac{n(Cu^{2+})}{n(e^-)} = \frac{1}{2}$$
$$n(Cu^{2+}) = \frac{1}{2} \times n(e^-)$$
$$= \frac{1}{2} \times 0.124$$
$$= 0.0622 \text{ mol}$$

Calculate the amount of Cu^{2+} initially present.
$$n(Cu^{2+}) \text{ initial} = c \times V$$
$$= 1.00 \times 0.250$$
$$= 0.250 \text{ mol}$$

Calculate the amount of Cu^{2+} remaining.
$$n(Cu^{2+}) \text{ remaining} = n(Cu^{2+}) \text{ initial} - n(Cu^{2+}) \text{ reduced}$$
$$= 0.250 - 0.0622$$
$$= 0.188 \text{ mol}$$

Calculate the concentration of Cu^{2+} remaining.
$$c(Cu^{2+}) = \frac{n}{V}$$
$$= \frac{0.188}{0.250}$$
$$= 0.752 \text{ M}$$

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26 **a** $Q = I \times t$

$= 7.50 \times (45.0 \times 60)$

$= 2.03 \times 10^4$ C

b A: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

B: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

C: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

D: $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

c $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

$$n(e^-) = \frac{Q}{F} = \frac{2.03 \times 10^4}{96500} = 0.210 \text{ mol}$$

$$\frac{n(Cu)}{n(e^-)} = \frac{1}{2}$$

$$n(Cu) = \frac{1}{2} \times n(e^-) = \frac{1}{2} \times 0.210 = 0.105 \text{ mol}$$

$$m(Cu) = n \times M = 0.105 \times 63.5 = 6.66 \text{ g}$$

d $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

$$n(e^-) = \frac{Q}{F} = \frac{2.03 \times 10^4}{96500} = 0.210 \text{ mol}$$

$$\frac{n(H_2)}{n(e^-)} = \frac{1}{2}$$

$$n(H_2) = \frac{1}{2} \times n(e^-) = \frac{1}{2} \times 0.210 = 0.105 \text{ mol}$$

$$V(H_2) = n \times V_m = 0.105 \times 24.8 = 2.60 \text{ L}$$

e $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

As the concentration of copper(II) ions increases in the solution due to the anode reaction, copper will be deposited on the cathode because Cu^{2+} is a stronger oxidising agent than H^+, so Cu^{2+} will be preferentially reduced.

27 **a** Write half-equations.

cathode: $Na^+(l) + e^- \longrightarrow Na(l)$

anode: $2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

$Q = I \times t$

$= 35 \times 10^3 \times (24 \times 60 \times 60)$

$= 3.0 \times 10^9$ C

$$n(e^-) = \frac{Q}{F} = \frac{3.0 \times 10^9}{96500} = 3.1 \times 10^4 \text{ mol}$$

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$\frac{n(\text{Na})}{n(\text{e}^-)} = \frac{1}{1}$

$n(\text{Na}) = n(\text{e}^-) = 3.1 \times 10^4$ mol

$m(\text{Na}) = n \times M$

$= 3.1 \times 10^4 \times 23.0$

$= 7.2 \times 10^5$ g

$= 7.2 \times 10^2$ kg

b $n(\text{Cl}_2) = \frac{1}{2} \times n(\text{e}^-)$

$= \frac{1}{2} \times 3.1 \times 10^4$

$= 1.6 \times 10^4$ mol

$V(\text{Cl}_2) = n \times V_m$

$= 1.6 \times 10^4 \times 24.8$

$= 3.9 \times 10^5$ L

28 **a** Write the half-equations.

cathode: Al^{3+} (in cryolite) + $3\text{e}^- \longrightarrow \text{Al(l)}$

anode: $\text{C(s)} + 2\text{O}^{2-}$ (in cryolite) $\longrightarrow \text{CO}_2\text{(g)} + 4\text{e}^-$

$m(\text{Al}) = 1.00$ tonne $= 1.00 \times 10^6$ g

$n(\text{Al}) = \frac{m}{M}$

$= \frac{1.00 \times 10^6}{27.0}$

$= 3.70 \times 10^4$ mol

$\frac{n(\text{e}^-)}{n(\text{Al})} = \frac{3}{1}$

$n(\text{e}^-) = 3 \times n(\text{Al})$

$= 3 \times 3.70 \times 10^4$

$= 1.11 \times 10^5$ mol

$Q = n(\text{e}^-) \times F$

$= 1.11 \times 10^5 \times 96\,500$

$= 1.07 \times 10^{10}$ C

$t = \frac{Q}{I}$

$= \frac{1.07 \times 10^{10}}{150\,000}$

$= 7.15 \times 10^4$ s

b $\frac{n(\text{C})}{n(\text{e}^-)} = \frac{1}{4}$

$n(\text{C}) = \frac{1}{4} \times n(\text{e}^-)$

$= \frac{1}{4} \times 1.11 \times 10^5$

$= 2.78 \times 10^4$ mol

$m(\text{C}) = n \times M$

$= 2.78 \times 10^4 \times 12.0$

$= 3.33 \times 10^5$ g

c $n(\text{CO}_2) = n(\text{C}) = 2.78 \times 10^4$ mol

$V(\text{CO}_2) = n \times V_m$

$= 2.78 \times 10^4 \times 24.8$

$= 6.89 \times 10^5$ L

d $E = V \times Q$

$= 5.00 \times 1.07 \times 10^{10}$

$= 5.35 \times 10^{10}$ J

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e Calculate the number of kilowatt hours required.

number of kWh = $\frac{5.35 \times 10^{10}}{3600000} = 1.49 \times 10^4$ kWh

Calculate the cost of electricity.

cost = $1.49 \times 10^4 \times 0.28 = \$4172 = \$4.2 \times 10^3$

29 **a** $n(\text{Ti}) = \frac{m}{M}$

$= \frac{14.37}{47.9}$

$= 0.300$ mol

b $Q = \frac{E}{V}$

$= \frac{463.2 \times 10^3}{4.0}$

$= 1.2 \times 10^5$ C

c $n(\text{e}^-) = \frac{Q}{F}$

$= \frac{1.2 \times 10^5}{96500}$

$= 1.2$ mol

d $\text{Ti}^{x+}(aq) + xe^- \longrightarrow \text{Ti}(s)$

$\frac{n(\text{e}^-)}{n(\text{Ti})} = \frac{x}{1}$

$x = \frac{n(\text{e}^-)}{n(\text{Ti})}$

$= \frac{1.2}{0.300}$

$= 4.0$

$x = 4$

The charge of the titanium ion is 4+.

e Therefore the empirical formula of rutile is TiO_2.

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Chapter 9 Designing for energy efficiency and sustainability

9.1 Optimising the yield of industrial processes

KEY QUESTIONS

Knowledge and understanding

1 In the production of methanol, both a higher reaction rate and a higher equilibrium yield could be achieved with a **higher** pressure. In addition, a moderate **temperature** needs to be used to ensure that a reasonable reaction rate and equilibrium yield are achieved. A **catalyst** is used to further increase the **reaction rate**.

2 High temperature and low pressure increase the equilibrium yield of NO_2.

3 **a** Gases under high pressure can be dangerous if there is a leak or faulty equipment. The risk is heightened if the gases involved are explosive or flammable. The equipment used to contain gases at high pressure is expensive.

b If gases are explosive or flammable, the risk involved will be greater if the temperature is increased. Increasing the temperature can also increase the pressure, adding to the danger.

Analysis

4 **a** The reaction is exothermic, so equilibrium yield will be increased at low temperatures. As 3 moles of gaseous reactants become 2 moles of gaseous products, high pressure would favour a higher equilibrium yield. An excess of a reactant can also be used to increase equilibrium yield.

b Reaction rate would be increased by increased pressure, high temperatures and the use of a catalyst.

c The use of high pressure is expensive and can be dangerous, so the reaction is run at 1 atm to reduce costs. The moderate temperature is used to ensure a reasonable rate of reaction without impacting too highly on the equilibrium yield. The decrease in reaction rate due to the lower temperature is offset by the addition of a catalyst. This compromise balances the yield and rate for the plant.

5 **a** The reaction is exothermic, the energy released increases the temperature of the system.

b As the reaction is an exothermic process, the gases are cooled before being pumped back into the reaction system to maximise equilibrium yield. Pumping hot gases into the reaction mixture would cause the temperature to rise and favour the reverse reaction, reducing the yield of ammonia.

6 Temperatures higher than 400°C are required to obtain an acceptably fast rate of reaction.

7 **a** Methane is usually sourced as a fossil fuel. When this happens, it is considered to be a non-renewable fuel and its extraction involves potential environmental damage. The other reactant is water—potentially this can be harvested from rainfall, limiting any negative impact on the environment.

b CO is a toxic gas. It is usually converted to CO_2, which is safer to handle, but presents greenhouse gas issues.

c The manufacture of hydrogen by this method will require significant energy as the reaction is highly endothermic.

9.2 Rechargeable cells and batteries

CASE STUDY: ANALYSIS

Secondary batteries: Car batteries

1 During discharge, Pb is **oxidised** at the **anode** and PbO_2 is **reduced** at the **cathode**. Energy is **released** in this cycle. During recharge, $PbSO_4$ is oxidised to **PbO_2** at the **anode** and $PbSO_4$ is reduced to **Pb** at the **cathode**.

2 Electrical energy is converted into chemical energy.

3 The reaction of PbO_2 at the cathode consumes H^+ ions. As discharge proceeds, the concentration of H^+ ions decreases, the solution becomes less acidic and the pH increases.

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KEY QUESTIONS

Knowledge and understanding

1 **a** Discharge – a spontaneous reaction occurs in a cell to produce electrical energy from chemical potential energy.
  b Recharge – a voltage is applied to the cell to reform the original reactants. This is an electrolytic process.

2 **a** secondary
  b primary
  c secondary

3 The voltage required needs to be >1.5 V for recharging to occur. It should, however, not be too much greater or the possibility of side reactions is increased.

4 Examples of applications that are increasing the demand for lithium-type batteries include electric cars, electricity storage batteries, miniaturised devices such as hearing aids, and portable appliances.

5 **a** True – the anode is defined as the electrode where oxidation occurs.
  b True – Primary cells cannot be recharged effectively because their reaction products are not in contact with the electrodes.
  c False – the anode will be positive during recharge.
  d True – it is too difficult to reverse the original reactions if the electrodes are consumed.
  e True – recharging a cell reverses the discharge reaction, reforming the original reactants

Analysis

6 **a** Lead is a very heavy metal. A series of lead-based cells in a car will make the car too heavy. Lead is a scarce metal and a toxic metal – it is desirable to use a safer alternative.
  b A laptop needs very small batteries. A small NiMH battery would not have a suitable capacity to run a laptop.
  c A laptop runs many functions at once and has a large screen. A primary cell would be drained too quickly in a laptop. The power demands of a basic calculator are not as great.

7 **a** Reduction half-reaction will occur at the positive cathode.
  b $OH^- + MH \longrightarrow H_2O + M + e^-$
  c Oxidation will be at the anode; the anode is positive during charging (recharge).

9.3 Producing ‘green’ hydrogen gas

KEY QUESTIONS

Knowledge and understanding

1 Brown hydrogen is sourced from fossil fuels, whereas the energy to produce green hydrogen comes from renewable energy sources.
  a brown
  b green
  c green
  d brown

2 Hydrogen gas produced from natural gas has two main issues: it depletes the supplies of natural gas, which is a non-renewable resource, and the process for manufacturing hydrogen releases CO_2.

3 The reaction is a very endothermic one. The covalent bonds in water that need to be broken are relatively strong.

4 **a** In artificial photosynthesis, sunlight is directed at a photosensitive electrode stored in a solution in an electrolytic cell. The energy from the Sun helps form molecules from the solution, such as methane or hydrogen.
  b The origin of the word photosynthesis is about forming molecules, using energy from the Sun. The molecule formed in plants is usually glucose, but in other mediums different molecules can be formed.

Analysis

5 **a** oxygen gas
  b Oxygen is a very useful gas, in medical situations as well as industrial applications.

6 **a** Anode, as it is an example of oxidation.
  b An electrolyser is an electrolytic cell, so the anode is positive in an electrolyser.
  c The reaction is not occurring in an aqueous environment.

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7 **a** Artificial photosynthesis is a one-step process, with hydrogen formed directly from the action of sunlight. Most hydrogen trial plants require at least two distinct phases, firstly for the generation and storage of electrical energy and then for the use of that energy to run an electrolytic cell to produce hydrogen gas.

b The direct conversion of energy in artificial photosynthesis offers potentially higher efficiencies as less energy transformations are required. The need for large-scale storage of electrical energy is also eliminated.

Chapter 9 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 C. The increase in temperature will increase the rate, but it will lower the yield of product in an exothermic reaction such as this.

Option A is incorrect as the amount of product will change. Options B and D are incorrect because an increase in temperature will increase the reaction rate.

2 D. Catalysts do not affect the yield of a reaction (so A is incorrect), but equilibrium will be attained faster. Catalysts do not change ΔH, so B is incorrect. C is incorrect – catalysts impact both forward and back reaction.

3 B. Oxidation always occurs at the anode. The anode will be the positive electrode in an electrolytic cell. A is incorrect – oxidation releases electrons. C is incorrect as the electrons flow in a different direction during recharge, and D is incorrect as oxidation is always at the anode.

4 A. The reaction needs to be oxidation as it is occurring at the anode. B and D are incorrect as they show reduction, and C is incorrect as hydrogen gas must be a product, not a reactant.

5 D. The likelihood of a cell being rechargeable is increased if the products remain in contact with the electrodes. A and B are incorrect as rechargeability is not linked to any particular chemical, and C is incorrect as high temperatures can damage a cell.

6 **a** Temperature: The impact of temperature on equilibrium yield depends upon whether a reaction is exothermic or endothermic. If the reaction is exothermic, an increase in temperature will lower the yield.

b Pressure: The impact of a pressure change on equilibrium yield depends upon the ratio of reactant particles to product particles. The position of equilibrium will shift to oppose any change of conditions.

7 Catalysts can be particularly useful in exothermic, reversible reactions, where a high equilibrium yield requires a low temperature. The catalyst negates some of the impact on reaction rate of the temperature being lowered, therefore improving the yield.

8 secondary cell: a galvanic cell that can be recharged. A commercial secondary cell needs to be able to go through multiple charging cycles

electrolyser: a system that uses electricity to break water into hydrogen and oxygen via electrolysis.

PEM: polymer exchange membrane – a polymeric electrolyte that allows conductivity of ions, usually protons.

hydrogen hub: precinct shared by a number of companies involved in the production and use of hydrogen.

photoelectrochemical: reactions involving an electric current generated by the action of light.

9 During discharge, a secondary cell acts as a **galvanic** cell. The reaction occurring is a **spontaneous** one. For this cycle, **reduction** occurs at the cathode and its polarity is **positive**. During the recharge cycle, the secondary cell operates as an **electrolytic** cell and a **non-spontaneous** reaction occurs. For the recharge cycle, **oxidation** occurs at the anode, and its polarity is **positive**.

10 **a** The rate of the forward reaction is increased.

b The rate of the back reaction is increased.

c The equilibrium yield will decrease as K_c is lower.

11 $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$ polarity +

$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$ polarity –

12 Fuel cells in cars, blended with domestic gas, manufacture of ammonia and export to other countries.

13 **a** $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

b Electrolysis of water requires energy.

c Green hydrogen is hydrogen that is produced using renewable energy. Its production does not drain supplies of non-renewable resources.

14 Hydrogen is an explosive gas. It is often stored at high pressures in high-quality containers and kept from any ignition sources. Its low density as a gas means that companies will liquify it before exporting or convert it to ammonia.

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Application and analysis

15 **a** $2Li(s) + 2H_2O(l) \longrightarrow 2LiOH(aq) + H_2(g)$

b Lithium cells need to have non-aqueous electrolytes so that this potentially dangerous reaction cannot occur.

16 **a** Lithium reacts at the anode, which is negative, and oxygen at the cathode, which is positive.

b Oxygen gas has an oxidation state of 0 and it is reduced to O^- during discharge.

c Li^+ ions.

d $2Li + O_2 \longrightarrow Li_2O_2$

e $Li_2O_2 \longrightarrow 2Li + O_2$

f Li_2O_2, as it is an oxidation reaction

17 **a** An electrolyser is a system that uses electricity to break water into hydrogen and oxygen via electrolysis.

b A PEM electrolyser does not operate in an aqueous environment like a simple electrolyser. It uses a conductive polymer electrolyte. The overall equation is the same, but the half-equations differ.

c The half-equations for both electrolysers will show the formation of oxygen and hydrogen gases, but the ions will differ.

d The overall equation for both will be $2H_2O \longrightarrow 2H_2 + O_2$. The states will differ. A simple electrolyser uses an aqueous environment, but the PEM does not.

18 **a** **i** decrease
- **ii** decrease
- **iii** increase
- **iv** no change
- **v** no change

b **i** increase
- **ii** increase
- **iii** increase
- **iv** increase
- **v** no change

19 **a** $2NiOOH(aq) + 2H_2O(l) + Cd(s) \longrightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$

b NiOOH reacts at the cathode and cadmium at the anode

c voltage = 0.48 – (–0.82) = 1.3 V

d $2Ni(OH)_2(s) + Cd(OH)_2(s) \longrightarrow 2NiOOH(aq) + 2H_2O(l) + Cd(s)$

e $Ni(OH)_2$ will react at the anode and cadmium at the cathode.

20 **a** Lead–acid batteries are made in a traditional way, with large parts and an aqueous electrolyte. The top of the cell is easily removed. Lithium-ion cells are high-technology devices using composites and complex membranes. It is not easy to access the individual components. The electrolyte in lithium-ion cells is not a simple ionic solution that the solid can easily be extracted from.

b Lithium batteries contain high proportions of cobalt, nickel and aluminium that could be recycled. The lithium compounds could also be re-used and the conductive membranes have potential to be re-used.

c It is not a good principle to use a material and to then throw it away. Sometimes the material is toxic and it should not be added to landfill and sometimes materials are scarce and need to be preserved.

21 $2H_2O(l) + 4e^- \longrightarrow 2H_2(g) + 2O^{2-}$

22

	Discharge	**Recharge**
Is the reaction spontaneous or non-spontaneous?	spontaneous	non-spontaneous
reactants	zinc, bromine	Zn^{2+}, Br^-
polarity of anode	negative	positive
direction of electron flow	negative to positive	positive to negative
Is the cell acting as a galvanic or electrolytic cell?	galvanic	electrolytic

23 **a** The Haber process is an energy-intensive process due to the need for elevated temperatures and pressures. In most instances the energy required is obtained from fossil fuels, producing CO_2 emissions. The use of methane as a source of hydrogen gas adds to the energy requirements of production and the methane is considered a relatively scarce resource.

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b If the hydrogen gas produced is green hydrogen, then the need to use fossil fuels in the production of ammonia is eliminated. Water is the source of hydrogen rather than methane, eliminating the emission of CO_2 gas.

c The production of ammonia via electrolysis is a very different process that offers significant potential energy savings. The process might be able to be conducted at room temperature, thus eliminating the need for expensive, energy-intensive heating of the gases. The electrolytic process removes the reversible nature of production, removing the need for considerations of reactant recycling and cooling. Using lower temperatures and pressures is likely to make the production a much safer process.

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Unit 3 Area of study 2

How can the rate and yield of chemical reactions be optimised?

Multiple-choice questions

1 C. A catalyst does not affect either the initial or the final states in a chemical reaction, so the amount of energy released or absorbed by a reaction is unchanged. However, a catalyst provides an alternative intermediate pathway with a lower activation energy threshold.

2 D. **I:** An increase in pressure for a gaseous reaction increases the concentration of the reactants, which increases the frequency of collisions between particles.

II: An increase in temperature increases the proportion of particles with $E \geq E_a$ and increases the frequency of collisions between particles.

III: Addition of Cl_2 increases the concentration of Cl_2, which increases the frequency of collisions between particles.

3 D.

$$\begin{aligned} n(CaCO_3) &= \frac{m}{M} \\ &= \frac{0.500}{100.1} \\ &= 0.00500 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(HCl) &= c \times V \\ &= 0.100 \times 0.100 \\ &= 0.0100 \text{ mol} \end{aligned}$$

So, neither reactant is limiting or in excess, since $n(HCl) = 2n(CaCO_3)$.

D is correct because the concentration of HCl is higher than the initial value, so the rate of reaction will increase, but the mass of $CaCO_3$ is lower than the initial value, so it becomes the limiting reactant so the volume of CO_2 produced would decrease.

A is incorrect because the rate will increase (due to increased HCl concentration), but the volume of CO_2 produced is unchanged ($CaCO_3$ is the limiting reactant and the mass is unchanged).

B is incorrect because the rate is unchanged (due to same HCl concentration), but the volume of CO_2 produced is decreased ($CaCO_3$ is the limiting reactant and the mass is decreased).

C is incorrect because the rate is unchanged (due to same HCl concentration) and the volume of CO_2 produced is unchanged ($CaCO_3$ is the limiting reactant and the mass is unchanged).

4 D. For this reaction $K = \frac{[Y]^2 \times [Z]^n}{[W]^2 \times [X]^2}$ and has the unit M^2. Hence $(2 + n) - (2 + 2) = 2$, so $n = 4$.

5 C. The reduction in volume will increase concentrations of all species and hence increase the net concentration of particles, inducing an equilibrium shift to the side with fewer particles. Hence, a net reverse reaction occurs, reducing the amount of products NO and Cl_2. However, this loss of Cl_2 does not completely offset the increase in concentration resulting from the initial volume change, so there is a net increase in the concentration of Cl_2.

6 A. Since these equations share a common species, $H_2CO_3(aq)$, changes that affect one will have a consequent effect on the other. Decreasing the pH means raising $[H_3O^+(aq)]$, which will cause a shift left in the second reaction. The consequent increase in $[H_2CO_3(aq)]$ will induce a shift left in the first reaction, also resulting in the loss of CO_2 from the solution.

B is incorrect because a decrease in the temperature of the solution favours the exothermic reaction, which is the forward reaction for the first equation, so more CO_2 dissolves.

C is incorrect because an increase in the concentration of CO_2 favours the forwards reaction for the first equation, so more CO_2 dissolves.

D is incorrect because an increase in the pressure of CO_2 increases the concentration of CO_2, which favours the forwards reaction for the first equation, so more CO_2 dissolves.

7 B. **I:** Zinc is a stronger reducing agent than tin and so will react with Sn^{2+} in solution.

II: Copper is a weaker reducing agent than tin and so will not react with Sn^{2+} in solution.

III and IV: Sn^{2+} ions will be the strongest oxidising agent in both cases and so will undergo reduction at the cathode.

8 A. The zinc electrode is the positive electrode, meaning it is the anode so it will be oxidised, releasing Zn^{2+} ions into the electrolyte. Therefore, the nickel rod is the negative electrode, meaning it is the cathode where Zn^{2+} ions, the strongest oxidising agent present would be reduced to form zinc metal (hence B and D are incorrect). The electrolyte must contain Zn^{2+} ions. If the electrolyte is a nickel(II) nitrate solution, Ni^{2+} ions would be the strongest oxidising agent present and would be reduced to nickel metal at the cathode (hence C is incorrect).

9 C. Increasing temperature increases the proportion of particles with $E \geq E_a$ and increases collision frequency (hence D is incorrect), but does not change the activation energy of the reaction (hence A is incorrect). Adding a catalyst lowers the activation energy of the reaction (hence B is incorrect), but does not change collision frequency (hence D is incorrect).

10 B. I is correct because the addition of a catalyst lowers the activation energy, resulting in a greater proportion of particles with energy greater than or equal to the lower activation energy, resulting in a greater proportion of successful collisions. II is incorrect because crushing a solid into a powder increases the surface area of the solid reactant, resulting in a greater frequency of collisions, but the proportion of successful collisions is unchanged. III is correct because increasing the temperature increases the proportion of particles with energy greater than or equal to the activation energy, resulting in a greater proportion of successful collisions.

11 B. Adding water means the system is diluted, so the concentration of the products decreases. The system partially opposes the change by shifting in the direction with more particles, so there is a net shift in the forward direction, the amount of the products increases and the equilibrium yield increases. A is incorrect because adding a catalyst will not affect the position of equilibrium, so there is no effect on the concentration of products nor the yield. C is incorrect because decreasing the temperature will cause the system to partially oppose the change by shifting in the exothermic direction, so there is a net shift in the reverse direction, so the concentration of products and the yield decreases. D is incorrect because adding reactant A will cause the system to partially oppose the change by removing reactant A, so there is a net shift in the forward direction, so the concentration of products and the yield increases.

12 B. $Q = I \times t$

$$= 3.5 \times (24 \times 60)$$
$$= 5.0 \times 10^3$$

$$n(e^-) = \frac{Q}{F}$$
$$= \frac{5.0 \times 10^3}{96\,500}$$
$$= 0.052 \text{ mol}$$

The half-equation for the reaction is: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

$$n(H_2) = \frac{1}{2} \times n(e^-)$$
$$= \frac{1}{2} \times 0.052$$
$$= 0.026 \text{ mol}$$

$$m(H_2) = n \times M$$
$$= 0.026 \times 2.0$$
$$= 0.052 \text{ g}$$

13 A. Reduction half-equations for the reactions occurring at the cathodes are:

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$

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

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

Since 1 F = 1 mol of electrons

$$n(e^-) = 0.60 \text{ mol}$$

$$n(Cr) = \frac{1}{3} \times n(e^-)$$
$$= \frac{1}{3} \times 0.60$$
$$= 0.20 \text{ mol}$$

$$n(Cu) = \frac{1}{2} \times n(e^-)$$
$$= \frac{1}{2} \times 0.60$$
$$= 0.30 \text{ mol}$$

$$n(Ag) = n(e^-)$$
$$= 0.60$$

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14 D. In molten LiBr, the reactions at the electrodes are:

anode: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$ (Note: the high temperature operating conditions of the cell will results in Br_2 gas forming)

cathode: $Li^+(l) + e^- \rightarrow Li(l)$

In aqueous LiBr, the reactions at the electrodes are:

anode: $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$

cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

15 B. $\frac{z}{2}$. In the $FeSO_4$ cell, $Q_1 = I \times t = y \times x$. In the $Cu(NO_3)_2$ cell, $Q_2 = I \times t = 4y \times \frac{x}{8} = \frac{y \times x}{2} = \frac{Q_1}{2}$, so the amount of charge passing through this cell is half of what passes through the $FeSO_4$ cell. Therefore, the amount of electrons passing through this cell is half the amount that passes through the $FeSO_4$ cell.

$Fe^{2+} + 2e^- \rightarrow Fe$
$Cu^{2+} + 2e^- \rightarrow Cu$

Mole ratio of $n(e^-) : n(\text{metal})$ for both cells is 2 : 1. Since half the amount of electrons is passing through the $Cu(NO_3)_2$ cell, the amount of Cu produced would be half that of Fe.

Short-answer questions

16 **a** anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
b anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
c anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
cathode: $Na^+(l) + e^- \rightarrow Na(l)$

17 **a** $Li^+(l) + e^- \rightarrow Li(l)$

b $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

c Water (H_2O) is a stronger oxidising agent than Li^+ and would be preferentially reduced at the cathode, producing hydrogen gas rather than lithium metal.

d A mixed electrolyte will have a lower melting temperature, making the process safer and less expensive. Potassium chloride is appropriate because K^+ will not be reduced in preference to Li^+.

e Like sodium, lithium is a very reactive metal. It must not be allowed to come into contact with air because it will spontaneously oxidise. Also, it must be separated from the chlorine produced, otherwise, the two products would spontaneously react together. In addition, it will react very quickly with water to produce hydrogen gas with the potential for explosion, so it must not be allowed to come in contact with water.

18 **a** $2H^+(aq) + 2e^- \rightarrow H_2(g)$

b $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

c Green hydrogen is hydrogen produced using renewable energy and resources instead of fossil fuels.

d $I = 5.25 \text{ kA} = 5.25 \times 10^3 \text{ A}$

$$Q = n(e^-) \times F = I \times t$$

$$n(e^-) = \frac{I \times t}{F}$$

$$= \frac{5.25 \times 10^3 \times (24 \times 60 \times 60)}{96500}$$

$$= 4.70 \times 10^3 \text{ mol}$$

$$n(H_2) = \frac{1}{2} \times n(e^-)$$

$$= \frac{1}{2} \times 4.70 \times 10^3$$

$$= 2.35 \times 10^3 \text{ mol}$$

$$p = 7.00 \times 10^4 \text{ kPa}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$pV = nRT$$

$$V(H_2) = \frac{nRT}{p}$$

$$= \frac{2.35 \times 10^3 \times 8.31 \times 298}{7.00 \times 10^4}$$

$$= 83.1 \text{ L}$$

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19 **a** The coating will appear on the spatula. Nickel metal is produced by a reduction reaction:

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

and reduction always occurs at the cathode (negative electrode in electrolysis).

b Positive electrode (anode): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Negative electrode (cathode): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

c $Q = I \times t$

$= 2.5 \times (15 \times 60)$

$= 2.3 \times 10^3 C$

$n(e^-) = \frac{Q}{F}$

$= \frac{2.3 \times 10^3}{96500}$

$= 0.023$ mol

$n(Ni) = \frac{1}{2} \times n(e^-)$

$= \frac{1}{2} \times 0.023$

$= 0.012$ mol

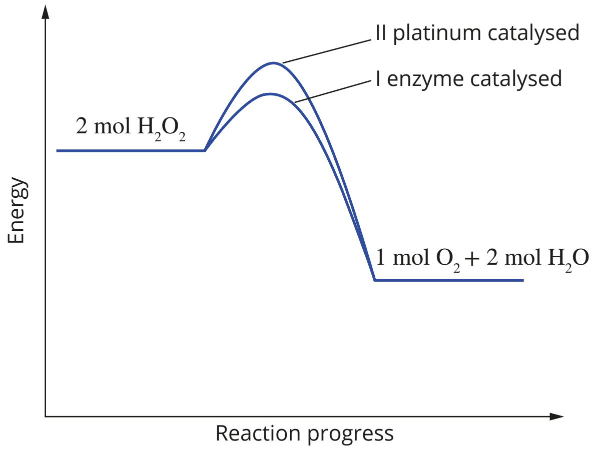
$m(Ni) = n \times M$

$= 0.012 \times 58.7$

$= 0.68$ g

20 **a** They function as catalysts, lowering the activation energy, and hence increasing the reaction rate.

b



c System I would be faster. The lower activation energy means that there is a greater proportion of reactant particles which have energy greater than or equal to the lower activation energy, so successful collisions will occur more frequently.

21 **a** The concentration of sodium thiosulfate is higher in experiment 2, so there will be more frequent collisions between reactant particles. While the probability of any particular collision being successful is unchanged, the higher frequency of collisions overall will increase the frequency of successful collisions and hence the rate of reaction.

b The higher temperature in experiment 3 means the particles in the mixture have a higher average kinetic energy and hence collide more frequently, and more significantly, there will be a higher proportion of particles with energy greater than or equal to the activation energy of the reaction. These two factors combine to give a higher frequency of successful collisions and hence a higher rate of reaction.

c The independent variable is the variable that is changed.

i Concentration of $Na_2S_2O_3$ solution.

ii Temperature of $Na_2S_2O_3$ solution.

d The dependent variable is the variable that is measured to determine the effect of changes to the independent variable. In this investigation, the dependent variable is the time taken for the cross to be obscured. This is used to determine the rate of reaction.

e Controlled variables are variables that are kept constant. Possible controlled variables are: volume of $Na_2S_2O_3$ solution, volume of HCl solution, concentration of HCl solution, same cross marked on paper, same stopwatch or other suitable device for measuring time.

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f **i** Multiple trials allow the experimenter to determine and improve the precision of the repeated measurements. Any outlying measurements could be due to a systematic error and excluded from the averaged measurement result.

ii Some possible factors that would affect the precision of the time measurements include:

- Uncertainty about when the mixture has become cloudy enough to mask the cross and so inconsistent stopping times.
- Human reaction time (random error) affecting when the stopwatch/time measurement device is started and stopped.
- There is inherent uncertainty (random error) in the time measured by the stopwatch/time measurement device.

g For the comparison between experiments 1 and 3 to be valid, the temperature of $Na_2S_2O_3$ solution must be the only independent variable. The concentrations of $Na_2S_2O_3$ and HCl solutions must not be changed as they are variables that would also affect the rate of reaction.

22

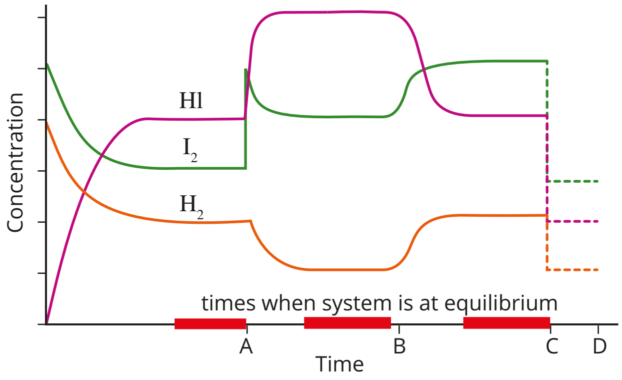
Change	Quantity	Increase/decrease/no change
increase temperature	*K*	increase because endothermic reaction
decrease temperature	amount of $H_2O(g)$	increase because equilibrium position shifts to the left
add $H_2(g)$	*K*	no change because no temperature change
add $CO_2(g)$	amount of $H_2(g)$	decrease because equilibrium position shifts to the left
double volume	amount of CO_2	increase because equilibrium position shifts to the right (to the side with more gas particles)
double volume	concentration of CO_2	decrease because initial volume increase causes an overall decrease in CO_2 concentration (not offset by increased amount)
remove CH_4	amount of CO_2	decreased because equilibrium position shifts to the left
add catalyst	amount of $H_2(g)$	no change because a catalyst does not affect the equilibrium position
add argon (an inert gas)	*K*	no change because no temperature change

23 **a** Iodine (I_2) has been added, followed by a net forward reaction to re-establish equilibrium.

b The temperature has been increased, resulting in a net back reaction (because the forward reaction is exothermic).

c Equilibrium exists when the concentrations are constant (see diagram).

d Doubling the volume will halve all concentrations. Because there are equal numbers of reactant (left-hand side) and product (right-hand side) particles, the mixture remains at equilibrium and there is no shift in the position of equilibrium (see diagram).



e **i**

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(0.400)^2}{(0.300)(0.100)}$$

$$= 5.33$$

$Q \neq K$, so the system is not at equilibrium.

ii Since $Q < K$, the system will shift in the forward direction until the value of Q increase to equal K.

iii $c(\text{HI}) = \frac{n}{V}$

$= \frac{0.940}{2.00}$

$= 0.470$ M

	H_2	I_2	HI
Initial	0.300 M	0.100 M	0.400 M
Change	–0.035	–0.035	+0.070
Equilibrium	0.265 M	0.065 M	0.470 M

24 a i $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

ii $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

b i They catalyse the reaction, which increases the reaction rate.

ii The equilibrium yield would be lower. Because the reaction is exothermic, increasing the temperature would favour the endothermic reaction which is the reverse reaction.

iii High pressure will increase the reaction rate so products form faster. Also, because the number of product particles (1 on the right-hand side) is smaller than the number of reactant particles (3 on the left-hand side), high pressure will favour the forward reaction and increase yield.

25 a i Positive electrode (anode): $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Negative electrode (cathode): $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

ii Brown I_2 forming at the positive electrode; bubbles forming at the negative electrode and increasing pH of electrolyte if tested with indicator.

b i Positive electrode (anode): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Negative electrode (cathode): $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

ii Bubbles forming at the positive electrode and decreasing pH of electrolyte if tested with indicator; lead solid/crystals deposited at the negative electrode.

c i Positive electrode (anode): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Negative electrode (cathode): $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

ii Copper positive electrode getting smaller, and appearance of blue colour (due to Cu^{2+}) in the electrolyte solution; bubbles forming at the negative electrode and increasing pH of electrolyte if tested with indicator.

26 a i $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

ii $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

iii For example, high NaCl(aq) concentrations are used so $Cl^-(aq)$ is oxidised at the anode; a semipermeable membrane prevents mixing of Cl^- and OH^- ions in the electrolyte while still allowing Na^+ ions to migrate from the anode to the cathode; the hydrogen and chlorine gases are separately removed after they have been produced, to prevent spontaneous reaction between the two gases.

b Water can itself act either as an oxidising agent or a reducing agent. Production of a chemical by electrolysis of an aqueous solution is only possible when the desired reaction involves a stronger oxidising or reducing agent than water, otherwise water will react preferentially. If the oxidising agent or reducing agent is a weaker oxidising agent or reducing agent than water, the desired reaction can only be achieved in the absence of water, either in an alternative solvent or in a molten electrolyte.

c Graphite is a good electrical conductor, relatively inexpensive, relatively inert and has a high sublimation point (in electrolytic cells operating at high temperatures, the graphite electrodes will not disintegrate).

d Metallic cathodes are always inert as the electrolytic process ensures only reduction can occur at their surface. However, the iron in a steel anode would likely be a better reducing agent than the target species so that the outcome would be the oxidation, and hence the consumption, of the electrode itself rather than the desired electrode reaction.

27 a i anode: H_2O is a stronger reducing agent than Cl^-, so

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

ii cathode: Sn^{2+} is a stronger oxidising agent than H_2O and H_2O is a stronger oxidising agent than Mg^{2+}, so

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

b Once Sn^{2+} has been consumed, H_2O is a stronger oxidising agent than Mg^{2+}, so

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

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28 **a** anode (+) electrode: $2Ni(OH)_2(s) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2NiOOH(s) + 2e^-$

cathode (–) electrode: $Zn(OH)_2(s) + 2e^- \rightarrow 2OH^-(aq) + Zn(s)$

b As in all forms of electrolysis, electrical energy is converted to chemical energy, so an external power source is used to drive a current through the cell to force non-spontaneous chemical reactions to occur. In a secondary cell, the non-spontaneous reactions are the reverse of the spontaneous reactions that occur during discharge.

c For recharging to be possible, the discharge products must remain in electrical contact with the electrodes. Any discharge products that migrate away from the electrode will not be available to participate in the reaction reversal during recharging, so that less reactant will be available on the next discharge cycle.

d
$$\begin{aligned} n(Zn) &= \frac{n}{M} \\ &= \frac{2.5}{65.4} \\ &= 0.038 \text{ mol} \end{aligned}$$

$$\begin{aligned} n(e^-) &= 2 \times n(Zn) \\ &= 2 \times 0.038 \\ &= 0.076 \text{ mol} \end{aligned}$$

$$\begin{aligned} t &= \frac{n(e^-) \times F}{I} \\ &= \frac{0.076 \times 96\,500}{0.83} \\ &= 8.9 \times 10^3 \text{ s} \end{aligned}$$

29 **a** The rates are equal up until the change was made.

b The addition of reactant W increases the frequency of collisions between reactant particles, so the rate of the forward reaction increases initially.

Because the forward reaction is now the faster, there will be a net forward reaction. This will consume the reactant particles, so the forward reaction will slow down, and generate product particles, so the reverse reaction speeds up. When the two rates become equal again, equilibrium has been re-established and no further change occurs.

c **i** Adding Y: This accounts for the initial increase in the rate of the reverse reaction; the subsequent changes reflect the re-establishment of equilibrium.

ii Adding a catalyst: Both rates increase equally and this is the characteristic effect of a catalyst.

Note: It doesn't apply here, but another case that would produce this change is that where a gas-phase reaction is compressed (volume decreased) and there are equal number of reactant and product particles in the equation.

iii Adding argon (an inert gas) at constant volume: This does not affect the concentrations of reactants or products and so does not affect the frequency of collisions between reactant or product particles. Hence, it does not affect the rate of either reaction.

d Lowering the temperature means the particles in the mixture have a lower average kinetic energy and hence collide less frequently, and there will be a lower proportion of particles with energy greater than or equal to the activation energies of the forward and reverse reactions. Hence, there will be a lower frequency of successful collisions and lower rates of reaction for both forward and reverse reactions.

e Because the forward reaction is faster (the reverse reaction has slowed to a greater extent), there will be a net forward reaction.

f Exothermic. Lowering the temperature will always induce a shift in the exothermic direction, which in this case must be the forward reaction since that is the direction of the shift.

g
$$\begin{aligned} c(Z) &= \frac{n}{V} \\ &= \frac{0.344}{0.500} \\ &= 0.688 \text{ M} \end{aligned}$$

	W	X	Y	Z
I	W	$c = \frac{n}{V} = \frac{2.00}{0.500} = 4.00$	0	0
C	–0.688	–1.376	+0.688	+0.688
E	W – 0.688	4.00 – 1.376 = 2.62	0.688	0.688

$$K = \frac{[Y][Z]}{[W][X]^2} = 1.50 \times 10^{-2}\ M^{-1}$$

$$= \frac{(0.688)^2}{(W - 0.688)(2.62)^2} = 1.50 \times 10^{-2}\ M^{-1}$$

$$W - 0.688 = \frac{(0.688)^2}{1.50 \times 10^{-2} \times (2.62)^2}$$

$$W - 0.688 = 4.58$$

$$W = 4.58 + 0.688$$

$$W = 5.27\ M$$

$$n(W) = c \times V$$

$$= 5.27 \times 0.500$$

$$= 2.64\ mol$$

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Chapter 10 Structure, nomenclature and properties of organic compounds

10.1 Diversity of organic compounds

KEY QUESTIONS

Knowledge and understanding

1 The carbon atoms in hydrocarbons have four bonds to other atoms. According to the valence shell electron pair repulsion theory, the angle around between each bond is 109.5° and the geometry around each carbon is tetrahedral. This means that carbon–carbon bonds are much less than 180°, and so the chain is zigzag shaped. Skeletal structures mainly show the bonds of the molecule, so the emphasis on shape is more important than in full structural formulas.

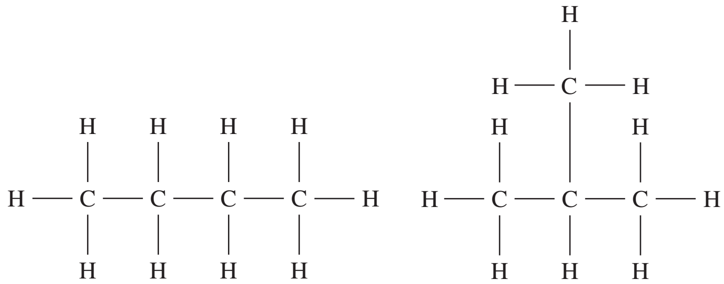
2 **a** Bond strength is directly related to the stability of a molecule. A molecule with strong chemical bonds is generally more stable than one with weaker bonds.

b The wide variety of compounds formed by carbon is due to its ability to form strong, stable covalent bonds with other carbon atoms and with atoms of other elements, such as hydrogen, oxygen, nitrogen, sulfur, phosphorus and the halogens. Carbon can also form strong, stable, single, double and triple bonds with itself, and it can form long chains and rings. The stability of these carbon compounds is related to their bond energies, which can be thought of as the strength of the bonds.

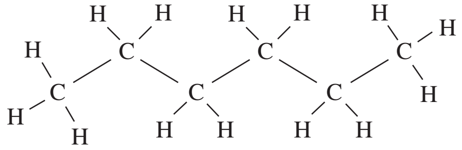
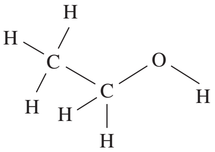
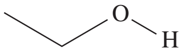
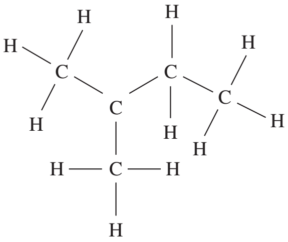
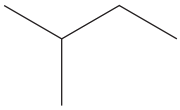
Analysis

3 **a** butane (C_4H_{10})

b



4

Molecular formula	Structural formula	Semi-structural formula	Skeletal formula
C_6H_{14}		$CH_3(CH_2)_4CH_3$	
C_2H_6O		CH_3CH_2OH	
C_5H_{12}		$CH_3CH(CH_3)CH_2CH_3$	

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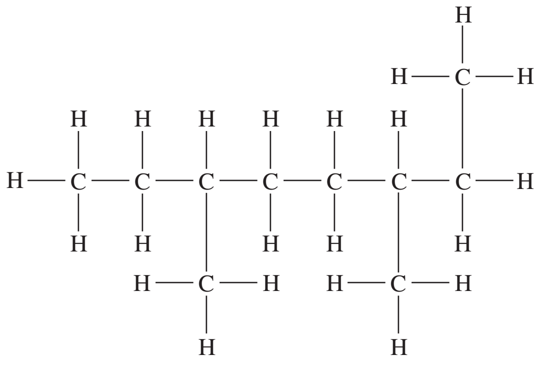
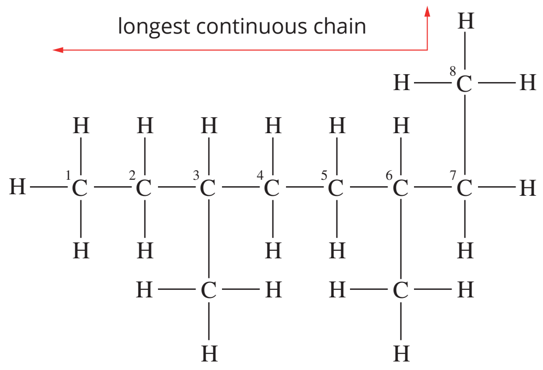
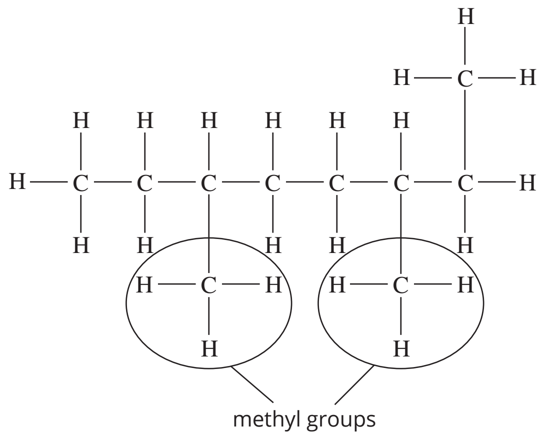
10.2 Hydrocarbons

Worked example: Try yourself 10.2.1

NAMING AN ISOMER OF AN ALKANE WITH MORE THAN ONE ALKYL BRANCH

Write the systematic name of the molecule with the following structure.



Thinking	**Working**
Identify the parent name by counting the longest continuous chain of carbon atoms.	 There are eight carbon atoms in the longest continuous chain, so the parent name is octane.
Identify any alkyl side chains by counting the number of carbon atoms in any branches.	 There is one carbon atom in each of the alkyl groups, so they are methyl groups. The prefix ‘di-’ is used because there are two methyl groups.

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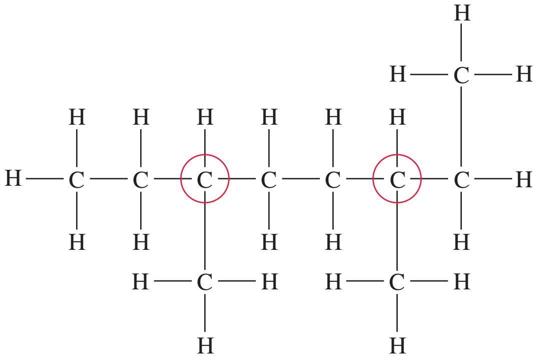
Identify the number(s) of the carbon atom(s) to which any alkyl group is attached. Count from the end that will give the lowest possible number to the carbons the groups are attached to.	 Each methyl group is attached to the third carbon from an end, so it does not matter which end to count from. This gives numbers 3 and 6 to the methyl groups.
Assemble the name of the isomer, listing alkyl groups in alphabetic order with the number of the carbon atom before each group.	The name of the isomer is 3,6-dimethyloctane.

Worked example: Try yourself 10.2.2

CALCULATING DEGREE OF UNSATURATION IN AN ORGANIC MOLECULE

Calculate the degree of unsaturation for a molecule with molecular formula C_6H_{12}.

Thinking	Working
Use the general formula for alkanes (C_nH_{2n+2}) to calculate the number of hydrogens that would be present in a fully saturated molecule.	Number of C atoms = 6 Hydrogens in fully saturated molecule $= (2 \times 6) + 2$ $= 14$
Calculate the degree of unsaturation using the formula degree of unsaturation = number of double bond or ring equivalents $= \frac{\text{maximum number of H possible per C} - \text{actual number of H per C}}{2}$	$= \frac{(14 - 12)}{2}$ $= 1$ The degree of unsaturation for C_6H_{12} is 1.

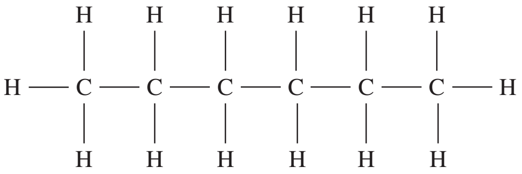
KEY QUESTIONS

Knowledge and understanding

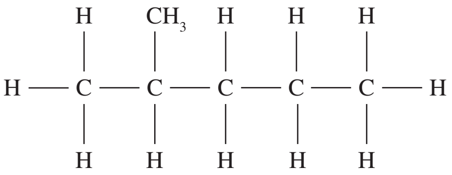
1 structural isomers

2 Alkyl branches are named in alphabetical order, before the parent molecule name.

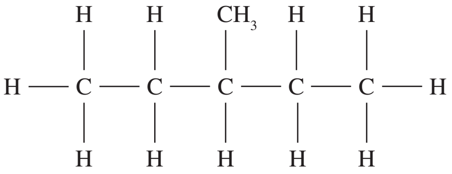
3 There are five possible isomers.



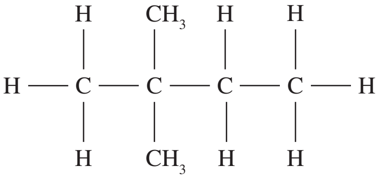
$$\begin{array}{ccccccccccccccc} & & H & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & \end{array}$$



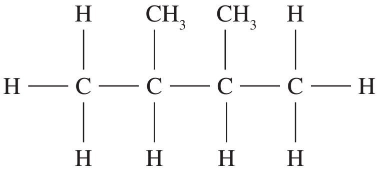
$$\begin{array}{ccccccccccccc} & & H & & CH_3 & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$



$$\begin{array}{ccccccccccccc} & & H & & H & & CH_3 & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$



$$\begin{array}{ccccccccccc} & & H & & CH_3 & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & CH_3 & & H & & H & & \end{array}$$



$$\begin{array}{ccccccccccc} & & H & & CH_3 & & CH_3 & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

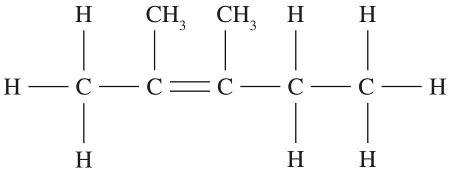
4 Alkenes are monounsaturated hydrocarbons, which means they contain one C=C double bond. Cyclohexane does not contain a C=C double bond. Its general formula has two fewer H atoms than a straight chain alkane, as two H atoms are removed when the ring is closed. Cycloalkanes form their own homologous series, which also follows the pattern C_nH_{2n}.

5 **a** benzene – C_6H_6
  b cyclohexane – C_6H_{12}

Analysis

6 **a** 2-methylbut-2-ene
  b 4-ethylhex-2-ene

7 **a**



$$\begin{array}{ccccccccccccc} & & H & & CH_3 & & CH_3 & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & = & C & - & C & - & C & - & H \\ & & | & & & & & & | & & | & & \\ & & H & & & & & & H & & H & & \end{array}$$

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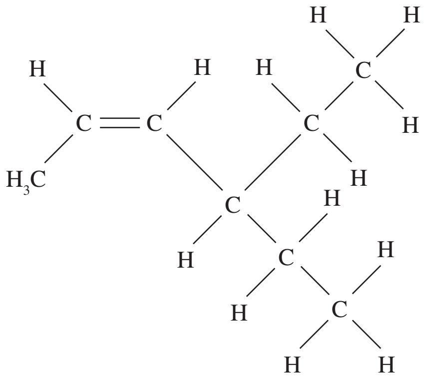
b



8 **a** Degree of unsaturation of $C_{10}H_{16}$

$$= \frac{(2n+2)-16}{2}$$

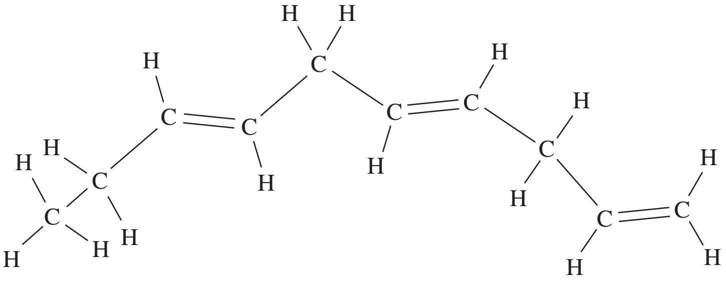
$$= \frac{22-16}{2}$$

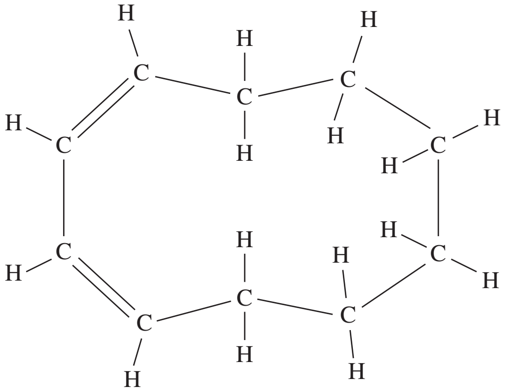
$$= \frac{6}{2}$$

$$= 3$$

This means the molecule must have 3 double bond or ring equivalents.

b Many answers are possible. These must contain 3 double bond or ring equivalents. Here are two possibilities:





10.3 Haloalkanes, alcohols and amines

KEY QUESTIONS

Knowledge and understanding

1 **a** halo (e.g. bromo, chloro, fluoro), hydroxyl, amino, respectively.

b haloalkanes: use a prefix (e.g. bromomethane)

alcohols: drop the final -e and add the suffix -ol (e.g. ethanol)

amines: drop final the -e and add the suffix -amine (e.g. ethanamine)

2 All prefixes (both branches and halo groups) are placed in alphabetical order before the parent alkane name.

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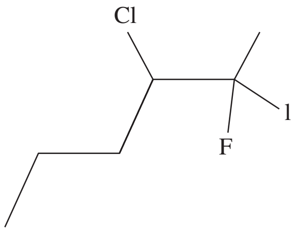
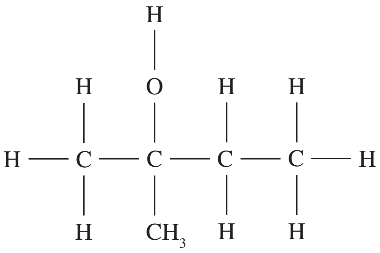
3 3-chloro-2-fluoro-2-iodohexane skeletal formula:



Analysis

4 2-methylbutan-2-ol

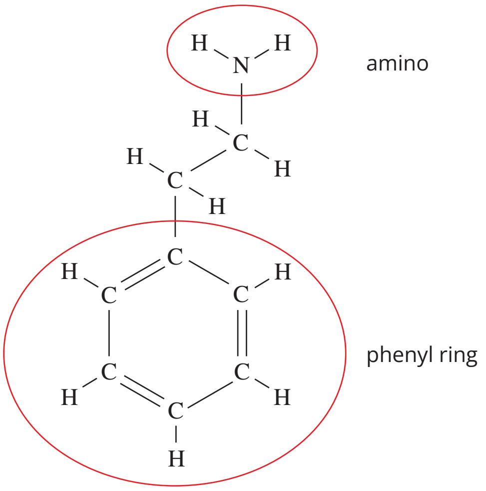


5 **a** 1-bromopropane
b 2-chloro-4-methylpentane
c pentan-1-ol
d octan-4-amine

6 Chloroethane has no isomers, so numbers are not needed. In propan-3-amine, the carbons should be numbered from the carbon atom closest to the amino functional group. The amino group is located on the first carbon instead of the third carbon. Hence, the correct name is propan-1-amine.

7 **a** $C_8H_{11}N$

b



c $M(C_8H_{11}N) = 121\ \text{g mol}^{-1}$

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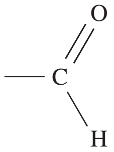
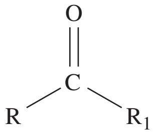
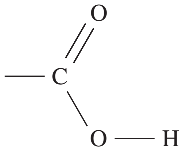
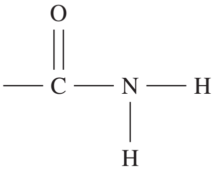
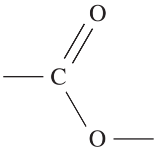
10.4 Molecules containing a carbonyl group

KEY QUESTIONS

Knowledge and understanding

1

Homologous series	Function group name	Structural formula	Semi-structural formula	Naming convention
aldehydes	carbonyl - end of molecule (aldehyde)		–CHO	suffix -al
ketones	carbonyl - not on end (ketone)		–CO–	suffix -one
carboxylic acids	carboxyl		–COOH	suffix -oic acid
primary amides	amide		$–CONH_2$	suffix -amide
esters	ester		–COO–	two-word name with suffixes -yl and -oate

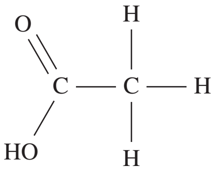
*R and R_1 are used to indicate the rest of the molecule – these are usually, but not always, alkyl chains.

2 **a** ketones
b aldehydes
c amides
d esters
e carboxylic acids

Analysis

3 **a** methyl methanoate
b methanoic acid
c propyl butanoate
d methyl ethanoate
e ethyl hexanoate
f 2,3-dimethylbutanal
g 3-methylpentan-2-one

4 ethanoic acid



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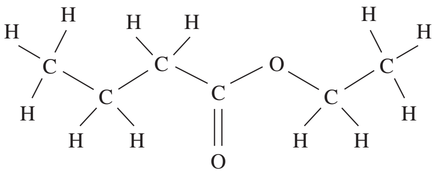
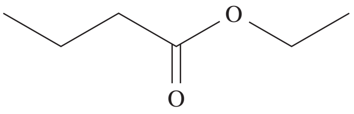
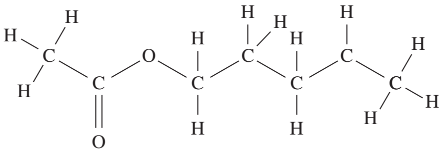
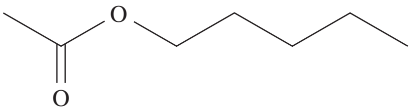
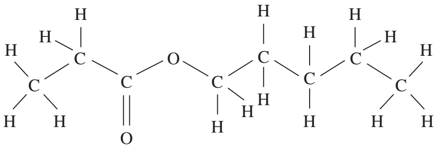
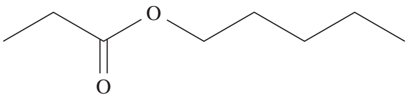
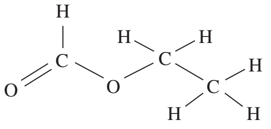
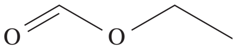
5

Name	Structural formula	Semi-structural formula	Skeletal formula
ethyl butanoate		$CH_3(CH_2)_2COOCH_2CH_3$	
pentyl ethanoate		$CH_3COO(CH_2)_4CH_3$	
pentyl propanoate		$CH_3CH_2COO(CH_2)_4CH_3$	
ethyl methanoate		$HCOOCH_2CH_3$	

10.5 An overview of IUPAC nomenclature

CASE STUDY: ANALYSIS

Trivial versus IUPAC systematic names

1 Sulflower is a compound with an eight-membered ring that contains sulfur. The structure looks somewhat like a sunflower, and the name is a combination of the words sulfur and sunflower. Quadratic acid is a square-shaped organic compound, which is sometimes also called squaric acid. Draculin is a compound found in the saliva of vampire bats.

2 Ethanoic acid is the systematic name for acetic acid. Methanoic acid is the systematic name for formic acid. Propan-2-one is the systematic name for acetone.

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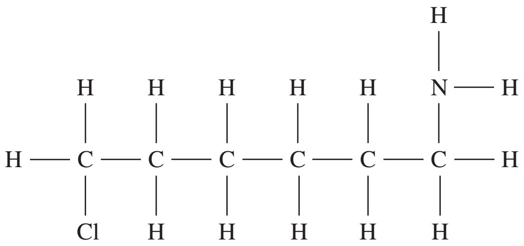
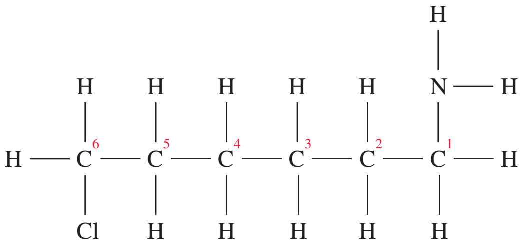
Worked example: Try yourself 10.5.1

NAMING AN ORGANIC MOLECULE WITH TWO FUNCTIONAL GROUPS

Name this molecule according to IUPAC rules.

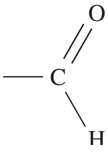


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	There are six carbons in the longest chain, so the parent name is hexane.
Identify the functional groups present.	The two functional groups present are chloro and amino.
Determine which functional group has the higher priority and determine the prefixes and suffixes to use.	The amino group has the higher priority, so the molecule will end in -amine. The chloro group has lower priority, so the prefix chloro- will be used.
Number the carbon chain, giving the higher priority group the lowest number possible.	
Determine the number of the carbon each functional group is attached to.	The $-NH_2$ is attached to carbon 1 and the –Cl is attached to carbon 6.
Use the functional group names and carbon numbers to construct the full name.	The name of the molecule is 6-chlorohexan-1-amine.

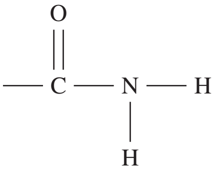
KEY QUESTIONS

Knowledge and understanding

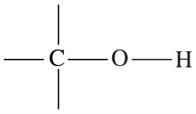
1 **a**



b



c



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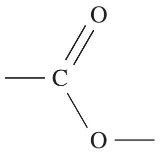
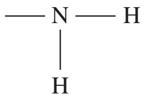
d



e



2 **a** -ol

b -amino

Hydroxyl groups have a higher priority than amino groups, therefore the amino group is named as a prefix with the hydroxyl naming '-ol' taking precedence as the suffix.

Analysis

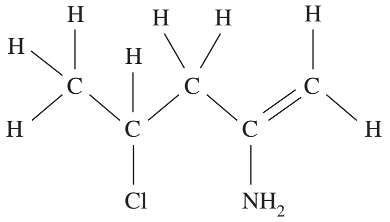
3 **a** 3-hydroxybutanoic acid

b 3-methylpentan-2-amine

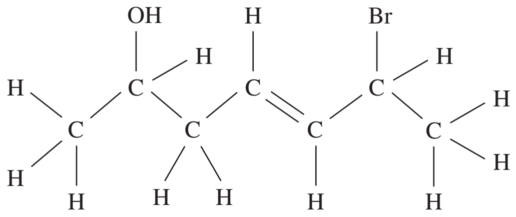
c 4-chloro-3-ethylpenan-2-ol

d butan-2-one

4 **a**



b



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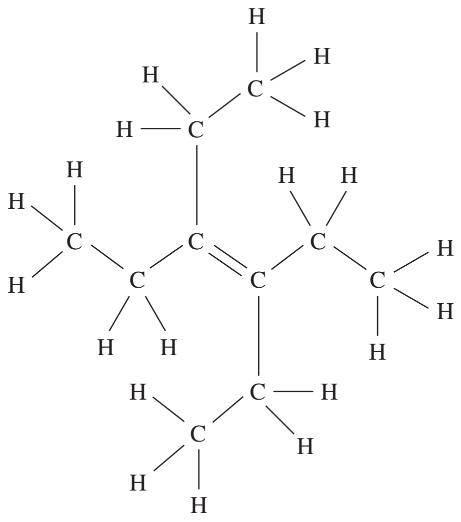
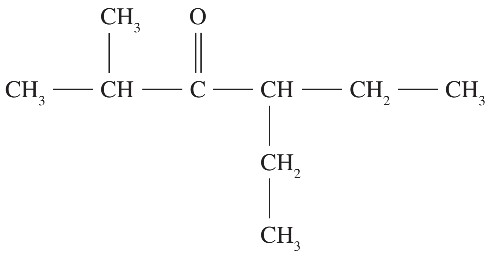


d



$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{\underset{|}{CH_2}}}{\underset{|}{CH}}-CH_2-CH_3$

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5 **a** Amino groups have priority over alkenes, so -amine should go at the end and have the lowest number. The correct name is prop-2-en-1-amine ($CH_2{=}CHCH_2NH_2$).

b Carboxylic acid groups always go at the end of the chain and contain carbon 1. The correct name is 4-chloropentanoic acid ($CH_3CHClCH_2CH_2COOH$).

c The ethyl chain is a part of the longest carbon chain. Hydroxyl groups have priority over alkenes, so –ol should go at the end. The numbering of the longest carbon chain should aim to minimise the number of the hydroxyl and alkene functional groups. Therefore, the carbon-carbon double bond is at carbon number 1 and the hydroxyl group is at carbon number 3. The correct name is pent-1-en-3-ol ($CH_2{=}CHCHOHCH_2CH_3$).

10.6 Trends in physical properties within homologous series

KEY QUESTIONS

Knowledge and understanding

1 Butane is a member of the **alkane** homologous series. The type of forces of attraction holding butane molecules to each other are **dispersion forces**. As the chain length of alkanes increases, their boiling points **increase**. In general, alkanes with branched chains have **lower** boiling points than straight-chain alkanes with the same number of carbon atoms.

2

Homologous series	Strongest form of intermolecular force of attraction between molecules
alcohols	hydrogen bonding
alkenes	dispersion forces
carboxylic acids	hydrogen bonding
esters	dipole–dipole interaction
haloalkanes	dipole–dipole interaction
amines	hydrogen bonding

3 $CH_3CH_2CH_3$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2Cl$, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COOH$

Propane and butane are both hydrocarbons, but butane is a longer molecule than propane, so will have stronger dispersion forces between its molecules and therefore a higher boiling point than propane. 1-chlorobutane is a polar molecule with dipole–dipole interaction forces between its molecules. These are stronger than dispersion forces, so 1-chlorobutane has a higher boiling point than the two hydrocarbons. Butan-1-ol has a hydroxyl functional group, so hydrogen bonding forces operate between its molecules. These forces are stronger than dipole–dipole interaction forces, so butan-1-ol has the next highest boiling point. Butanoic acid has the highest boiling point because its molecules are held together by hydrogen bonds, and also because its molecules form dimers between the carboxyl groups of neighbouring molecules.

4 As the viscosity of a liquid increases, it flows **less** readily. The viscosity of pentane is **lower/less** than that of octane at the same temperature. This is because pentane molecules have **shorter** hydrocarbon chains than octane. In samples of liquid pentane, there will be **fewer/less** points of contact between molecules, and overall, the strength of dispersion forces holding them together will be **weaker** than those holding octane molecules together.

Liquids consisting of molecules made up of a straight hydrocarbon chain with a functional group attached will generally have a **greater** viscosity than a liquid consisting of hydrocarbon chains of similar length with no functional group. This is because forces of attraction (dipole–dipole or hydrogen bonds) between the polar functional groups are **stronger** than dispersion forces.

Analysis

5 pentane; hexane; 1-chloroheptane; heptan-1-ol.

Pentane and hexane molecules have shorter hydrocarbon chains than the other two compounds, so have weaker overall dispersion forces between their molecules. Pentane molecules are shorter than hexane molecules, so have weaker overall dispersion forces and pentane has a lower viscosity than hexane. Dipole–dipole forces of attraction operate between 1-chloroheptane molecules. These forces are stronger than the dispersion forces between the alkane molecules, so 1-chloroheptane has greater viscosity than pentane and hexane. Dipole–dipole interaction forces are weaker than the hydrogen bonding forces operating between heptan-1-ol molecules, so 1-chloroheptane has lower viscosity than heptan-1-ol.

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6 2,2-dimethylpropane, 2-methylbutane, pentane.

Straight-chain hydrocarbon molecules can ‘pack’ together closely, so that there are many points of contact between the molecules. This means that overall the intermolecular forces (dispersion forces) are stronger than for branched chain hydrocarbon molecules and that is why pentane has the highest boiling point of the three compounds. In branched chain hydrocarbon molecules, the side chains reduce the ability of the hydrocarbon chains to come into close contact, so the overall strength of dispersion forces is decreased. Generally, the more side chains there are, the lower will be the boiling point of compounds with similar molar mass. This is the reason why the boiling point of 2-methylbutane is higher than that of 2,2-dimethyl pentane.

Chapter 10 Review

REVIEW QUESTIONS

Knowledge and understanding

1 D. C_6H_{14} Noncyclic alkanes follow the pattern C_nH_{2n+2}. D is the only option that fits this pattern.

2 B. $C_{17}H_{30}$ contains 3 degrees of unsaturation: $= \frac{(36 - 30)}{2} = 3$. A, C and D contain 2, 0 and 1 degree/s of unsaturation respectively.

3 B. Incorrect—isomers have identical molecular formulas. The other statements are all true for isomers.

4 A. hydroxyl (–OH). The carbonyl functional group (C=O) is present in carboxylic acids and amides. ‘Carboxyl’ is the name of the complete functional group in carboxylic acids (–COOH). ‘Alcohol’ is not the name of a functional group at all. It is the name of a family of compounds that contain the hydroxyl (–OH) group.

5 D. The parent molecule contains five carbon atoms. The ‘-ene’ refers to the fact that the molecule is an alkene. The ‘–2-ene’ refers to the location of the C=C. ‘Methyl’ indicates that the molecule has an alkyl side chain.

6 **a** N and H
b C, N, H and O
c Cl
d H and O
e C, O and H
f C and O

7 Propan-1-ol is a primary alcohol; the carbon to which the hydroxyl group is attached has only one alkyl group attached to it. Propan-2-ol is a secondary alcohol; the carbon to which the hydroxyl group is attached has two alkyl groups attached to it.

8 A carboxylic acid has a carbonyl group with a hydroxyl group attached to the carbon; an amide has a carbonyl group with an amino group attached to the carbon.

9 Carboxyl and amide carbons have three bonds to the carbon atom within the functional group. The carbon atom in this group can therefore only make one bond to connect to a carbon chain, so the group can never be within a chain.

10 B. The weaker the intermolecular forces between organic compounds, the less energy is needed to separate them from each other, so the lower their boiling points will be. Therefore, B is the incorrect statement.

A is true—molecular shape can affect the boiling points of compounds. For example, more branched hydrocarbon chains will lead to fewer points of contact between molecules, and so cause a lower boiling point.

C is true—as the length of a hydrocarbon chain increases, there are more points of contact between molecules, dispersion forces become stronger and boiling points increase.

D is also true—the intermolecular forces of attraction between non-polar molecules are dispersion forces. These are weaker forces than the dipole–dipole forces or hydrogen bonding forces between polar molecules, so non-polar molecules will have lower boiling points than polar molecules.

11 A. Each of the molecules contain four carbon atoms, so their hydrocarbon chain lengths are similar and will not result in much difference in the strength of the intermolecular forces between them.

But-2-ene molecules and 2-methylpropane molecules are non-polar, so the intermolecular forces between them are weak dispersion forces. Butan-2-ol has a polar OH group, so hydrogen bond forces operate between them. The intermolecular forces between ethyl ethanoate molecules are dipole–dipole interactions. These forces are not as strong as hydrogen bonds, so butan-2-ol will have the greatest viscosity of the four compounds.

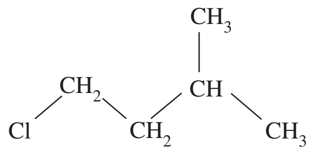
12 Octane has the higher viscosity. Intermolecular forces determine the viscosity of organic compounds. This is because octane has the higher molar mass and is the larger molecule. Both octane and pentane are non-polar hydrocarbons, so the only intermolecular forces are dispersion forces. As the size of the molecules increases, so does the strength and number of dispersion forces between molecules.

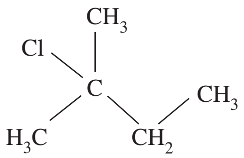
13 CH_3CH_3 (ethane), $CH_3CH_2CH_2CH_3$ (butane) and $CH_3CH(CH_3)CH_3$ (2-methylpropane) are all hydrocarbons, so they are non-polar and the only intermolecular forces present are dispersion forces. The ethane molecule is shorter than the butane molecule, so there will be less intermolecular forces between ethane molecules and ethane has a lower boiling point than butane. Both butane and 2-methylpropane molecules have four carbon atoms, but the latter molecule is branched. This means the molecules do not pack together as closely as butane molecules, so butane molecules will have the higher boiling point. Both $CH_3CH_2CH_2CH_2OH$ (butan-1-ol) and $CH_3CH_2CH_2COOH$ (butanoic acid) have intermolecular forces of hydrogen bonds between their molecules, so they will have higher boiling points than the alkane molecules. Typical of carboxylic acids, butanoic acid can form dimers (Figure 10.6.16), held together by hydrogen bonds. These intermolecular forces are stronger than the hydrogen bonds holding butan-1-ol molecules together (Figure 10.6.12). Therefore the boiling point of butanoic acid will be higher than that of butan-1-ol.

Application and analysis

14 **a** 8

b


1-chloro-3-methylbutane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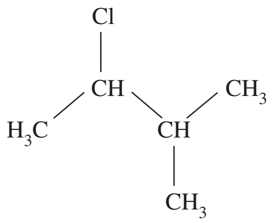
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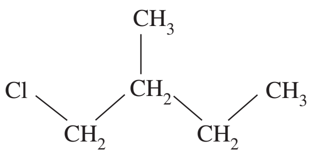
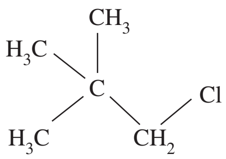
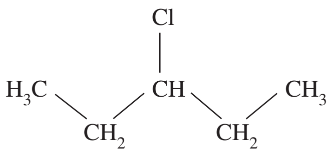
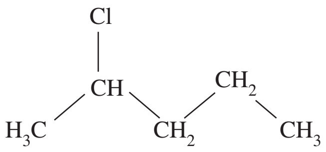
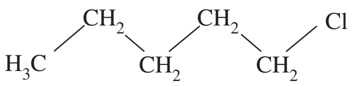

1-chloro-2-methylbutane


1-chloro-2, 2-dimethylpropane


3-chloropentane


2-chloropentane


1-chloropentane

15 $CH_2{=}CHCH_2CH_3$ (but-1-ene), $CH_3CH{=}CHCH_3$ (but-2-ene), $(CH_3)_2C{=}CH_2$ (2-methylprop-1-ene)

16 **a** C_5H_{12}
b C_6H_{12}
c C_4H_8
d C_7H_{14}

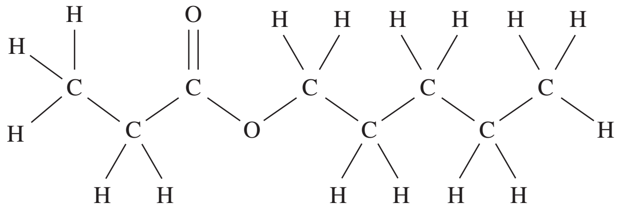
17 3 (pentane, 2-methylbutane and 2,2-dimethylpropane)

18 If an ethyl group is on the second carbon atom, then the longest chain is 6 carbon atoms long and the name would be 3-methylhexane.

19 **a** 2-aminopropan-1-ol
b 8-chlorooctan-2-ol
c 2-iodoheptan-3-amine

20 **a** but-3-enoic acid
b 4-aminobutan-2-ol
c butyl ethanoate
d 2-methylhex-3-ene
e 1-bromobut-2-ene

21 **a**



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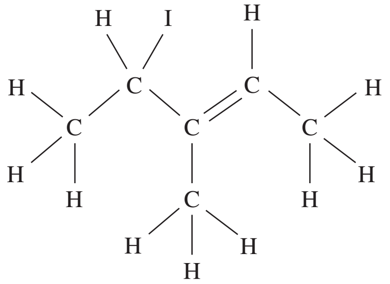
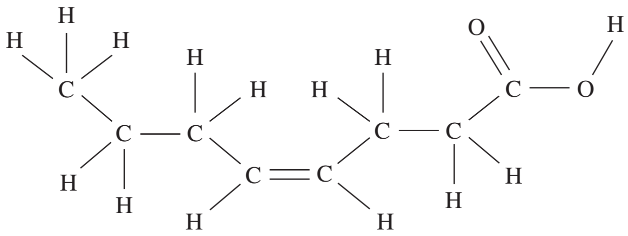
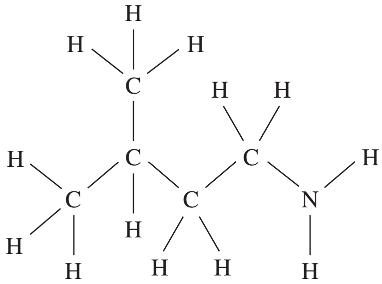


c



d



22 **a** $CH_3CH_2CH_2CH_2CH{=}CHCH_2COOH$
b $CH_3CH_2CH_2CH_2CH_2COOCH_3$
c $CH_2FCH_2CH_2OH$
d $CH_2OHCH_2CH_2COOH$
e $CH_3CH_2CH(CH_3)CH(CH_3)CH_2NH_2$

23 **a** $CH_3CH_2CH_2COCH_3$
b $CH_3CH(CH_3)CH_2CH_2OH$
c $CH_3CH_2CONH_2$
d $CH_3CH_2COOCH_2CH_3$

24 **a** The double bond cannot be in the ‘4’ position because it must be between two carbon atoms. If the 4-carbon is involved in a double bond it should have priority in the name, and so be called but-1-ene.
b The hydroxyl group has higher priority than the amino group, so the name should be 2-aminoethan-1-ol.
c The C=C bond has higher priority than the chloro group, so the name should be 3-chlorohex-1-ene.
d The longest chain in this arrangement is 5 carbon atoms long, so the stem should be pent- and the branch should be methyl. The correct name is 2-chloro-3-methylpentane.

25 **a** **i** primary alcohol
  ii heptan-1-ol
b **i** chloroalkane
  ii 4-chloroheptane
c **i** secondary alcohol
  ii hexan-2-ol
d **i** amine
  ii butan-2-amine

26 **a** structural isomers
b unrelated
c structural isomers

27 Boiling points of compounds are determined by the strength of the intermolecular forces. Weak dispersion forces are present in all molecules, polar or non-polar, so must be kept as close to constant as possible when making comparisons on the effect of changing functional groups. Because dispersion forces increase with molecular size, it is important to select compounds of a similar molar mass.

28 **a** The boiling point within a homologous series increases as the carbon chain length increases. The boiling points of alcohols are higher than the boiling points of alkanes with a similar molecular mass. The boiling points of carboxylic acids are higher than those of alcohols with a similar molecular mass.

b The boiling point of pentanoic acid ($CH_3(CH_2)_3COOH$) from experiment 3 is much lower than expected. The experimental data shows it to have a similar boiling point to that of hexan-1-ol ($CH_3(CH_2)_4CH_2OH$), but this is an anomaly in the trend. As can be seen from the data from experiments 1 and 2, carboxylic acids have higher boiling points than alkanes and alcohols of a comparable molecular mass.

c Boiling points within a homologous series increase as the carbon chain length increases because the dispersion forces between neighbouring molecules become stronger. The boiling points of alcohols are greater than the boiling points of alkanes with a similar molecular mass because alcohol molecules form hydrogen bonds with each other in addition to dispersion forces (alkane molecules only have dispersion holding them to each other). Carboxylic acids have a higher boiling point than alcohols of a similar molecular mass because intermolecular hydrogen bonds result in the formation of dimers that effectively double their molecular mass and increase the strength of the dispersion forces formed between neighbouring molecules. While this did not show here for pentanoic acid, this has been justified by identifying that the result is due to experimental error.

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Chapter 11 Reactions of organic compounds

11.1 Reactions of alkanes and haloalkanes

KEY QUESTIONS

Knowledge and understanding

1 Alkanes will undergo complete combustion in air to produce **carbon dioxide** and **water**. The first organic product formed when methane reacts with bromine in the presence of **ultraviolet** light is **bromomethane**. This is an example of **a substitution** reaction. The organic product formed when chloromethane reacts with sodium hydroxide is **methanol**. This is also an example of **substitution** reaction.

2 $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

3 **a** butan-2-ol
  b ethanamine
  c carbon dioxide

4 **a** $CH_3Cl(g) + NaOH(aq) \rightarrow CH_3OH(aq) + NaCl(aq)$
  b $CH_3CHBrCH_3(l) + NH_3(aq) \rightarrow CH_3CH(NH_2)CH_3(l) + HBr(aq)$
  c $CH_3CH_2CH_2Cl(l) + NaOH(aq) \rightarrow CH_3CH_2CH_2OH(l) + NaCl(aq)$

Analysis

5

Homologous series	Reactant	Type of organic product(s)	Type of reaction
alkane	**$O_2(g)$**	carbon dioxide and water	**combustion**
haloalkane	NaOH	**alcohol**	**substitution**
haloalkane	ammonia	**amine**	substitution
alkane	**chlorine**	chloroalkane	**substitution**

6 The reactants are methane and an excess of chlorine gas. The reaction conditions are the presence of UV light. The dichloromethane could be separated from other chloromethane products by fractional distillation.

11.2 Reactions of alkenes

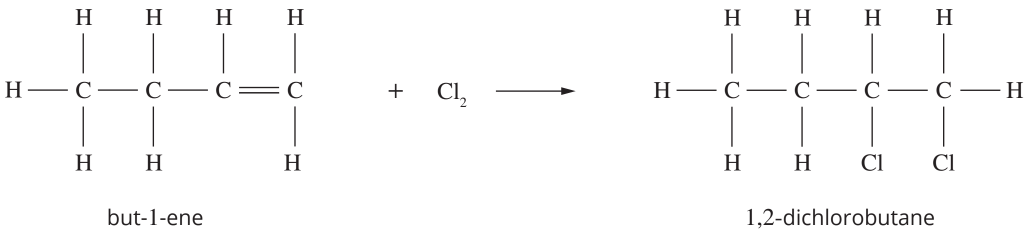
KEY QUESTIONS

Knowledge and understanding

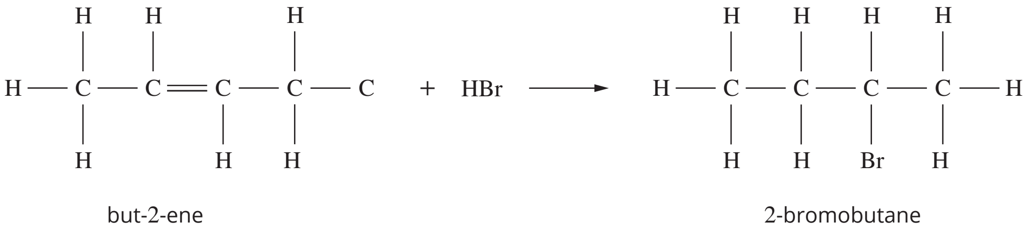
1 Alkenes will undergo combustion reactions in air to produce **carbon dioxide** and **water**. The product formed when but-2-ene reacts with bromine is **2,3-dibromobutane**. This is an example of an **addition** reaction.

The product formed when ethene reacts with hydrogen chloride is **chloroethane**. This is an example of an **addition** reaction.

2 **a**



b



3 $CH_3CH_2CHCHCH_2CH_3(l) + HCl(g) \rightarrow CH_3CH_2CHClCH_2CH_2CH_3(l)$

Analysis

4

Homologous series	Reactant	Type of organic product(s)	Type of reaction
alkene	halogen	dihaloalkane	addition
alkene	hydrogen gas, H_2 + Ni or Pt catalyst	**alkane**	**addition**
alkene	**air (oxygen)**	$CO_2 + H_2O$	**combustion**
alkene	**water + catalyst**	alcohol	**addition**
alkene	hydrogen halide	**haloalkane**	**addition**

5 **a** Propene could react with water to form two different products, propan-1-ol and propan-2-ol. This is because the OH group from water can react at either of the two carbon atoms in the carbon–carbon double bond in the propene molecule, resulting in two different compounds.

b But-2-ene will only form one product, butan-2-ol, when it reacts with water. The OH group from water can attach to either of the two carbon atoms in the carbon–carbon double bond of but-2-ene. The carbon atom to which the OH group is attached will be given the number 2 in each of the two product molecules.

6 C is correct. Pent-2-ene is not symmetrical and will form two possible products, one with a chlorine atom on carbon atom number 2 in the compound and the other with a chlorine atom on carbon atom number 3 (similar to the example in Figure 11.2.7).

Hex-3-ene and oct-4-ene are symmetrical and will only produce one product in their reactions with water (similar to the example in Figure 11.2.6).

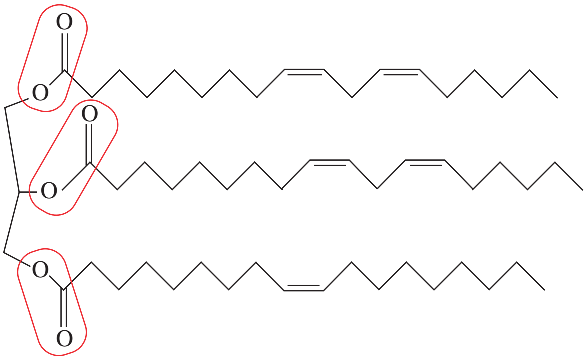
Chlorine, Cl_2, is symmetrical and so will only form one product with alkenes, whether they are symmetrical or not.

11.3 Reactions of alcohols, carboxylic acids and esters

CASE STUDY: ANALYSIS

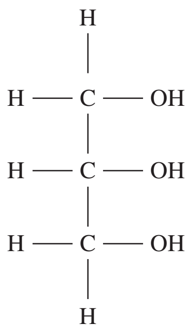
Making margarine

1



2 Three. A carboxyl group from each carboxylic acid molecule will react with one of the three hydroxyl groups of a glycerol molecule (see the diagram below).

3



4 Three molecules of hydrogen. There are five carbon–carbon double bonds in the original vegetable oil and two in the margarine, so three of the double bonds have reacted with hydrogen molecules. Each carbon–carbon double bond will react with one H_2 molecule in an addition reaction, so a total of three hydrogen molecules will react with one vegetable oil molecule.

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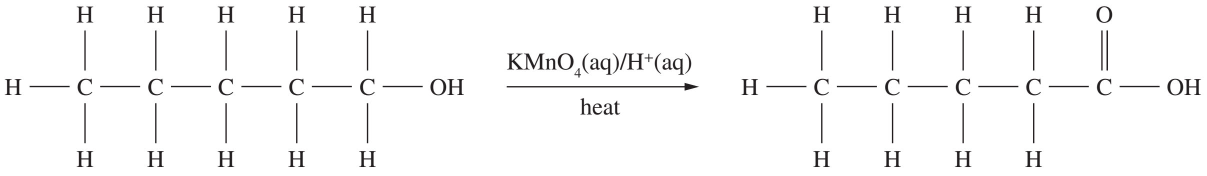
KEY QUESTIONS

Knowledge and understanding

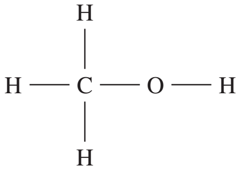
1 **a** ester
  b carboxylic acid
  c alcohol and carboxylic acid

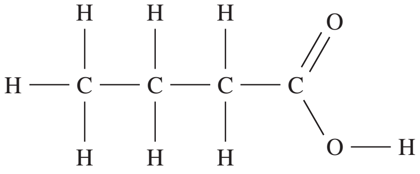
2 **a** $2C_5H_{12}O(g) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(g)$
  b Pentan-3-ol is a secondary alcohol; pentan-1-ol is a primary alcohol.
  c Pentan-1-ol would oxidise to the carboxylic acid. The solution would change from deep purple to clear as the reaction proceeded.



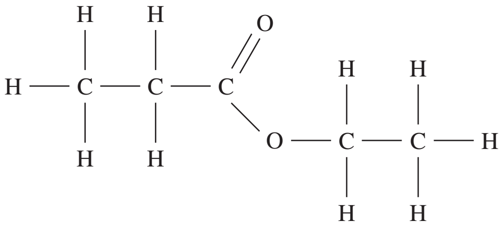
3 When pentanoic acid reacts with propan-1-ol, the organic product called **propylpentanoate** is formed. The other product in this reaction is **water**. This is an example of a **condensation** reaction.

4 **a** Methanol and sodium butanoate are initially formed; however, the addition of acid to the sodium butanoate will form butanoic acid.


methanol


butanoic acid

b


ethyl propanoate

Analysis

5

Homologous series compound	Reactant	Product(s)	Type of reaction
alcohol	air	**carbon dioxide and water**	combustion
primary alcohol	$H^+/Cr_2O_7^{2-}$ or H^+/MnO_4^-	**carboxylic acid**	**oxidation**
alcohol	**carboxylic acid + acid (H_2SO_4)**	ester + water	**esterification**
carboxylic acid	water	carboxylate ion + H_3O^+	**ionisation**
ester	water + acid	**carboxylic acid + alcohol**	**hydrolysis**
triglyceride	methanol	**biodiesel + glycerol**	**transesterfication**

6 **a** $CH_3CH_2COOCH_3(l) + H_2O(l)$
  b $CH_3COOH(l) + CH_3(CH_2)_3CH_2OH(l)$

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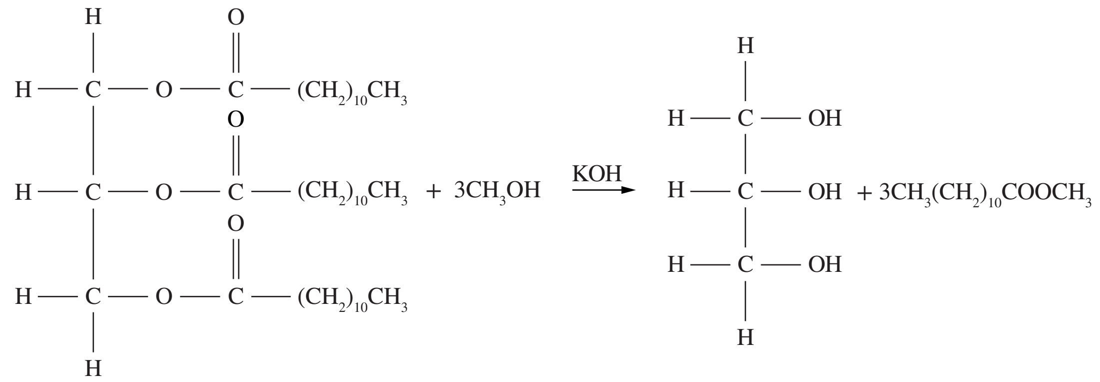

11.4 Reaction pathways and atom economy

Worked example: Try yourself 11.4.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

80.0 g of propan-1-ol was oxidised to propanoic acid using an acidified solution of $K_2Cr_2O_7$. The propanoic acid obtained at the end of the reaction had a mass of 55.0 g. Calculate the percentage yield of this oxidation reaction.

Thinking	Working
Write an equation for the reaction.	$C_3H_7OH(l) \xrightarrow{K_2Cr_2O_7/H^+} C_2H_5COOH$
Use the formula $n = \frac{m}{M}$ to determine the amount of reactant.	$n(C_3H_7OH) = \frac{m(C_3H_7OH)}{M(C_3H_7OH)}$ $= \frac{80.0}{60.0}$ $= 1.33$ mol
Use the mole ratio for the reaction to determine the amount, in moles, of the product that would be made if all of the reactant reacts.	mole ratio $= \frac{n(C_3H_7OH)}{n(C_2H_5COOH)} = \frac{1}{1}$ $n(C_2H_5COOH) = \frac{1}{1} \times n(C_3H_7OH)$ $= 1.33$ mol
Use the formula $m = n \times M$ to determine the mass of the product if all of the reactant reacts. This is the theoretical yield of the product.	$m(C_2H_5COOH) = n \times M$ $= 1.33 \times 74$ $= 98.42$ g
Calculate the percentage yield for this reaction from the formula: $\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$	$\text{percentage yield} = \frac{55.0}{98.42} \times \frac{100}{1}$ $= 55.9\%$

Worked example: Try yourself 11.4.2

CALCULATING THE PERCENTAGE YIELD OF A MULTI-STEP SYNTHESIS

Calculate the overall percentage yield for the preparation of D from A if it proceeds by a three-step synthesis:

$$A \longrightarrow B \text{ followed by } B \longrightarrow C \text{ followed by } C \longrightarrow D$$

The yield of A ⟶ B is 90%, the yield of B ⟶ C is 80% and the yield of C ⟶ D is 60%.

Thinking	Working
Calculate the overall yield of D by multiplying the percentage yields together and expressing as a percentage (multiplying by 100).	The overall yield of D is: $\frac{90}{100} \times \frac{80}{100} \times \frac{60}{100} \times \frac{100}{1}$ $= 43\%$

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Worked example: Try yourself 11.4.3

CALCULATING ATOM ECONOMY

Calculate the atom economy in the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol. The equation for the reaction is:

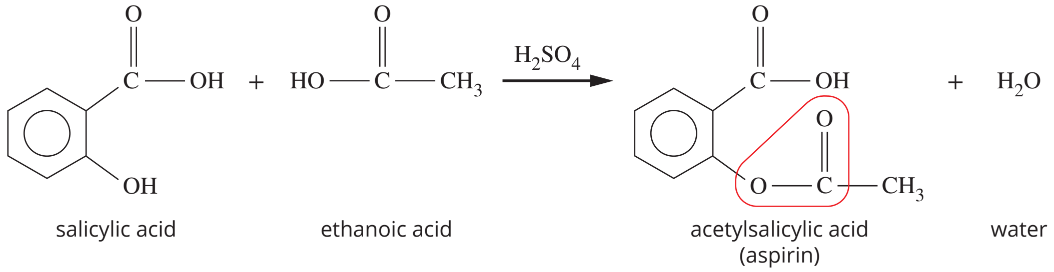
$$CH_3CH_2CH_2OH(aq) + NaI(aq) + H_2SO_4(aq) \longrightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$$

Thinking	Working
Calculate the total molar mass of the reactants.	$M(CH_3CH_2CH_2OH) + M(NaI) + M(H_2SO_4)$ $= [(3 \times 12.0) + (8 \times 1.00) + 16.0] + (23.0 + 127) + [(2 \times 1.00) + 32.0 + (4 \times 16.0)]$ $= 308 \text{ g mol}^{-1}$
Calculate the molar mass of the required product.	M(iodopropane) $= (3 \times 12.0) + (7 \times 1.00) + 127$ $= 170 \text{ g mol}^{-1}$
Calculate the atom economy for the reaction using the formula: $\text{atom economy} = \dfrac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$	$\text{atom economy} = \dfrac{170}{308} \times 100$ $= 55.2\%$

CASE STUDY: ANALYSIS

Aspirin, an ester derived from a herbal remedy

1



2 Total molar mass of all reactants = M(salicylic acid) + M(acetic acid)

$= 138 + 60 = 198 \text{ g mol}^{-1}$

Molar mass of desired product = M(aspirin)

$= 180 \text{ g mol}^{-1}$

$$\text{atom economy} = \left(\frac{\text{molar mass of desired product}}{\text{total molar mass of reactants}}\right) \times 100$$

$$= \left(\frac{180}{198}\right) \times 100$$

$$= 90.9\%$$

3 salicylic acid $(C_7H_6O_3)(s)$ + ethanoic acid $(C_2H_4O_2)(l) \longrightarrow$ aspirin $(C_9H_8O_4)(s) + H_2O(l)$

$n(\text{salicylic acid}) = \dfrac{m}{M} = \dfrac{10.5}{138} = 0.0760 \text{ mol}$

From the equation, n(aspirin) = n(salicylic acid)

$= 0.0760 \text{ mol}$

theoretical yield aspirin $= 0.076 \times 180$

$= 13.7 \text{ g}$

$\text{percentage yield of aspirin} = \dfrac{4.50}{13.7} \times 100$

$= 32.8\%$

KEY QUESTIONS

Knowledge and understanding

1 **a** The theoretical yield of a reaction is the maximum amount of product that can be formed using calculations based on the stoichiometric ratio of the limiting reactant and assumes 100% conversion.

b The percentage yield compares the actual yield to the theoretical yield and is a measure of the efficiency of a production process. It is found using:

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

c The atom economy for a chemical reaction is the percentage of the atoms in the reactants that end up in the desired product. It is found using:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100\%$$

2 Compound A is propan-1-ol; reactant B is acidified dichromate ions or acidified permanganate ions.

3 **a** $n(\text{ethene}) = \frac{120}{28.0} = 4.29 \text{ mol}$

theoretical yield of 1,2-dibromoethane = 4.29 × 188 = 806 g

b percentage yield of 1,2-dibromoethane $= \frac{280}{806} \times 100 = 34.7\%$

4 **a** overall yield $= \frac{80}{100} \times \frac{40}{100} \times \frac{30}{100} \times 100 = 9.6\%$

b overall yield $= \frac{25}{100} \times \frac{40}{100} \times \frac{30}{100} \times 100 = 3.0\%$

5 **a** Step 2: atom economy $= \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} = \frac{(2 \times 46)}{180} \times 100 = 51\%$

b The chemical by-product for the overall process is carbon dioxide, CO_2.

Analysis

6 **a** $H_2O(g)/H_3PO_4$ catalyst

b butanoic acid

c butyl ethanoate

7 **a** butanoic acid

b methanol with acid catalyst

c butan-1-ol

d $H^+/Cr_2O_7^{2-}$ and heat or H^+/MnO_4^-

e NaOH

8 This synthesis is carried out in three steps: (1) synthesis of ethanol, (2) synthesis of propanoic acid, and (3) synthesis of ethyl propanoate.

1 $\text{ethene} \xrightarrow{HCl} \text{chloroethane} \xrightarrow{OH^-} \text{ethanol}$

2 $\text{propene} \xrightarrow{H_2O/\text{catalyst}} \text{propan-1-ol} \xrightarrow{Cr_2O_7^{2}/H^+} \text{propanoic acid}$

3 $\text{ethanol} + \text{propanoic acid} \xrightarrow{H^+} \text{ethyl propanoate}$

After the first stage of the second step, fractional distillation would be required to separate the isomers propan-1-ol and propan-2-ol.

11.5 Sustainable production of chemicals

KEY QUESTIONS

Knowledge and understanding

1 **a** Using renewable raw materials (feedstocks)

b Using catalysts

c Designing safer chemicals and products.

2 Cellophane is biodegradable and is made from cellulose, which can be obtained from plant materials.

Polyvinyl chloride is made by the polymerisation of vinyl chloride. This compound is made from one of the fractions obtained in the fractional distillation of crude oil. It is therefore non-renewable.

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3 When catalysts are used in chemical reactions:

- lower temperatures are required, so heating costs are reduced.
- reaction rates are increased, so more product is formed in a shorter time.
- they are not consumed, so can be used repeatedly.

Analysis

4 **a** PFAS chemicals are useful ingredients in fire-fighting foams because they are surfactants which allow the foam to spread over the fire. They are also stable, not broken down by heat and are also oil- and water-resistant.

b The fact that PFAS chemicals are so stable means that they do not break down easily in soil or water. They therefore persist in the environment, and so can move long distances through soil, aquifers and waterways without decomposing. PFAS compounds are known to be toxic to some animals and there are also concerns that they may have an impact on human health.

5 There are no polar groups in polypropene, whereas the cellulose polymer is made up of glucose monomers with many hydroxyl groups, so polypropene is more hydrophobic than cellulose. Polypropene will interact less with aqueous solutions of any kind in the environment, than cellulose will. In addition, the carbon–carbon bonds which form the backbone of polypropene are very strong.

The polar hydroxyl groups in cellulose will interact readily with water and the carbon–oxygen bonds in cellulose are more readily hydrolysed than the strong carbon–carbon bonds in polypropene.

Chapter 11 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 B. Esters are formed when a carboxylic acid and an alcohol react together using a small amount of an acid, such as sulfuric acid as catalyst. Compounds **i** and **iii** are carboxylic acids and alcohols, respectively. None of the other pairs of compounds include both an alcohol and a carboxylic acid.

2 C. The atom economy of a reaction is calculated by the formula:

$$\text{atom economy} = \frac{\text{molar mass of the desired product} \times \text{its mole ratio in the equation}}{\text{molar mass of all reactants} \times \text{their mole ratios in the equation}} \times 100$$

In this question, ethanol is the desired product. Its molar mass is 46. In the equation, the mole ratio of ethanol to the reactant (glucose) is 2 : 1. The molar mass of glucose, the reactant, is 180.

3 **a** $CH_3CHCH_2(g) + Cl_2(g) \longrightarrow CH_3CHClCH_2Cl(l)$

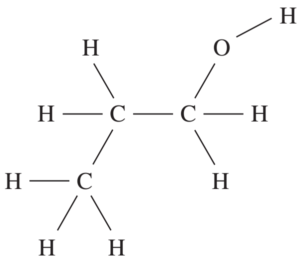
b $CH_3CH_2CH_2CH_2Cl(l) + OH^-(aq) \longrightarrow CH_3CH_2CH_2CH_2OH(aq)$

c $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

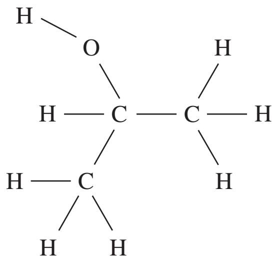
4 **a** The original compound reacted with hydrogen and a nickel catalyst to form propane, so it must have been propene. This is confirmed by the fact that it decolourised a bromine solution.

b Propene would react with chlorine in an addition reaction to produce 1,2-dichloropropane.

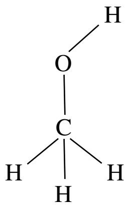
5 **a**



or



b



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6

Reactants	Products	Reaction type
pent-2-ene and bromine	1,2-dibromopentane	addition
ethanol burning in excess oxygen	**carbon dioxide and water**	**combustion or oxidation**
ethene and water, H_3PO_4 catalyst	**ethanol**	**addition**
bromoethane and hydroxide ion	**ethanol**	**substitution**
propene and hydrogen, Ni catalyst	**propane**	**addition**
chloromethane and ammonia	**methanamine**	**substitution**
hex-3-ene and hydrogen chloride	**3-chlorohexane**	**addition**
methyl propanoate and a dilute solution of HCl	**methanol and propanoic acid**	**hydrolysis**

7 **a** $CH_3CH_2CH_2COOH$
b CH_3COCH_3
c CH_3COOH

8 **a** $CH_3CH_2CH_2COOH$, CH_3OH
b $CH_3CH_2CH_2OH$, CH_3COOH
c CH_3CH_2OH, HCOOH

9 The term 'natural gas' sometimes causes confusion, but it is a fossil fuel. It is often found in deposits with crude oil. It is a non-renewable commodity.

10 Turpentine is made from plant material, which is a renewable resource. Mineral spirits are made from crude oil, a non-renewable resource. The fact that turpentine is more flammable and more toxic than mineral spirits means that more care needs to be taken when using it. For example, it would be important to use turpentine in a well-ventilated area.

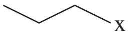
11 The tar is produced from the spinifex plant which is a renewable resource. The heat used to melt the spinifex resin is produced by burning wood, another renewable resource. The tar itself is biodegradable.

Crude oil is a fossil fuel and is non-renewable. The bitumen produced using tar persists in the environment and only biodegrades very slowly.

Application and analysis

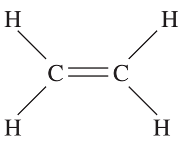
12 **A** ethene
B 1,2-dibromoethane
C chloroethane
D carbon dioxide and water

13 **a** $CH_3CH_2CH_2OH$
b (In the diagram, X represents a halogen atom.)

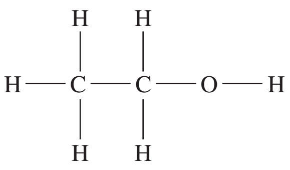


c NaOH

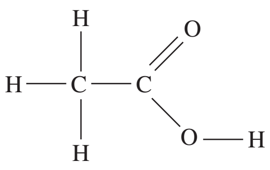
14



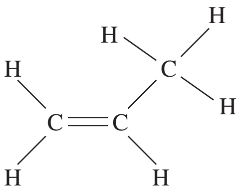
Compound A



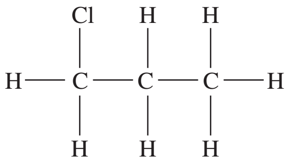
Compound B



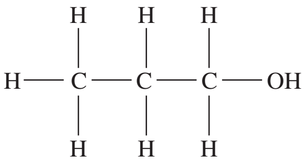
Compound C



Compound D



Compound E



Compound F

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15 **a** 3.26 g

$$\frac{n(\text{salicylic acid})}{n(\text{aspirin})} = \frac{1}{1}$$

$M(C_7H_6O_3) = 138\text{ g mol}^{-1}$

$$n(C_7H_6O_3) = \frac{2.5}{138}$$

$= 0.0181$ mol

$n(\text{aspirin}) = 0.0181$ mol

$M(\text{aspirin}) = M(C_9H_8O_4)$

$= 180\text{ g mol}^{-1}$

$m(\text{aspirin}) = 0.0181 \times 180$

$= 3.26$ g

b $\text{percentage yield} = \frac{2.35}{3.26} \times 100$

$= 72.1\%$

16 $CH_2CH_2 \xrightarrow{H_2O/H_3PO_4} CH_3CH_2OH \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3COOH$

17 $\text{Overall percentage yield} = \frac{46}{100} \times \frac{67}{100} \times 100 = 31\%$

In the two-step reaction:

$$n(C_2H_4) = \frac{m}{M} = \frac{54}{28} = 1.9\text{ mol}$$

If the yield from the reaction were 100%:

from the two equations, $n(C_2H_5OH) = n(C_2H_4)$

$= 1.9$ mol

$m(C_2H_5OH) = n \times M$

$= 1.9 \times 46$

$= 89$

But the yield was only 31%, so actual yield $= 89 \times \frac{31}{100}$

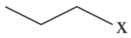
$= 28$ g

18 $$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

$$\text{mass of all reactants} = \frac{\text{mass of desired product} \times 100}{\text{atom economy}}$$

$$= \frac{2.00 \times 100}{55.2}$$

$= 3.62$ kg

19 **a** 

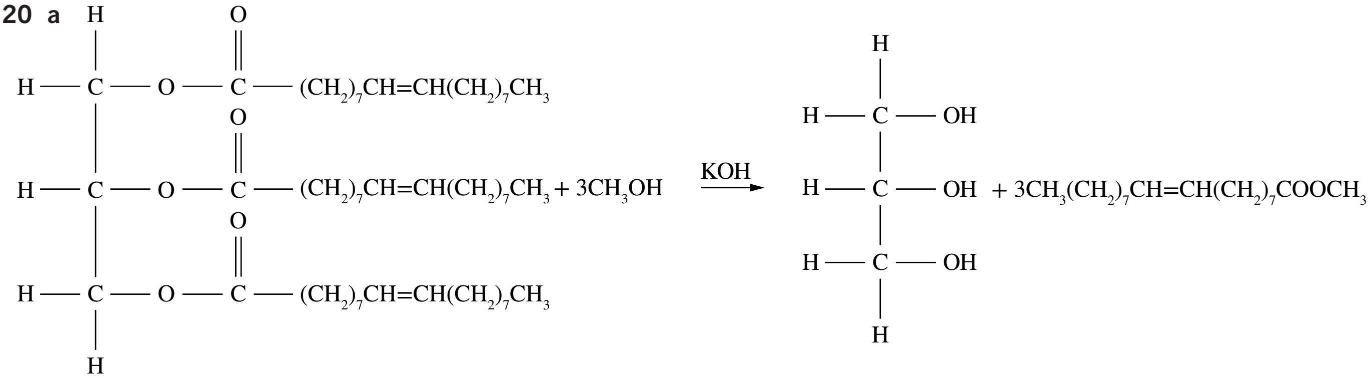
b $H^+/Cr_2O_7^{2-}$ or H^+/MnO_4^-

c propanoic acid

d $CH_3CH_2CH_2CH_2OH$

e $H_2SO_4(aq)$

f $CH_3CH_2CH_2CH_2OCOCH_2CH_3$ or $CH_3CH_2COOCH_2CH_2CH_2CH_3$

20 **a** 

triglyceride (palm oil) methanol glycerol fatty acid methyl esters (biodiesel)

b atom economy $= \dfrac{\text{molar mass of desired product}}{\text{molar mass of all reactants}}$

$= \dfrac{3 \times 296.0}{884.0 + (3 \times 32.0)} \times \dfrac{100}{1}$

$= 90.61\%$

c The mass of the triglyceride is used to determine the theoretical yield of biodiesel:

$n(\text{triglyceride}) = \dfrac{m}{M}$

$= \dfrac{44.20}{884.0}$

$= 0.05000$ mol of triglyceride

$\dfrac{n(\text{biodiesel})}{n(\text{triglyceride})} = \dfrac{3}{1}$

So, $n(\text{biodiesel}) = 3n(\text{triglyceride})$

$= 3 \times 0.05000$

$= 0.1500$ mol

$M(\text{biodiesel}) = 296.0 \text{ g mol}^{-1}$

$m(\text{biodiesel}) = 0.1500 \times 296.0$

$= 44.40$ g

So, the theoretical yield of biodiesel is 44.40 g.

percentage yield $= \dfrac{\text{actual yield}}{\text{theoretical yield}} \times \dfrac{100}{1}$

$= \dfrac{28.42}{44.40} \times \dfrac{100}{1}$

$= 64.01\%$

d The biodiesel has the semi-structural formula of $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$, so it will have the molecular formula of $C_{19}H_{36}O_2$. An equation for the combustion of this biodiesel is:

$$C_{19}H_{36}O_2(l) + 27O_2(g) \longrightarrow 19CO_2(g) + 18H_2O(l)$$

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Chapter 12 Reactions of biologically important compounds

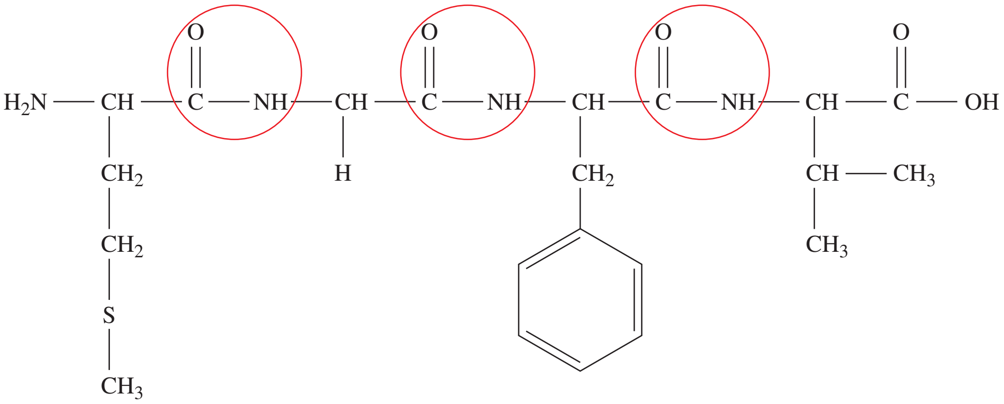
12.1 Synthesis of proteins

CASE STUDY: ANALYSIS

Ada Yonath and the structure of the ribosome

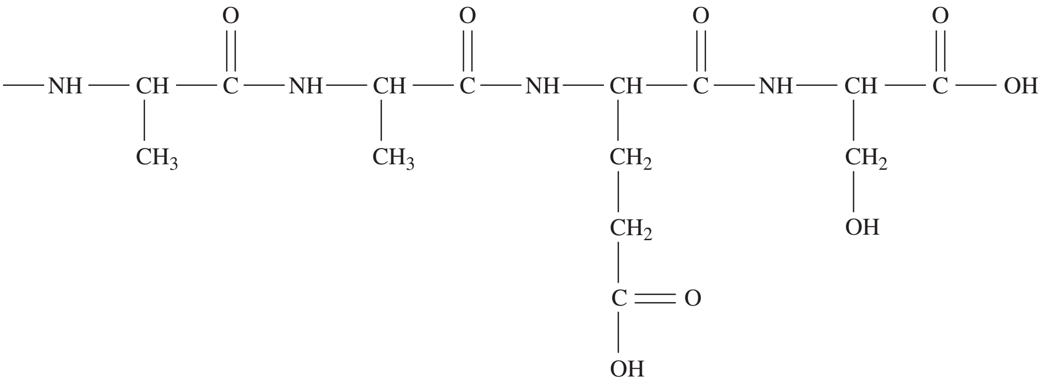
1 **a** Four. Count the number of C=O bonds in the molecule.

b



c methionine, glycine, phenylalanine, valine (Met-Gly-Phe-Val)

2



3 The ribosomes are large and dynamic, with rapidly moving atoms, and all of these things disturb crystallisation.

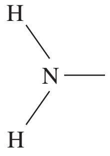
KEY QUESTIONS

Knowledge and understanding

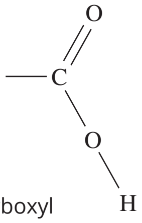
1 The figure shows a section of a polypeptide. It consists of **nine** amino acid residues that are linked together by **peptide/amide** groups. It was produced by a **condensation polymerisation** reaction. In this polypeptide there are two units of leucine residues, two units of **alanine**, two units of **lysine** and one unit each of **valine and methionine**.

2 Proteins are organic **biopolymers**. The monomers required to make proteins are **amino acids**. The formation of a protein is an example of a condensation polymerisation where the other product formed is **water**. The functional group that forms between monomers is an **amide**/a **peptide** group.

3 **a**



amine



carboxyl

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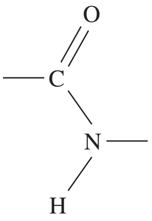
b



amide

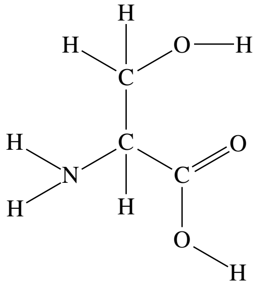
Analysis

4 B is a 2-amino acid because carbon number 2 is attached to the amino and R-functional group/methyl group. A is not a 2-amino acid because there are too many carbons in the chain. C is not a carboxylic acid.

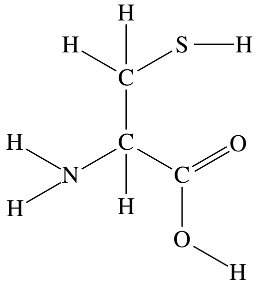
5 **a** A—amino group; B—peptide or amide link or bond or group; C—R group; D—carboxyl group

b alanine, serine, leucine

6 **a**

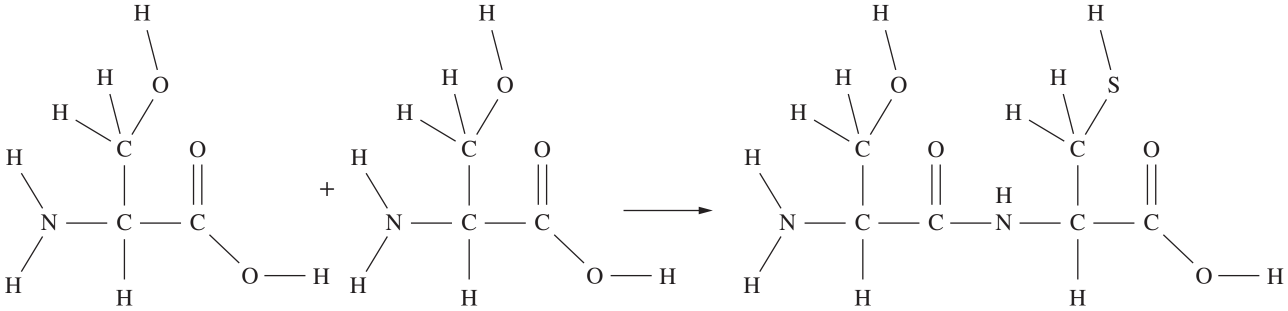


serine

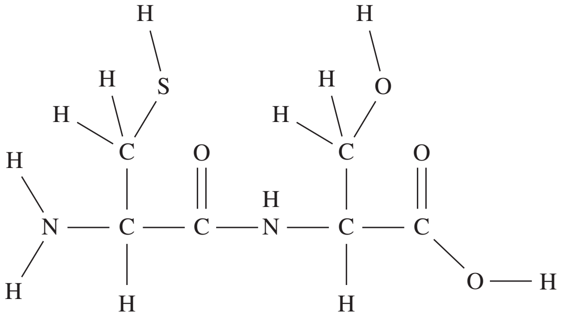


cysteine

b



c



If you drew this structure in your answer to part **b**, then the product in part **b** should be your answer to part **c**.

d condensation reaction—because two functional groups are reacting together

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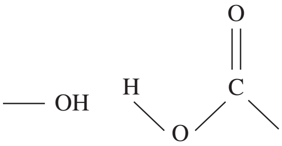
12.2 Synthesis of starch, glycogen and lipids

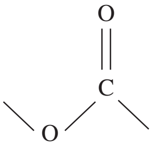
KEY QUESTIONS

Knowledge and understanding

1 **a** Hydroxyl groups (–OH) on both molecules react.
   b A glycosidic (or ether) link (–O–) is formed.
   c A hydroxyl group reacts with a carboxylic acid.



   d An ester functional group is formed.



2

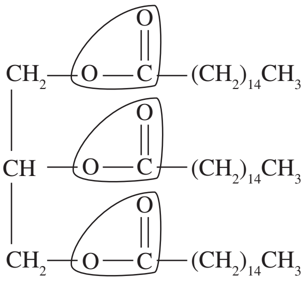
amylose	polysaccharide
fructose	monosaccharide
sucrose	disaccharide
lactose	disaccharide
cellulose	polysaccharide

3 **a** Glucose is a monosaccharide, made up of single ring structures of 5 carbon atoms and 1 oxygen atom. Maltose is made up of two monosaccharide molecules bonded together by a glycosidic linkage (ether functional group) –O–. Starch is a polymer of many monosaccharide molecules joined together by glycosidic linkages.
   b condensation

4 B, D, F and G. Starch is a polysaccharide formed from glucose monosaccharide units. It is the storage molecule of glucose in plants and is found in two forms: amylose and amylopectin. Amylose is largely insoluble in water due to the shape of the molecule, in which the hydroxyl groups face each other rather than being in contact with water. Amylopectin is more soluble in water because its branching shape leaves the –OH groups exposed and able to interact with water. Therefore, B, D, F and G are all correct.

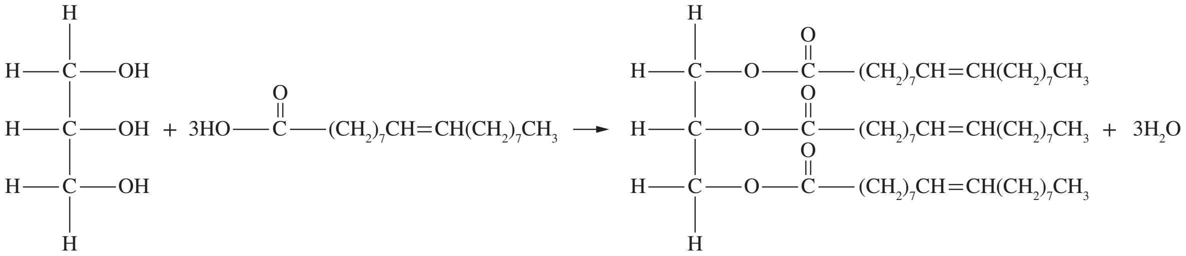
Analysis

5 **a**



   b The fat is saturated because the alkyl groups in the molecules ($CH_3(CH_2)_{14}$) contain only single carbon–carbon bonds. Alkyl groups with the general formula C_nH_{2n+1} are saturated.

6 **a**



$$\begin{array}{l}\text{H—C—OH}\\ \text{H—C—OH}\\ \text{H—C—OH}\end{array} + 3HO-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH{=}CH(CH_2)_7CH_3 \rightarrow \begin{array}{l}H-C-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH{=}CH(CH_2)_7CH_3\\ H-C-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH{=}CH(CH_2)_7CH_3\\ H-C-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH{=}CH(CH_2)_7CH_3\end{array} + 3H_2O$$

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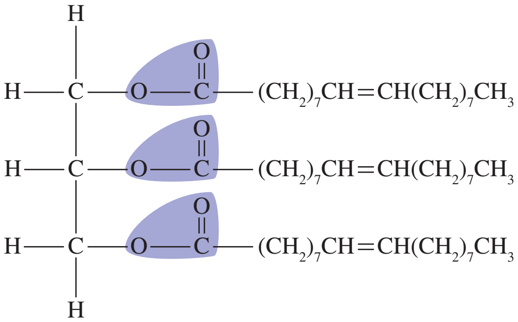
b



7 Fatty acids are relatively insoluble due to their long hydrocarbon chain. The hydrocarbon chain is non-polar and will not form hydrogen bonds with water.

12.3 Hydrolysis of biomolecules

KEY QUESTIONS

Knowledge and understanding

1 Amino acids can combine to form **polypeptides** in **condensation** reactions. **Water** is also formed in this reaction. The reverse of this reaction is a **hydrolysis** reaction.

Polysaccharides are formed in condensation reactions involving **monosaccharides**.

Fatty acids and **glycerol** can combine in a condensation reaction to form a **triglyceride**.

2 polysaccharide $\xrightarrow{\text{hydrolysis}}$ monosaccharides $\xrightarrow{\text{condensation}}$ **polysaccharide**

triglyceride $\xrightarrow{\text{hydrolysis}}$ glycerol and fatty acids $\xrightarrow{\text{condensation}}$ **triglyceride**

protein $\xrightarrow{\text{hydrolysis}}$ amino acids $\xrightarrow{\text{condensation}}$ **polypeptide/protein**

3 Enzymes catalyse many of the important hydrolysis reactions. They are essential for the breakdown by hydrolysis of proteins, carbohydrates and triglyceride molecules obtained from food into smaller molecules.

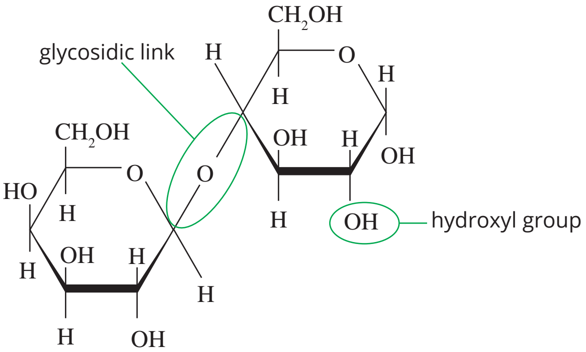
4 **a** $C_6H_{12}O_6$

b glycosidic links

Analysis

5 **a** A hydrolysis reaction is one in which water is a reactant. In the hydrolysis of lactose, the molecule is broken into two smaller parts by breaking the glycosidic link with the help of a catalyst.

b



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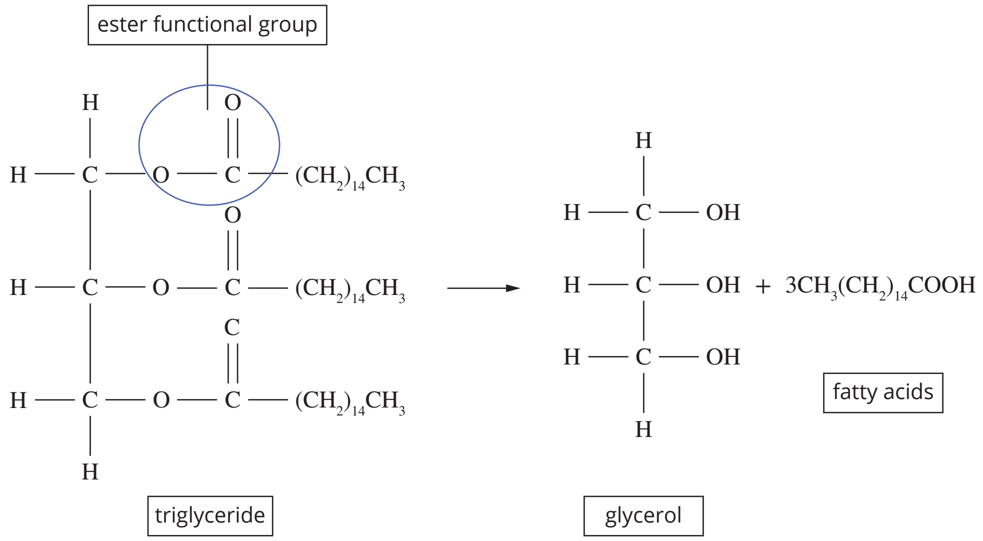
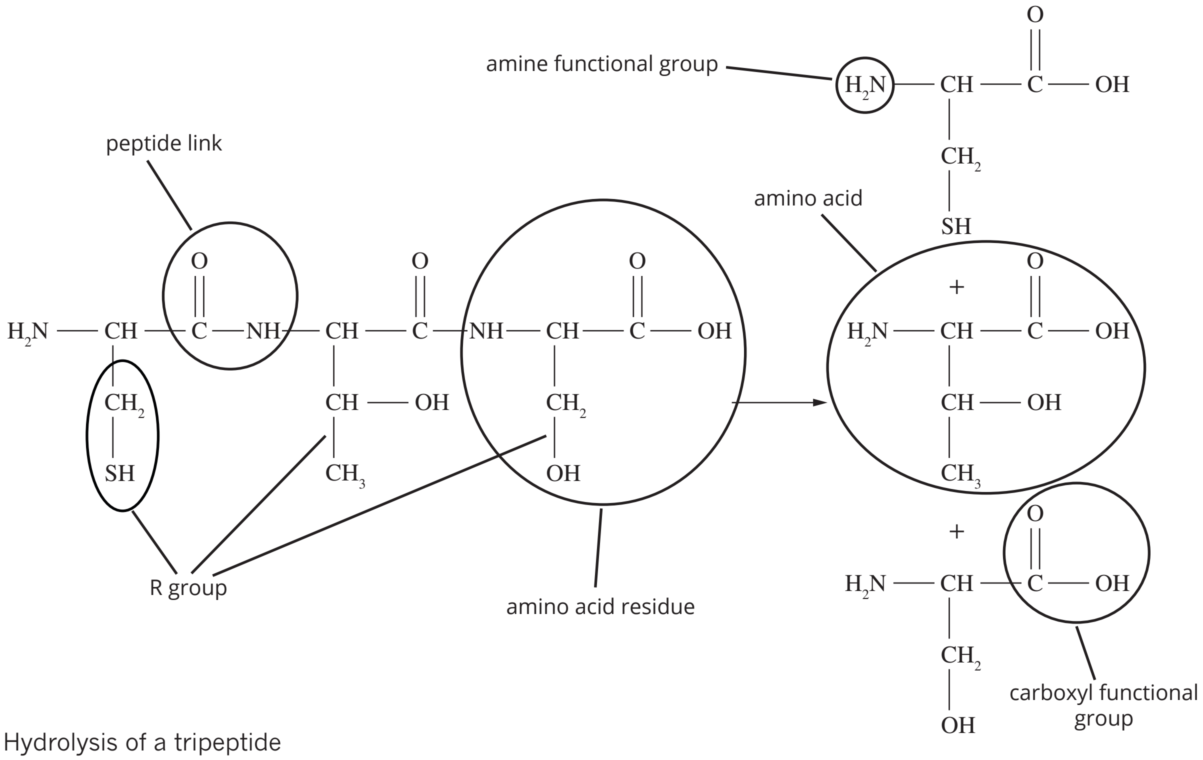


7 **a** Two water molecules are needed as extra reactants to give a balanced equation.

b



Hydrolysis of a tripeptide

Chapter 12 Review

REVIEW QUESTIONS

Knowledge and understanding

1 C. A is incorrect because R groups can contain additional atoms to C, H, O and N (such as sulfur).

B is incorrect because amino acids are the product of the hydrolysis of proteins, not carbohydrates.

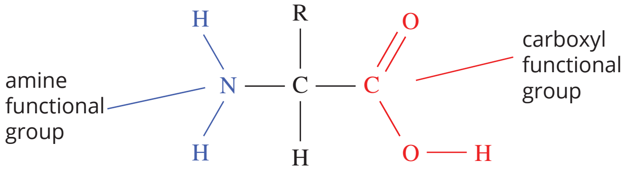
C is correct because amino acid R groups often contain additional N atoms.

D is incorrect because the side chains of amino acids can be acidic, basic, polar or non-polar.

2 A. The amine and carboxy groups are not attached to the same carbon. The amine group of B is pointing towards the bottom of the page and it is attached to the same carbon as the carboxy group, with the R group to the left. In C and D, the amino group and carboxy groups are attached to the same carbon, with the R group of C to the bottom and the R group of D to the top.

3 B. The hydroxyl groups on neighbouring molecules react to form a glycosidic linkage. The peptide linkage described in alternative A is found in a polypeptide, the ester functional group in alternative C is found in tryglycerides and in alternative D, a glycosidic linkage is incorrectly described as being formed from a hydroxyl group and a carboxyl. It is actually formed from the reaction between two hydroxyl groups.

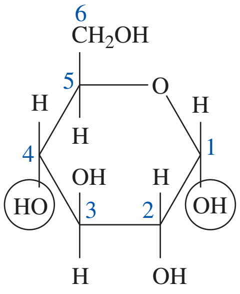
4



The amine is coloured blue (on the left-hand side) and the carboxy group is in red (on the right-hand side).

5 **a** The presence of several polar hydroxyl groups makes glucose soluble in water.

b The usual reactions of glucose involve the hydroxyls at positions 4 and 1.



6 **a** galactose or fructose

b maltose or lactose

c starch, cellulose or glycogen

7 Glycogen is the main storage polysaccharide in animals. Therefore, it fulfills the same role in animals that starch does in plants.

8 **a** carboxyl and hydroxyl groups; lipids

b two hydroxyl groups; carbohydrates

c carboxyl and amino groups; proteins

9 **a** all

b triglyceride

c all

d protein

e triglyceride

10

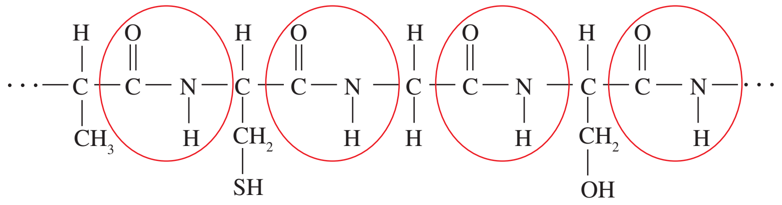
	Names of links between units	Functional groups formed when links break	Monomer or smallest components
Carbohydrate	**glycosidic**	hydroxyl	**monosaccharide**, often **glucose**
Fat	**ester**	hydroxyl and **carboxyl**	**fatty acids** and glycerol
Protein	**peptide/amide**	**amine** and carboxyl	**amino acid**

Analysis and application

11 **a** $H_2NCHCH_3CONHCH_2COOH$, $H_2NCH_2CONHCHCH_3COOH$

b 6 (using each amino acid once in each peptide)

c



d alanine-cysteine-glycine-serine

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12 During condensation reactions, small molecules join together to form larger molecules. Large food molecules undergo hydrolysis to form smaller molecules.

- **a** condensation
- **b** condensation
- **c** condensation
- **d** hydrolysis
- **e** hydrolysis
- **f** hydrolysis

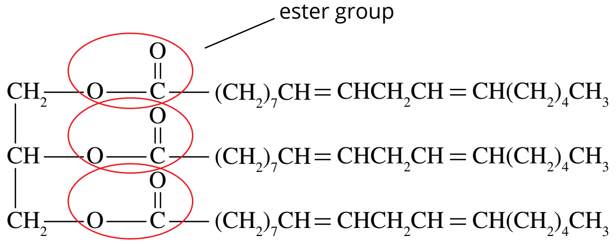
13
- **a** stearic acid + glycerol ⟶ ester
- **b** glucose + fructose ⟶ glycosidic (ether)
- **c** glycine + glycine ⟶ peptide (amide)
- **d** glucose + glucose ⟶ glycosidic (ether)
- **e** linoleic acid + glycerol ⟶ ester

14
- **a** It is not a protein as it does not contain N atoms.
- **b** A fatty acid is likely to be much smaller and to contain only two oxygen atoms.
- **c** It is far too big a molecule to be a monosaccharide.
- **d** The molecule is a typical polysaccharide – it is big, contains only carbon, hydrogen and oxygen and there are approximately 2 hydrogens for every oxygen, as there is in glucose.

15 Sucrose is a disaccharide formed from glucose and fructose (an isomer of glucose, with the same molar mass) – its molar mass will be (2 × 180) – 18 = 342 g mol^{-1}.

40 mol = 40 × 342 = 13680 g

16
- **a** glycerol
- **b**



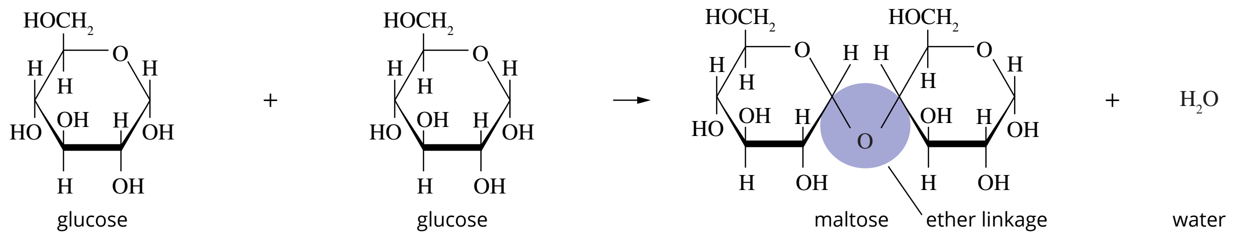
- **c** ester group (circled in part **b**)
- **d** Linoleic acid is an unsaturated fatty acid because it has two carbon–carbon double bonds in its structure.

17
- **a** carbon dioxide
- **b** glucose
- **c** disaccharide
- **d** glycosidic link
- **e** polysaccharide

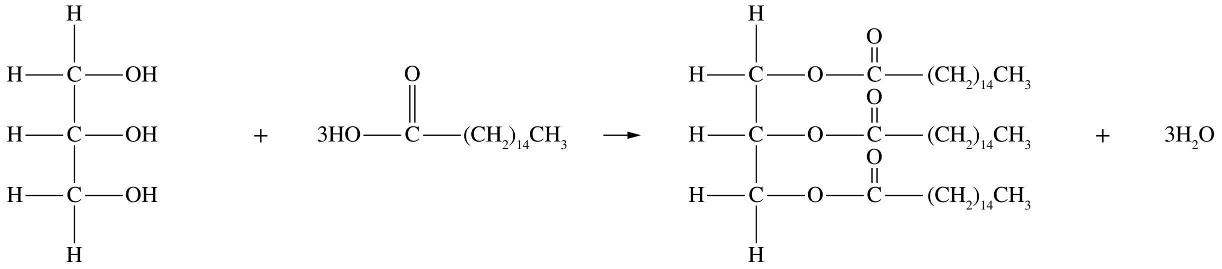
18

Molecule	The molecule is best described as a/an	A functional group it contains
glycine	**amino acid**	**amine or carboxyl**
glycogen	**polysaccharide**	**glycosidic or ether or hydroxyl**
glucose	**monosaccharide**	**hydroxyl or ether**
glycerol	**alcohol**	**hydroxyl**

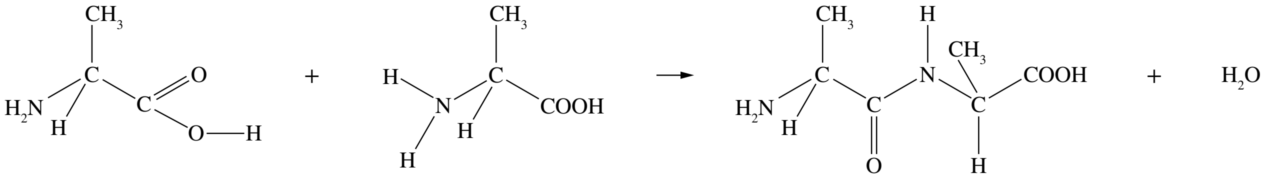
19
- **a** Condensation reactions involve the linking together of two small molecules and the elimination of a small molecule, usually water. Hydrolysis reactions consume water, produce two small molecules from one larger molecule, and they can often be regarded as the reverse of condensation reactions.
- **b** Vital biochemical processes include condensation reactions (e.g. synthesis of lipids, proteins and polysaccharides) and hydrolysis reactions (e.g. digestion).
- **c** **i**



ii


H
H—C—OH
H—C—OH
H—C—OH
H
+
3HO—C—(CH$_2$)$_{14}$CH$_3$
O
→
H—C—O—C—(CH$_2$)$_{14}$CH$_3$
H—C—O—C—(CH$_2$)$_{14}$CH$_3$
H—C—O—C—(CH$_2$)$_{14}$CH$_3$
O
O
O
H
H
+
3H$_2$O

iii


CH$_3$
H$_2$N
H
C
C
O
O—H
+
CH$_3$
H
N
H
C
H
COOH
→
CH$_3$
H$_2$N
H
C
C
O
H
N
CH$_3$
C
H
COOH
+
H$_2$O

Unit 4 Area of Study 1

How are organic compounds categorised and synthesised?

Multiple-Choice questions

1 A. The C–C bond energy (348 kJ mol^{-1}) is higher than that for C–Si bonds (318 kJ mol^{-1}), implying that C–C bonds are stronger. Hence, more energy will be required to break the C–C bonds in diamond than the C–Si bonds in silicon carbide.

2 B. The longest continuous chain is 5 carbons and there are no double bonds present, so the parent molecule is pentane. An additional methyl (CH_3) group is attached at carbon 2. A is incorrect because it does not recognise the longest chain of 5 carbons. C is incorrect as there is no carbon-to-carbon double bond present. D is incorrect as the methyl group is bonded to carbon 2, not carbon 1.

3 D. Propane is a non-polar molecule which will only form dispersion forces between molecules. It is also the smallest molecule presented; thus the dispersion forces will be weaker than in the other compounds. Weaker intermolecular forces lead to a lower boiling point, as less energy is required to separate the molecules so they can become a gas. A is incorrect as propan-1-ol contains a hydroxyl group which can form hydrogen bonds. These stronger intermolecular forces will increase the boiling point. B is incorrect as butane is a larger molecule than propane, and thus forms stronger dispersion forces, leading to a higher boiling point. C is incorrect as the chloro group will introduce a dipole in the molecule, and dipole–dipole interactions will be present between molecules, increasing the boiling point.

4 B. A glycosidic link, the functional group that is formed between glucose molecules in starch, forms from two hydroxyl groups. A is incorrect as it describes the groups involved in a peptide (amide) link, found in protein molecules. C is incorrect as it describes the groups involved in an ester link, found in triglycerides. D is incorrect as glycosidic links do not form between an amino group and a hydroxyl group.

5 A. The reaction involves formation of peptide links between the carboxyl functional group of one amino acid and the amine functional group of another. Option B is incorrect as it describes the formation of a glycosidic (ether) link. C is incorrect as it describes the formation of an ester link. D is incorrect as it does not include a carboxyl group.

6 D. Links between fatty acids and glycerol result from condensation of a hydroxyl (–OH) group and a carboxyl (–COOH) group. This results in an ester linkage (–COO–). A is incorrect as this is not the way these links are named. B is incorrect as peptide links occur in proteins. C is incorrect as ether (glycosidic) links occur in disaccharides and polysaccharides.

7 C. Successive members of a homologous series differ by a CH_2 unit. Primary alcohols can be oxidised to form carboxylic acids. Statement II is incorrect because hydroxyl groups are not significantly acidic or basic, therefore A, B and D are incorrect.

8 A. CH_2CH_2 (ethene) is unsaturated and undergoes an addition reaction with bromine, where one Br atom adds to each side of the double bond. B and D are incorrect as after an addition reaction the molecule will become saturated, whereas both these molecules contain a carbon-to-carbon double bond. C is incorrect as both Br atoms will be added into the product.

9 A. Reaction I involves the addition of HCl across the double bond in ethene. Reaction II substitutes a hydroxyl group (–OH) for a chloro group (–Cl). Reaction III converts a primary alcohol to a carboxylic acid, which involves oxidation. A is the only option that matches these reactions.

10 C. Acidified dichromate ($Cr_2O_7^{2-}/H^+$) is an oxidising agent typically used to convert a primary alcohol into a carboxylic acid. Heating ensures that the intermediate aldehyde, ethanal, is completely oxidised. A, B and D are incorrect as they are not carboxylic acids.

11 D. The '-oate' component of an ester derives from the carboxylic acid used, so this ester derives from ethanoic acid. The '-yl' component derives from the alcohol used, which must be methanol. A is incorrect as this combination would make ethyl ethanoate. B is incorrect as this combination would make ethyl methanoate. C is incorrect as this combination would make methyl propanoate.

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12 C. IV is the only structure where the hydroxyl group is not highest ranked when naming the compound, because in this case it is the carboxyl group that has the highest rank. IV is named 1-hydroxybutanoic acid. I is butan-1-ol. II is butan-2-ol. III contains both a hydroxyl group and an amino group. In this situation, the hydroxyl group takes precedence, and it is named 4-aminobutan-2-ol.

13 C. Option C is not true (and thus the correct answer), as all H atoms are in an oxidation state of +1 throughout. A and B are true, because acidified potassium dichromate is a strong oxidising agent that oxidises the methanol to methanoic acid. The dichromate ions are themselves reduced. D is a true statement as the sulfate ions are spectator ions in this reaction.

14 B. When a fat (a triglyceride) undergoes hydrolysis, it produces three fatty acids and glycerol. III is glycerol; II and V are fatty acids, but only V is saturated with a general formula of $C_nH_{2n+1}COOH$. Option A is incorrect, as it contains molecule II, an unsaturated fatty acid. Options C and D are incorrect as they do not contain glycerol.

15 B. $3x + 92(M(\text{glycerol})) = 878 + 54$ ($3 \times 18 = 54$; the mass of the three water molecules are incorporated in the hydrolysis step)

$$3x + 92 = 878 + 54$$
$$3x = 840$$
$$x = 840 \div 3$$
$$x = 280\ \text{g mol}^{-1}$$

Short-answer questions

16 **a** **i** C_7H_{16} **ii** e.g. $CH_3CH_2CH_2CH(CH_3)CH_2CH_3$
b **i** $C_4H_{10}O$ **ii** e.g. $CH_3CH_2CHOHCH_3$
c **i** $C_3H_6O_2$ **ii** e.g. CH_3CH_2COOH
d **i** $C_5H_{11}OCl$ **ii** e.g. $CH_2Cl(CH_2)_4OH$
e **i** $C_6H_{12}O$ **ii** e.g. $CH_3CH_2CH(CH_3)CH_2CHO$
f **i** $C_6H_{12}O$ **ii** e.g. $CH_3CHCHC(OH)(CH_3)CH_3$

17 **a** heptan-3-ol
b 3-fluorobutanal
c pent-2-ene
d 4-ethylhexan-3-amine
e 1-aminopropan-2-ol
f 5-chlorohexan-3-ol
g 6-hydroxyoctanoic acid
h 2-bromo-3-methylpentane
i 2-chlorohexan-3-one

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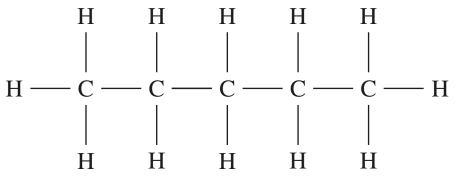
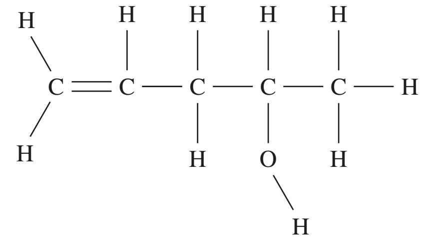
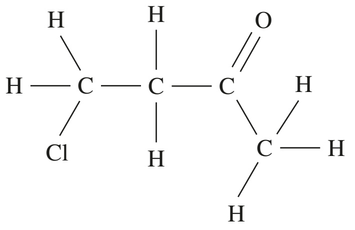
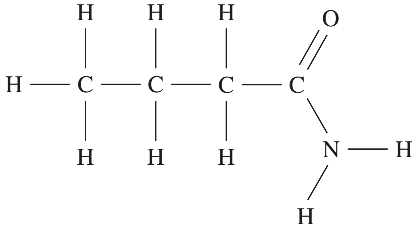
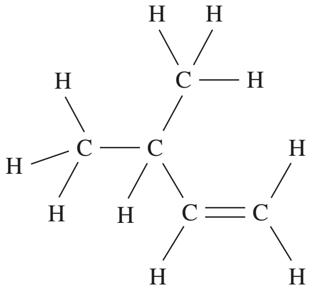
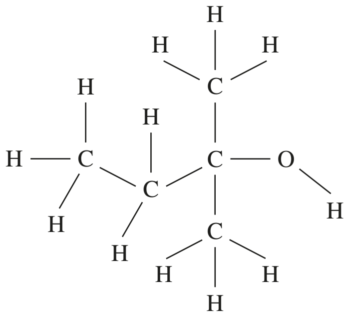
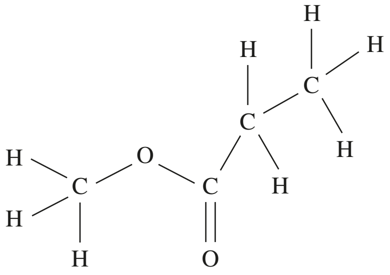
18

a	
b	
c	
d	
e	
f	
g	

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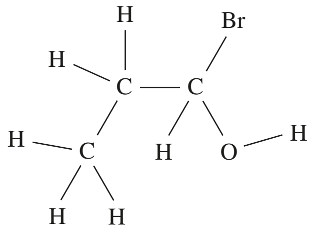
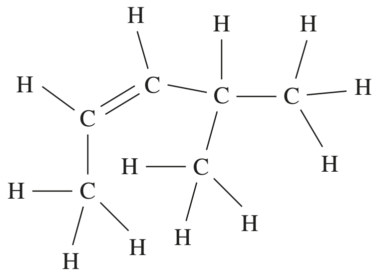
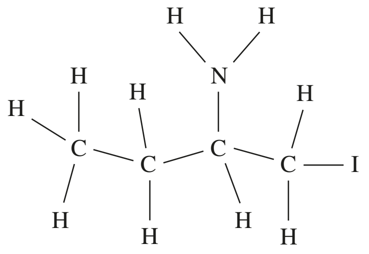
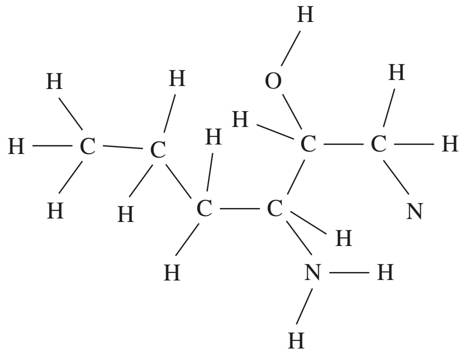
h	
i	
j	
k	

19 **a** Warm with an alkali metal hydroxide (e.g. KOH, NaOH)

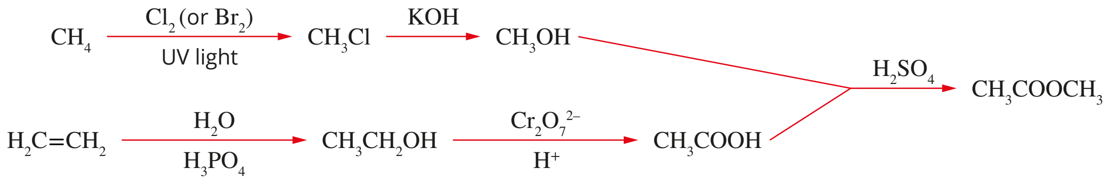
b Acidified dichromate ($Cr_2O_7^{2-}/H^+$) or acidified permanganate (MnO_4^-/H^+)

c NH_3

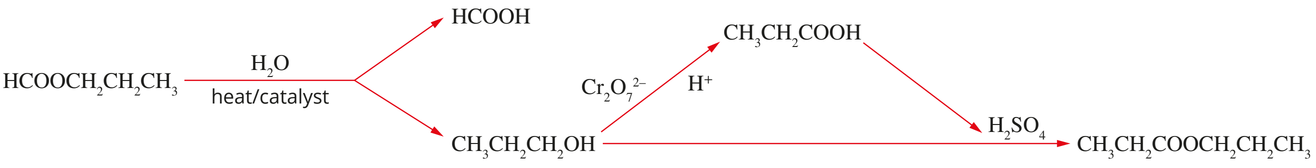
20 **a**

$$CH_3CH_2CH_3 \xrightarrow[\text{UV light}]{Cl_2\text{ (or }Br_2)} CH_3CH_2CH_2Cl \xrightarrow{KOH} CH_3CH_2CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3CH_2COOH$$

b



c



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21 a $CH_3CH_2CH_2OH + H_2O \rightarrow CH_3CH_2COOH + 4H^+ + 4e^-$

b $CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$

22 a Viscosity is a measure of the resistance to flow. Low-viscosity-liquids are 'runnier'.

b i Viscosity increases from methanol to ethanol to propan-1-ol because larger molecules have stronger dispersion forces between them, tending to restrict movement.

ii Ethane-1,2-diol has one more hydroxyl group than ethanol. The additional hydrogen bonding that this allows accounts for the higher viscosity and boiling point of ethane-1,2-diol compared to that of ethanol.

iii Benzene has a comparable molecular mass to butan-1-ol, but is non-polar and can only form relatively weak intermolecular dispersion forces. Weak bonding between benzene molecules results in low viscosity. A comparison of propanone and propan-1-ol also illustrates the point.

23 a $M(CHCl_3) = 119.4 \text{ g mol}^{-1}$

$M(CH_4) = 16.0 \text{ g mol}^{-1}$

$M(Cl_2) = 70.9 \text{ g mol}^{-1}$

$$\text{Atom economy} = \frac{\text{molar mass of product}}{\text{total molar mass of reactants}} \times 100 = \frac{119.4}{16.0 + (3 \times 70.9)} \times 100 = 52.2\%$$

b $$n(CH_4) = \frac{m}{M} = \frac{1000}{16.0} = 62.5 \text{ mol}$$

$n_{max}(CHCl_3) = n(CH_4) = 62.5$ mol; this is the maximum yield

$m_{max}(CHCl_3) = nM = 62.5 \times 119.4 = 7.46 \times 10^3 \text{ g} = 7.46 \text{ kg}$

$$m_{yield}(CHCl_3) = \frac{75}{100} \times 7.46 \text{ kg} = 5.60 \text{ kg}$$

c Sodium hydroxide and sodium ethanoate

d $M(CHCl_3) = 119.4 \text{ g mol}^{-1}$

$M(CH_3COCH_3) = 58.1 \text{ g mol}^{-1}$

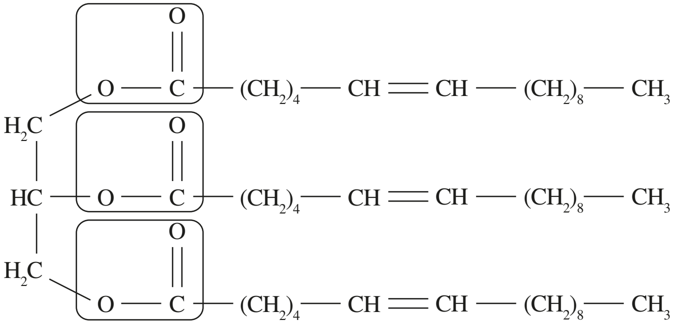
$M(NaOCl) = 74.4 \text{ g mol}^{-1}$

$$\text{Atom economy} = \frac{\text{molar mass of product}}{\text{total molar mass of reactants}} \times 100 = \frac{119.4}{58.1 + 3 \times 74.4} \times 100 = 42.4\%\text{; slightly lower}$$

e Addition reactions of alkenes have an atom economy of 100%, since in addition reactions the atoms of a small molecule add across a C=C double bond and there are no other products formed.

24 I a	$C_{22}H_{40}O_2$; $C_{21}H_{39}COOH$	**b**	polyunsaturated
II a	$C_{18}H_{28}O_2$; $C_{17}H_{27}COOH$	**b**	polyunsaturated
III a	$C_{20}H_{40}O_2$; $C_{19}H_{39}COOH$	**b**	saturated
IV a	$C_{16}H_{30}O_2$; $C_{15}H_{29}COOH$	**b**	monounsaturated

25 a, b



26 a $C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2C_6O_{12}O_6(aq)$

b $3C_{11}H_{23}COOH(l) + C_3H_8O_3(aq) \rightarrow C_{39}H_{74}O_6(l) + 3H_2O(l)$

27 a Independent variable: type of vegetable oil; Dependent variable: yield of biodiesel

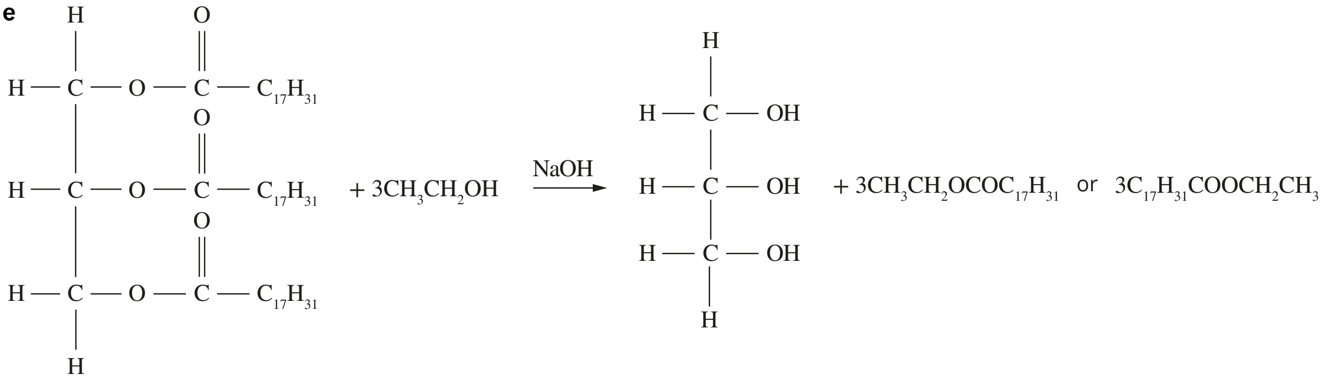
b The students wish to investigate the yield of biodiesel, so they would need to measure the quantity produced. Looking at the procedure they followed, the biodiesel is poured into a measuring cylinder. The students would need to identify which layer is the biodiesel, then use the increments on the measuring cylinder to measure the volume of biodiesel produced.

c i The measuring cylinder contains approximately 15.5 mL of biodiesel.

ii The bottom, polar layer, would contain glycerol, sodium hydroxide and unreacted ethanol.

d The mixture would become frothy. The NaOH present would react with the fatty acid molecules to form soap. This would decrease the yield of the biodiesel.

e



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Chapter 13 Laboratory analysis of organic compounds

13.1 Qualitative testing of organic compounds

Worked example: Try yourself 13.1.1

DETERMINING THE IDENTITY OF ORGANIC COMPOUNDS USING CHEMICAL TESTS

A student tests five colourless liquids labelled A, B, C, D and E. The identity of each individual liquid is unknown, but they are known to be pentane, but-2-ene, propan-1-ol, ethanoic acid and 2-methylpropan-2-ol. The student performs a number of qualitative tests on each liquid. Identify each liquid using the results shown below.

	A	B	C	D	E
Solubility in water	insoluble	soluble	soluble	insoluble	soluble
Addition of red-coloured bromine (Br_2) solution	colour disappears	no immediate reaction	no immediate reaction	no immediate reaction	no immediate reaction
Addition of sodium hydrogen carbonate ($NaHCO_3$) powder	no reaction	no reaction	no reaction	no reaction	gas evolved
Addition of acidified potassium permanganate ($KMnO_4$)	no colour change	colour change from purple to colourless	no colour change	no colour change	no colour change

Thinking	Working
Identify the homologous series to which each unknown liquid in the original list belongs.	Pentane is an alkane. But-2-ene is an alkene. Propan-1-ol is an alcohol. Ethanoic acid is a carboxylic acid. 2-methylpropan-2-ol is an alcohol.
Identify the polarity of each of the listed compounds. Remember that alkanes and alkenes are non-polar, and alcohols and carboxylic acids are polar.	Pentane and but-2-ene are non-polar. Propan-1-ol, ethanoic acid and 2-methylpropan-2-ol are polar.
The test for solubility in water is used to group the unknown liquids as polar or non-polar. Non-polar compounds are insoluble in water, and small alcohols and carboxylic acids are soluble in water.	Liquids A and D are insoluble in water, so must be the alkane and alkene. Liquids B, C and E are soluble in water, so these are the two alcohols and the carboxylic acid.
Use the bromine test to identify the presence of a carbon–carbon double bond. When bromine is added to a substance containing a carbon–carbon double bond, the bromine rapidly decolourises. Use this test to decide which of the non-polar liquids is an alkene.	The red colour of bromine disappears when added to liquid A, so A must contain a carbon–carbon double bond. Liquid A is but-2-ene. Liquid D is pentane.
Sodium hydrogen carbonate can be used to test for the presence of the carboxyl group. The reaction between an acid and sodium hydrogen carbonate produces carbon dioxide gas.	A gas is evolved when sodium hydrogen carbonate is added to liquid E. Liquid E is ethanoic acid.
The addition of acidified potassium permanganate is used to identify a primary or secondary alcohol. The primary or secondary alcohol is oxidised by the permanganate ion. As the permanganate ion is reduced to Mn^{2+}, the liquid changes from purple to colourless.	Butan-1-ol is a primary alcohol. 2-methylpropan-2-ol is a tertiary alcohol. A colour change from purple to colourless occurs with liquid B. Liquid B is propan-1-ol. Liquid C is 2-methylpropan-2-ol.

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Worked example: Try yourself 13.1.2

CALCULATING THE NUMBER OF CARBON–CARBON DOUBLE BONDS IN AN ORGANIC COMPOUND

A 0.0050 mol sample of linolenic acid reacts completely with 50.0 mL of a 0.30 M iodine solution (I_2). Determine the number of carbon–carbon double bonds present in each linolenic acid molecule.

Thinking	**Working**
Calculate the amount, in mol, of iodine that reacted with the fatty acid sample using: $n = cV$	$n(I_2) = cV$ $= 0.30 \times 0.0500$ $= 0.015$ mol
Calculate the value of the ratio: $\frac{n(I_2)}{n(\text{fatty acid})}$	$\frac{n(I_2)}{n(\text{linolenic acid})}$ $= \frac{0.015}{0.0050}$ $= 3$
Determine the number of carbon–carbon double bonds in one fatty acid molecule using the value of the ratio: $\frac{n(I_2)}{n(\text{fatty acid})}$	3 mole of iodine reacts with 1 mole of linolenic acid, so this means that there are 3 carbon–carbon double bonds in each linolenic acid molecule.

Worked example: Try yourself 13.1.3

CALCULATING IODINE NUMBER

Eicosapentaenoic acid is a polyunsaturated fatty acid found in fish oil. The semi-structural formula of eicosapentaenoic acid is $CH_3(CH_2CH{=}CH)_5(CH_2)_3COOH$ and the molar mass is 302.0 g mol^{-1}. Calculate the iodine number for this fatty acid.

Thinking	**Working**
Determine the number of carbon–carbon double bonds present in 1 molecule of the fatty acid.	From the semi-structural formula, there are 5 carbon–carbon double bonds in 1 molecule of eicosapentaenoic acid.
Convert 100 g of fatty acid to amount, in mol, using the formula: $n = \frac{m}{M}$	$n(\text{eicosapentaenoic acid}) = \frac{100}{302.0}$ $= 0.331$ mol
Calculate the amount of I_2, in mol, required to react with 1 mol of the fatty acid using: $n(I_2) = n(\text{fattyacid}) \times \text{number of C=C double bonds}$	$n(I_2) = n(\text{eicosapentaenoic acid}) \times 5$ $= 0.331 \times 5$ $= 1.66$ mol
Calculate the mass of iodine that will react with 100 g of the fatty acid using: $m(I_2) = n \times M$	$m(I_2) = 1.66 \times (126.9 \times 2)$ $= 420$ g
The iodine number is equal to the mass of I_2 that will react with 100 g of the fatty acid.	iodine number of eicosapentaenoic acid = 420

KEY QUESTIONS

Knowledge and understanding

1 Simple distillation is used to **separate** mixtures of two or more liquids. The mixture is placed in a round-bottom flask with anti-**bumping** granules to allow smooth **boiling**, and then heated to the **boiling point** of the liquid to be collected. The **vapour** rises up the flask and enters the **condenser**. The vapour is **cooled** to below its boiling point and condenses back to a liquid. This pure liquid is called the **distillate** and is collected in a separate flask. The liquid with the **higher** boiling point remains in the round-bottom flask.

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2 B. The presence of impurities will lower the melting point and broaden the melting point range of an organic compound.

A is incorrect because the presence of impurities lowers the melting point.

C is incorrect because the presence of impurities both lowers and broadens the melting point range.

D is incorrect—the identities of the compounds are not required because the two compounds have different melting points, so there will be an effect on the melting point of the first compound when the second compound is mixed in.

3 **a** An addition reaction occurs when bromine is added to a compound containing a carbon–carbon double bond. The bromine is said to be decolourised, as the red-brown colour of the bromine rapidly disappears when mixed with a compound containing a carbon–carbon double bond.

b $C_2H_4(g) + Br_2(aq) \longrightarrow CH_2BrCH_2Br(aq)$

4

$$
\begin{aligned}
n(CH_3CH_2OH) &= \frac{m}{M} \\
&= \frac{100}{328.0} \\
&= 0.305 \text{ mol}
\end{aligned}
$$

$$
\begin{aligned}
n(I_2) &= 5 \times n(C_{22}H_{32}O_2) \\
&= 5 \times 0.305 \\
&= 1.52 \text{ mol}
\end{aligned}
$$

$$
\begin{aligned}
m(I_2) &= n(I_2) \times M(I_2) \\
&= 1.52 \times 253.8 \\
&= 387 \text{ g}
\end{aligned}
$$

Iodine number = 387

Analysis

5 C.

$$
\begin{aligned}
n(I_2) &= 0.0250 \times 0.48 \\
&= 0.012 \text{ mol}
\end{aligned}
$$

$$
\begin{aligned}
\frac{n(I_2)}{n(\text{fatty acid})} &= \frac{0.012}{0.0040} \\
&= 3
\end{aligned}
$$

The fatty acid contains 3 carbon–carbon double bonds, which matches alternative C.

The molecules in the four alternatives have:

A: 1 carbon–carbon double bond

B: 2 carbon–carbon double bonds

C: 3 carbon–carbon double bonds

D: 4 carbon–carbon double bonds

6 **a** The unknown chemical could be ibuprofen or the unknown chemical could be a different substance that happens to have the same melting point as ibuprofen.

b Add pure ibuprofen to the chemical and determine the melting point of the mixture. If the melting point is exactly 75°C, then the unknown chemical is ibuprofen. If the melting point is lower than 75°C, then the unknown chemical is not ibuprofen.

7

$$
\begin{aligned}
n(I_2) &= \frac{m}{M} \\
&= \frac{22.84}{253.8} \\
&= 0.08999 \text{ mol}
\end{aligned}
$$

$$
\begin{aligned}
n(I_2) &: n(\text{fatty acid}) \\
&= 0.08999 : 0.045 \\
&= 2 : 1
\end{aligned}
$$

The fatty acid molecule contains 2 carbon–carbon double bonds.

8 A is propan-2-ol. The colour change from orange to green when acidified potassium dichromate was added indicates a primary alcohol.

B is pent-1ene. The bromine is decolourised, indicating the presence of a carbon–carbon double bond.

C is propanoic acid. A gas is produced (CO_2) on addition of sodium hydrogen carbonate.

D is hexane. Alkanes are insoluble in water and do not react rapidly with bromine.

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E is 2-methylpropan-2-ol. This can be identified as an alcohol because it is soluble in water, but undergoes no reaction with sodium hydrogen carbonate. No colour change when acidified potassium dichromate is added indicates a tertiary alcohol.

9 The mixture of volatile liquids can be separated by fractional distillation. The mixture is placed in the distillation flask and heated. The most volatile compound with the lowest boiling point (bromomethane) is the first to reach the top of the fractionating column and condense. The fraction condensing in a narrow range of temperatures around the boiling point 65°C is collected. The next fraction to be collected at around 80°C will contain the ester, methyl propanoate, which is collected as the distillate. The higher boiling point components from the reaction mixture, water and propanoic acid, remain in the distillation flask.

13.2 Redox titrations of organic compounds

Worked example: Try yourself 13.2.1

VOLUMETRIC ANALYSIS OF AN ALCOHOL

The concentration of a solution of methanol (CH_3OH) was determined by titration with a standard solution of acidified potassium permanganate ($KMnO_4$). The ionic equation for the reaction is:

$$5CH_3OH(aq) + 4MnO_4^-(aq) + 12H^+(aq) \rightarrow 5HCOOH(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$$

A 10.00 mL aliquot of CH_3OH solution was titrated with a 0.125 M solution of $KMnO_4$. Titres of 14.13, 14.18, 14.28 and 14.11 mL were required to reach the end point when the orange solution turned green. Determine the molar concentration of the methanol solution.

Thinking	Working
Calculate the average volume of the concordant titres.	The titre of 14.28 mL is discarded because it is not concordant, i.e. it is not within a range of 0.10 mL from highest to lowest titre volumes. $\text{average titre} = \frac{14.13+14.18+14.11}{3}$ $= 14.14\text{ mL}$
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(MnO_4^-) = c \times V$ $= 0.125 \times 0.01414$ $= 1.77 \times 10^{-3}\text{ mol}$
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	$\text{mole ratio} = \frac{n(CH_3OH)}{n(MnO_4^-)} = \frac{5}{4}$ $\text{so } n(CH_3OH) = \frac{5}{4} \times n(MnO_4^-)$ $= 2.21 \times 10^{-3}\text{ mol}$
Determine the concentration of the unknown substance. Express your answer to the appropriate number of significant figures.	$c(CH_3OH) = \frac{n}{V}$ $= \frac{2.21 \times 10^{-3}}{0.01000}$ $= 0.221\text{ M}$ The final result is rounded to 3 significant figures, corresponding to the smallest number of significant figures in the original data. All figures are kept in the calculator throughout the calculation to avoid rounding errors.

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Worked example: Try yourself 13.2.2

VOLUMETRIC ANALYSIS THAT INVOLVES DILUTION

The concentration of sodium hypochlorite, NaOCl, in a sample of disinfectant, was found by diluting 25.00 mL of bleach to 250.0 mL. Excess potassium iodide and sulfuric acid is added to each of the 20.00 mL aliquots of the diluted bleach in a conical flask.

The initial reaction between the hypochlorite ions, iodide ions and the acid in the conical flask is:

$$OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + H_2O(l)$$

and the mixture turns brown due to the production of iodine.

The mixture is titrated with 0.0235 M sodium thiosulfate ($Na_2S_2O_3$) solution. Titres of 25.08, 26.40, 25.05 and 25.10 mL are required to reach the end point which is determined using starch indicator:

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

Calculate the molar concentration of NaOCl in the original sample of disinfectant.

Thinking	Working
Determine the average volume of the concordant titres.	The titre of 26.40 mL is discarded because it is not concordant, i.e. it is not within a range of 0.10 mL from the highest to lowest titre volumes. $\text{average titre} = \frac{25.08+25.05+25.10}{3}$ $= 25.08 \text{ mL}$
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(S_2O_3^{2-}) = c \times V$ $= 0.0235 \times 0.025\,08$ $= 5.89 \times 10^{-4} \text{ mol}$
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	$\text{mole ratio} = \frac{n(I_2)}{n(S_2O_3^{2-})} = \frac{1}{2}$ In this example, $n(I_2) = n(OCl^-) = \frac{1}{2} \times n(S_2O_3^{2-})$ $n(OCl^-) = \frac{1}{2} \times n(S_2O_3^{2-})$ $= \frac{1}{2} \times 5.89 \times 10^{-4}$ $= 2.95 \times 10^{-4} \text{ mol}$
Determine the concentration of the unknown substance in the diluted solution by dividing the amount of unknown in one aliquot by the volume of the aliquot (in litres).	$c(OCl^-) = \frac{n}{V}$ $= \frac{2.95 \times 10^{-4}}{0.02000}$ $= 0.0147 \text{ M}$
Multiply by the dilution factor to determine the concentration of the unknown substance in the undiluted solution. Express your answer to the appropriate number of significant figures.	$\text{Dilution factor} = \frac{250.0}{25.00} = 10.00$ So undiluted $c(OCl^-)$ = diluted $c(OCl^-) \times 10.00$ $= 0.0147 \times 10.00$ $= 0.147 \text{ M}$ The final result is rounded to 3 significant figures, corresponding to the smallest number of significant figures in the original data. All values are kept in the calculator in the earlier steps of the calculation to avoid rounding errors.

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Worked example: Try yourself 13.2.3

SOLUTION STOICHIOMETRY: A LIMITING REACTANT PROBLEM

17.5 mL of a 0.645 M potassium dichromate ($K_2Cr_2O_7$) solution is added to 28.2 mL of a 0.560 M ethanol (C_2H_5OH) solution. The overall ionic equation for the reaction is:

$$3C_2H_5OH\text{(aq)} + 2Cr_2O_7^{2-}\text{(aq)} + 16H^+\text{(aq)} \rightarrow 3CH_3COOH\text{(aq)} + 4Cr^{3+}\text{(aq)} + 11H_2O\text{(l)}$$

a Determine the limiting reactant.

b Calculate the mass of CH_3COOH in the reaction mixture when the reaction is complete.

Thinking	**Working**
a Calculate the number of moles of each of the reactants using $n = cV$. Remember to convert mL to L.	$n(K_2Cr_2O_7) = n(Cr_2O_7^{2-})$ $= c \times V$ $= 0.645 \times 0.0175$ $= 0.0113$ mol $n(C_2H_5OH) = c \times V$ $= 0.560 \times 0.0282$ $= 0.0158$ mol
Identify the limiting reactant as follows: Choose one reactant and use the coefficients in the equation to find the amount of the other reactant needed for it to completely react.	The equation shows that 2 mol of $Cr_2O_7^{2-}$ reacts with 3 mol of C_2H_5OH. $n(Cr_2O_7^{2-})$ needed to react $= \frac{2}{3} \times n(C_2H_5OH)$ $= \frac{2}{3} \times 0.0158$ $= 0.0105$ mol
Compare the values for the amount required of the second reactant and the amount actually present to determine which is the limiting reactant.	0.0105 mol of $Cr_2O_7^{2-}$ is needed for all of the C_2H_5OH to react. There is 0.0113 mol of $Cr_2O_7^{2-}$ present. The $K_2Cr_2O_7$ is in excess. C_2H_5OH is the limiting reactant.
b Find the mole ratio of the unknown substance to the limiting reactant from the equation coefficients: $\frac{\text{coefficient of unknown}}{\text{coefficient of known (limiting reactant)}}$	The unknown substance is CH_3COOH. From the equation coefficients: $\frac{n(CH_3COOH)}{n(C_2H_5OH)} = \frac{3}{3}$
Calculate the number of moles of the unknown substance using the mole of limiting reactant calculated using the original data: n(unknown) = mole ratio × n(limiting reactant)	$n(CH_3COOH) = n(C_2H_5OH)$ $= 0.0158$ mol
Calculate the mass of the unknown substance using: m(unknown) = n(limiting reactant) × molar mass Express your answer to the appropriate number of significant figures.	$M(CH_3COOH) = 60.0$ g mol^{-1} $m(CH_3COOH) = n \times M$ $= 0.0158 \times 60.0$ $= 0.948$ g

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CASE STUDY: ANALYSIS

Determination of vitamin C content

Analysis

1 Iodine is unstable and, immediately before its use as a standard solution, it must be reacted with another chemical (usually sodium thiosulfate) to accurately determine its concentration.

2 and **3**

Trial	1	2	3
Mass of vitamin C tablet (g)	0.342	0.336	0.338
Titre iodine (mL)	25.68	25.47	25.53
$n(I_2) = c \times V$ (mol)	0.0525×0.02568 $= 0.001348$	0.0525×0.02547 $= 0.001337$	0.0525×0.02553 $= 0.001340$
$n(C_6H_8O_6) = n(I_2)$ (mol)	0.001 348	0.001 337	0.001 340
Mass of ascorbic acid in each tablet: $m(C_6H_8O_6) = n(C_6H_8O_6) \times M(C_6H_8O_6)$	0.001348×176.0 $= 0.2373$ $= 0.237$ g	0.001337×176.0 $= 0.2353$ $= 0.235$ g	0.001340×176.0 $= 0.2359$ $= 0.236$ g
Percentage purity = $\frac{m(C_6H_8O_6)}{m(\text{tablet})} \times 100\%$	$\frac{0.237}{0.342} \times \frac{100}{1}$ $= 69.38\ \%$	$\frac{0.235}{0.336} \times \frac{100}{1}$ $= 70.04\ \%$	$\frac{0.236}{0.338} \times \frac{100}{1}$ $= 69.79\ \%$

average % purity = $\frac{(69.38 + 70.04 + 69.79)}{3} = 69.7\%$ (3 significant figures)

4 C is correct.

A: Rinsing the conical flask only with deionised water would have no effect on the calculated mass of ascorbic acid because it does not change the number of moles of ascorbic acid in the conical flask.

B: The final rinse for the burette should be with the iodine solution. Rinsing only with deionised water would dilute the iodine solution, resulting in a higher titre as more iodine would be needed to oxidise the ascorbic acid. The calculated mass of ascorbic acid would be higher.

C: If the concentration of the iodine solution was higher than specified, then a lower titre would be required to neutralise the ascorbic acid. The calculated mass of ascorbic acid would be lower.

5 Gloves and safety glasses must be worn to prevent skin and eye damage.

6 The tablet may also include binders to hold the ingredients of the tablet together and sweeteners to improve the taste.

KEY QUESTIONS

Knowledge and understanding

1 **a** A standard solution is a solution of accurately known concentration. A primary standard is a substance that is readily obtained in a pure form, has a known formula and can be stored without deteriorating or reacting with the atmosphere. It should also be cheap and have a high molar mass.

b A burette is a piece of equipment capable of delivering different volumes of a liquid accurately (generally up to 50.00 mL). Pipettes usually deliver only a fixed volume of liquid (e.g. 20.00 mL).

c An aliquot is the volume of liquid delivered from a pipette. A titre is delivered by a burette and is the volume needed to reach the end point of a titration.

2 $CH_3CH_2CH_2CH_2OH(aq) + H_2O(l) \rightarrow CH_3CH_2CH_2COOH(aq) + 4H^+(aq) + 4e^-$

3 **a** $n(MnO_4^-) = c \times V = 0.450 \times 0.02301 = 0.0104$ mol

b $n(CH_3CH_2OH) = \frac{5}{4} \times n(MnO_4^-) = 0.01294$ mol in 20.00 mL of cider

c $c(CH_3CH_2OH)$ in the cider = $n = \frac{n}{V} = \frac{0.01294}{0.02000}$

$= 0.647$ M

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Analysis

4 **a** $n(C_6H_8O_6) = c \times V$

$= 0.235 \times 0.0198$

$= 4.65 \times 10^{-3}$ mol

$n(I_2) = c \times V$

$= 0.195 \times 0.0202$

$= 3.94 \times 10^{-3}$ mol

The equation shows that 1 mole of $C_6H_8O_6$ reacts with 1 mole of I_2.

0.004 65 mol of I_2 is needed for all of the $C_6H_8O_6$ to react.

There is 0.003 94 mol of I_2 present.

The $C_6H_8O_6$ is in excess.

I_2 is the limiting reactant.

b From the equation coefficients:

$$\frac{n(C_6H_6O_6)}{n(I_2)} = \frac{1}{1}$$

$$n(C_6H_6O_6) = n(I_2)$$

$$= 3.94 \times 10^{-3} \text{ mol}$$

Molar mass of $C_6H_6O_6$ = 174.0 g mol^{-1}

$m(C_6H_6O_6) = n \times M$

$= 3.94 \times 10^{-3} \times 174.0$

$= 0.685$ g

5 The titre of 14.54 mL is discarded because it is not concordant, i.e. it is not within a range of 0.10 mL from the highest to lowest titre volumes.

$$\text{average titre} = \frac{14.32 + 14.27 + 14.25}{3}$$

$= 14.28$ mL

The equation for the reaction is:

$2MnO_4^-(aq) + 5CH_3CHO(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5CH_3COOH(aq) + 3H_2O(l)$

$$n(MnO_4^-) = c \times V = 0.104 \times 0.014\,28 = 1.485 \times 10^{-3} \text{ mol}$$

$$n(CH_3CHO) = \frac{5}{2} \times n(MnO_4^-) = \frac{5}{2} \times 1.485 \times 10^{-3} = 3.713 \times 10^{-3} \text{ mol}$$

$$c(CH_3CHO) \text{ in the 20.00 mL sample} = \frac{n}{V} = \frac{3.713 \times 10^{-3}}{0.020\,00}$$

$= 0.186$ M

6 **a** $n(Cr_2O_7^{2-}) = c \times V = 0.103 \times 0.024\ 61 = 2.535 \times 10^{-3}$ mol

$$n(CH_3CH_2OH) = \frac{3}{2} \times n(Cr_2O_7^{2-}) = \frac{3}{2} \times 2.535 \times 10^{-3} = 3.802 \times 10^{-3} \text{ mol}$$

$$c(CH_3CH_2OH) \text{ in the 20.00 mL aliquot of diluted wine} = \frac{n}{V} = \frac{3.802 \times 10^{-3}}{0.020\,00}$$

$= 0.190$ M

$$\text{dilution factor} = \frac{100.0}{10.00} = 10.00$$

$c(CH_3CH_2OH)$ in the 10.00 mL sample of wine = diluted $c(CH_3COOH) \times 10.00$

$= 0.190 \times 10.00$

$= 1.90$ M

b The calculated concentration would be higher than its actual value. Rinsing the burette with deionised water would slightly dilute the potassium dichromate solution. This means more potassium dichromate solution would need to be added to reach the equivalence point. It would then appear that a greater amount of potassium dichromate reacted; hence, it would appear that a greater amount of ethanol had reacted, resulting in a reported ethanol concentration higher than it actually is.

7 **a** $CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$

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

c $2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$

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d **i** $n(\text{Cr}_2\text{O}_7{}^{2-}) = c \times V = 0.125 \times 0.015\,24 = 1.905 \times 10^{-3}$ mol

$n(\text{CH}_3\text{CH}_2\text{OH}) = \frac{3}{2} \times n(\text{Cr}_2\text{O}_7{}^{2-}) = \frac{3}{2} \times 1.905 \times 10^{-3} = 0.002\,858$ mol

$c(\text{CH}_3\text{CH}_2\text{OH})$ in the 10.00 mL aliquot of diluted whiskey $= \frac{n}{V} = \frac{0.002858}{0.01000}$

$= 0.2858$ mol L^{-1}

dilution factor $= \frac{500.0}{20.00} = 25.00$

$c(\text{CH}_3\text{CH}_2\text{OH})$ in the 20.00 mL sample of whiskey = diluted $c(\text{CH}_3\text{CH}_2\text{OH}) \times 25.00$

$= 0.2858 \times 25.00$

$= 7.14$ M

ii $c(\text{g L}^{-1}) = c(\text{M}) \times M = 7.14 \times 46.0 = 328$ g L^{-1}

Chapter 13 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 **a** 24.22, 24.20 and 24.16 mL

b 24.19 mL

2 **a** The carbon–carbon double bond in but-1-ene could be identified by reaction with bromine solution. The bromine would be decolourised if a double bond is present.

b The hydroxyl group in ethanol could be identified by reaction with ethanoic acid and a little sulfuric acid. The characteristic smell of an ester (ethyl ethanoate) would be observed if the compound is ethanol.

c The carboxyl group in propanoic acid could be identified by the addition of sodium hydrogen carbonate powder. Effervescence would be observed because of the production of carbon dioxide gas.

3 $3\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH(aq)} + 2\text{Cr}_2\text{O}_7{}^{2-}\text{(aq)} + 16\text{H}^+\text{(aq)} \longrightarrow 3\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH(aq)} + 4\text{Cr}^{3+}\text{(aq)} + 11\text{H}_2\text{O(l)}$

4 $n(\text{H}_2\text{C}_2\text{O}_4.2\text{H}_2\text{O}) = \frac{m}{M} = \frac{2.436}{126.0} = 0.01933$ mol

$c(\text{H}_2\text{C}_2\text{O}_4.2\text{H}_2\text{O}) = \frac{n}{V} = \frac{0.01933}{0.1000} = 0.1933$ M

5 The volumetric flask should be rinsed with deionised water, the pipette with the iodine standard solution, the burette with vitamin C solution and the conical flask with deionised water.

6 **a** A primary standard has a very high level of purity; has a known formula; is stable (e.g. will not react with atmospheric gases, such as carbon dioxide and water vapour); has a high molar mass to minimise errors in weighing; is readily available; and is relatively inexpensive.

b
- Accurately weigh an empty weighing bottle, add the primary standard and reweigh.
- Transfer the weighed sample to a volumetric flask using a dry glass funnel.
- Rinse out the weighing bottle and glass funnel using a wash bottle.
- Half-fill the volumetric flask with water and shake to dissolve the sample.
- When the sample has dissolved, add water to the calibration mark and shake the flask again.
- Determine the concentration of the primary standard.

7 **a** $n(\text{KMnO}_4) = c \times V$

$= 1.05 \times 0.0200$

$= 0.0210$ mol

$n(\text{CH}_3\text{OH}) = c \times V$

$= 1.12 \times 0.0305$

$= 0.0342$ mol

b The equation shows that 4 mol of $\text{MnO}_4{}^-$ reacts with 5 mol of CH_3OH.

$$\frac{n(\text{CH}_3\text{OH})}{n(\text{Cr}_2\text{O}_7^{2-})} = \frac{5}{4}$$

$$n(\text{CH}_3\text{OH}) = \frac{5}{4} \times 0.0210$$

$= 0.0263$ mol

0.0263 mol of CH_3OH is needed for all of the $\text{MnO}_4{}^-$ to react.

c There is 0.0342 mol of CH_3OH present, but only 0.0263 mol is needed for all of the $\text{MnO}_4{}^-$ to react.

The CH_3OH is in excess.

KMnO_4 is the limiting reactant.

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d From the equation coefficients:

$$\begin{aligned}\frac{n(\text{HCOOH})}{n(\text{KMnO}_4)} &= \frac{5}{4}\\ n(\text{HCOOH}) &= \frac{5}{4}\times n(\text{KMnO}_4)\\ &= \frac{5}{4}\times 0.0210\\ &= 0.0263\text{ mol}\end{aligned}$$

Molar mass of HCOOH = 46.0 g mol^{-1}

$$\begin{aligned}m(\text{HCOOH}) &= m\times M\\ &= 0.0263\times 46.0\\ &= 1.21\text{ g}\end{aligned}$$

8 $$\begin{aligned}n(\text{C}_{18}\text{H}_{28}\text{O}_2) &= \frac{m}{M}\\ &= \frac{100}{276.0}\\ &= 0.362\text{ mol}\end{aligned}$$

$$\begin{aligned}n(I_2) &= 4\times n(\text{C}_{18}\text{H}_{28}\text{O}_2)\\ &= 4\times 0.362\\ &= 1.448\text{ mol}\end{aligned}$$

$$\begin{aligned}m(I_2) &= n(I_2)\times M(I_2)\\ &= 1.448\times 253.8\\ &= 368\text{ g}\end{aligned}$$

Iodine number = 368

9 Determine the melting point of the sample. If the melting point range is sharp and between 157°C and 159°C, then the sample is likely to be pure salicylic acid. If the melting point is lower than 159°C and the range is broad, then the sample contains impurities.

Application and analysis

10 $$\begin{aligned}n(\text{I}_2) &= c\times V\\ &= 0.50\times 0.0380\\ &= 0.019\text{ mol}\end{aligned}$$

$$\begin{aligned}m(\text{I}_2) &= n\times M\\ &= 0.019\times 253.8\\ &= 4.8\text{ g}\end{aligned}$$

5.0 g of vegetable oil reacts with 4.8 g of I_2.

Let 100 g of vegetable oil react with m g of I_2:

$$\begin{aligned}m(I_2) &= \frac{100}{5.0}\times 4.8\\ &= 96\text{ g}\end{aligned}$$

Iodine number of the vegetable oil = 96

11 a The molar mass of nervonic acid = 366.0 g mol^{-1}

$$\begin{aligned}n(I_2) &= \frac{m}{M}\\ &= \frac{7.69}{253.8}\\ &= 0.0303\text{ mol}\end{aligned}$$

$$\begin{aligned}n(\text{C}_{24}\text{H}_{46}\text{O}_2) &= \frac{m}{M}\\ &= \frac{11.1}{366.0}\\ &= 0.0303\text{ mol}\end{aligned}$$

$$\begin{aligned}n(\text{I}_2) &: n(\text{C}_{24}\text{H}_{46}\text{O}_2)\\ &= 1:1\end{aligned}$$

So, a nervonic acid molecule contains 1 carbon–carbon double bond (monounsaturated).

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b Calculate the amount, in mol, of 100 g of nervonic acid:

$$n(C_{24}H_{46}O_2) = \frac{m}{M}$$
$$= \frac{100}{366.0}$$
$$= 0.273 \text{ mol}$$

Nervonic acid molecules contain 1 carbon–carbon double bond:

$$n(I_2) = n(C_{24}H_{46}O_2)$$
$$= 0.273 \text{ mol}$$
$$n(I_2) = n(C_{24}H_{46}O_2)$$
$$= 0.273 \text{ mol}$$
$$m(I_2) = n \times M$$
$$= 0.273 \times 253.8$$
$$= 69.3 \text{ g}$$

The iodine number of nervonic acid = 69.3

12 The mixture of volatile liquids can be separated by fractional distillation. The mixture is placed in the distillation flask and heated. The components in the mixture are separated in order of their boiling points, with the most volatile component (lowest boiling point), bromoethane, being the first fraction to condense. This is followed by the fraction containing 1,1-dibromoethane. The fraction condensing in a narrow range of temperatures around the boiling point of 1,2-dibromoethane, 131°C, is then collected in a new receiving flask. The higher boiling point component from the reaction mixture, 1,1,2-tribromoethane, remains in the distillation flask.

13 $n(I_2) = \frac{m}{M}$

$n(I_2)$ added to 10.0 g of plant oil = $\frac{15.0}{253.8} = 0.0591$ mol

$n(I_2)$ reacting with 10.0 g of plant oil = $0.0591 - 0.0201 = 0.0380$ mol

$m(I_2)$ reacting with 10.0 g of plant oil = $n(I_2) \times M = 0.0390 \times 258.3 = 9.90$ g

$m(I_2)$ reacting with 100 g of plant oil = $9.90 \times \frac{100}{10.0} = 99.0$ g

Iodine number of the plant oil = 99.0

14 **a** Rinsing with water would dilute the standard solution.

b The calculated concentration would be higher as a smaller titre of the unknown solution would be required to react with the standard solution.

15 $n(K_2Cr_2O_7) = c \times V = 0.0988 \times 0.0181$

$= 1.79 \times 10^{-3}$ mol

$n(CH_3CH_2OH) = c \times V = 0.114 \times 0.0253$

$= 2.88 \times 10^{-3}$ mol

The equation shows that 2 moles of $K_2Cr_2O_7$ reacts with 3 mole of CH_3CH_2OH.

$n(CH_3CH_2OH)/n(CR_2O_7^{2-}) = \frac{3}{2}$

$n(CH_3CH_2OH) = \frac{3}{2} \times 1.79 \times 10^{-3}$

$= 2.685 \times 10^{-3}$ mol

0.00268 mol of CH_3CH_2OH is needed for all of the $K_2Cr_2O_7$ to react.

There is 2.88×10^{-3} mol of CH_3CH_2OH present.

The CH_3CH_2OH is in excess.

$K_2Cr_2O_7$ is the limiting reactant.

From the equation coefficients:

$$\frac{n(CH_3COOH)}{n(K_2Cr_2O_7)} = \frac{3}{2}$$
$$n(CH_3COOH) = \frac{3}{2} \times n(K_2Cr_2O_7)$$
$$= \frac{3}{2} \times 1.79 \times 10^{-3}$$
$$= 2.68 \times 10^{-3} \text{ mol}$$

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Molar mass of CH_3COOH = 60.0 g mol^{-1}

$m(CH_3COOH) = n \times M = 2.68 \times 10^{-3} \times 60.0$

$= 0.161$ g

16 a $n(I_2) = c \times V = 0.0243 \times 0.019\,76 = 4.802 \times 10^{-4}$ mol

b $n(SO_2) = n(I_2) = 4.802 \times 10^{-4}$ mol

c $m(SO_2) = n(SO_2) \times M = 4.802 \times 10^{-4} \times 64.1 = 0.0308$ g

d percentage $SO_2 = \frac{0.03078}{20.97} \times \frac{100}{1} = 0.147$ % m/m

17 a Oxidation of ethanol to ethanoic acid: $CH_3CH_2OH(aq) + H_2O(l) \longrightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$

Reduction of permanganate: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

b $5CH_3CH_2OH(aq) + 4MnO_4^-(aq) + 12H^+(aq) \longrightarrow 5CH_3COOH(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$

c $n(MnO_4^-) = c \times V$

$= 0.450 \times 0.02301$

$= 0.01035$ mol

$n(CH_3CH_2OH) = \frac{5}{4} \times n(MnO_4^-)$

$= \frac{5}{4} \times 0.01035$

$= 0.0129$ mol

$n(CH_3CH_2OH)$ in the 10.00 mL sample of cider = 0.0129 mol

d $m(CH_3CH_2OH) = n \times M$

$= 0.0129 \times 46.0$

$= 0.595$ g

$V(CH_3CH_2OH) = \frac{m}{d}$

$= \frac{0.595}{0.789}$

$= 0.755$ g

$\%CH_3CH_2OH = \frac{V(CH_3CH_2OH)}{V(\text{cider sample})}$

$= \frac{0.755}{10.00} \times \frac{100}{1}$

$= 7.55\%\ v/v$

Concentration of ethanol in the cider = 7.55 % v/v

e i The calculated concentration of ethanol in the cider solution would be lower. Rinsing the pipette with deionised water would slightly dilute the cider solution. This means less potassium permanganate would need to be added to oxidise the ethanol. It would then appear that a smaller amount of potassium permanganate reacted; hence, it would appear that a smaller amount of ethanol had reacted.

ii The calculated concentration of ethanol in the cider solution would be higher. Rinsing the burette with deionised water would slightly dilute the potassium permanganate solution. This means more potassium permanganate solution would need to be added to oxidise the ethanol. This would give the impression that the ethanol solution was more concentrated than it actually was.

iii The calculated concentration of ethanol in the cider solution would not be affected. Rinsing the conical flask with deionised water would have no effect on the titre volume as the amount of ethanol in the conical flask is accurately known.

18 a $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ (multiply by a factor of 2)

$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e^-$ (multiply by a factor of 5)

Add the equations:

$2MnO_4^-(aq) + 16H^+(aq) + 10e^- + 5C_2O_4^{2-}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g) + 10e^-$

Simplify:

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

b $n(Na_2C_2O_4) = \frac{m}{M} = \frac{0.161}{134.0} = 1.201 \times 10^{-3}$ mol

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From the equation: $n(\text{MnO}_4^-) = \frac{2}{5} \times n(\text{C}_2\text{O}_4^{2-})$

$= \frac{2}{5} \times 1.201 \times 10^{-3}$ mol

$= 4.806 \times 10^{-4}$ mol

$c(\text{MnO}_4^-) = \frac{n}{V}$

$= \frac{0.0004806}{0.02670}$

$= 0.0180$ M

This answer is given to 3 significant figures because the original mass of sodium oxalate was only given to 3 significant figures.

19 **a** First, write a balanced equation: $\text{C}_6\text{H}_8\text{O}_6(aq) + \text{I}_2(aq) \longrightarrow \text{C}_6\text{H}_6\text{O}_6(aq) + 2\text{H}^+(aq) + 2\text{I}^-(aq)$

Calculate the amount of the given reactant, I_2:

$n(\text{I}_2) = c \times V = 0.105 \times 0.026\,34 = 2.766 \times 10^{-3}$ mol

From the equation, 1 mol of ascorbic acid reacts with 1 mol of I_2:

$\frac{n(\text{C}_6\text{H}_8\text{O}_6)}{n(\text{I}_2)} = \frac{1}{1}$

$n(\text{C}_6\text{H}_8\text{O}_6) = 2.766 \times 10^{-3}$ mol

Calculate the mass of ascorbic acid:

$m(\text{C}_6\text{H}_8\text{O}_6) = n \times M = 2.766 \times 10^{-3} \times 176.0$

$= 0.487$ g

b percentage ascorbic acid in the vitamin C tablet $= \frac{0.487}{2.592} \times 100$

$= 18.8\%$

c fillers, binders, sweeteners, flavours and colouring

20 **a** Calculate the average volume of the concordant titres:

average titre $= \frac{9.20 + 9.16 + 9.22}{3} = 9.19$ mL $= 0.009\,19$ L

Calculate the amount of the $\text{Cr}_2\text{O}_7^{2-}$ present in the average titre:

$n(\text{Cr}_2\text{O}_7^{2-}) = c \times V = 0.0500 \times 0.00919$

$= 4.60 \times 10^{-4}$ mol

b From the equation, 3 mol of $\text{CH}_3\text{CH}_2\text{OH}$ reacts with 2 mol of $\text{Cr}_2\text{O}_7^{2-}$:

$\frac{n(\text{CH}_3\text{CH}_2\text{OH})}{n(\text{Cr}_2\text{O}_7^{2-})} = \frac{3}{2}$

$n(\text{CH}_3\text{CH}_2\text{OH})$ in 20.00 mL $= \frac{3}{2} \times 4.60 \times 10^{-4}$

$= 6.89 \times 10^{-4}$ mol

c Calculate the amount of $\text{CH}_3\text{CH}_2\text{OH}$ in the 250.0 mL flask, remembering that only 20.00 mL was removed from the 250.0 mL flask for the titration. This is the amount of $\text{CH}_3\text{CH}_2\text{OH}$ in the 10.00 mL beer sample.

$n(\text{CH}_3\text{CH}_2\text{OH})$ in 250.0 mL $= 6.89 \times 10^{-4} \times \frac{250.0}{20.00}$

$= 8.62 \times 10^{-3}$ mol

d Calculate the mass of $\text{CH}_3\text{CH}_2\text{OH}$ in the beer sample.

$m(\text{CH}_3\text{CH}_2\text{OH}) = n \times M = 8.62 \times 10^{-3} \times 46.0$

$= 0.396$ g

Calculate the volume of ethanol using the density:

$V(\text{CH}_3\text{CH}_2\text{OH}) = \frac{m}{d}$

$= \frac{0.3963}{0.785}$

$= 0.505$ mL

Calculate the volume of volume (% v/v) of $\text{CH}_3\text{CH}_2\text{OH}$ in the sample of beer.

% v/v $\text{CH}_3\text{CH}_2\text{OH} = \frac{0.5049}{10.00} \times 100$

$= 5.05\%$

e No, this product would not conform with the regulations for low-alcohol beer.

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21 a $(MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)) \times 4$

$(\text{alcohol}(aq) + H_2O(l) \longrightarrow \text{carboxylic acid}(aq) + 4H^+(aq) + 4e^-) \times 5$

$4MnO_4^-(aq) + 5 \times \text{alcohol}(aq) + 12H^+(aq) \longrightarrow 4Mn^{2+}(aq) + 5 \times \text{carboxylic acid}(aq) + 11H_2O(l)$

$$\text{mole ratio} = \frac{n(\text{alcohol})}{n(MnO_4^-)} = \frac{5}{4}$$

b $n(MnO_4^-) = c \times V$

$= 0.184 \times 0.020\ 00$

$= 3.680 \times 10^{-3}$ mol

$$n(\text{alcohol}) = \frac{5}{4} \times n(MnO_4^-)$$

$$= \frac{5}{4} \times 3.680 \times 10^{-3}$$

$= 4.600 \times 10^{-3}$ mol

$m(\text{alcohol}) = c \times V$

$= 17.00 \times 0.020\ 02$

$= 0.3403$ g

$$M(\text{alcohol}) = \frac{m}{n}$$

$$= \frac{0.3403}{4.600 \times 10^{-3}}$$

$= 74.0$ g mol^{-1}

c butan-1-ol

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Chapter 14 Instrumental analysis of organic compounds

14.1 Mass spectrometry

Worked example: Try yourself 14.1.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkene has a molecular ion peak at $m/z = 56$. Determine the molecular formula of the alkene and give its name.

Thinking	Working
The *m/z* value of the molecular ion is equal to the relative molecular mass of the molecule.	The relative molecular mass of the alkene is 56.
Identify the general formula for the molecule.	The general formula for an alkane is C_nH_{2n}.
Use the general formula to set up an equation linking the relative molecular mass to the relative atomic masses of the constituent atoms.	$M_r(C) = 12$ $M_r(H) = 1$ $(12 \times n) + (1 \times 2n) = 56$
Solve the equation for *n*.	$12n + 2n = 56$ $14n = 56$ $n = 4$
Use the value of *n* to find the molecular formula and the name.	C_4H_8, which is butene.

KEY QUESTIONS

Knowledge and understanding

1. a $12 + (3 \times 1) = 15$
   b $(3 \times 12) + (7 \times 1) = 43$
   c $12 + (3 \times 1) + 81 = 96$
   d $12 + 1 + 16 = 29$
   e $12 + 1 + (2 \times 35) = 83$
2. All fragments must have a positive charge. The correct formula is CHO^+.
3. 186 ($CH_3CH^{79}Br_2^+$), 188 ($CH_3CH^{79}Br^{81}Br^+$), 190 ($CH_3CH^{81}Br_2^+$)
4. CH_2OH^+

Analysis

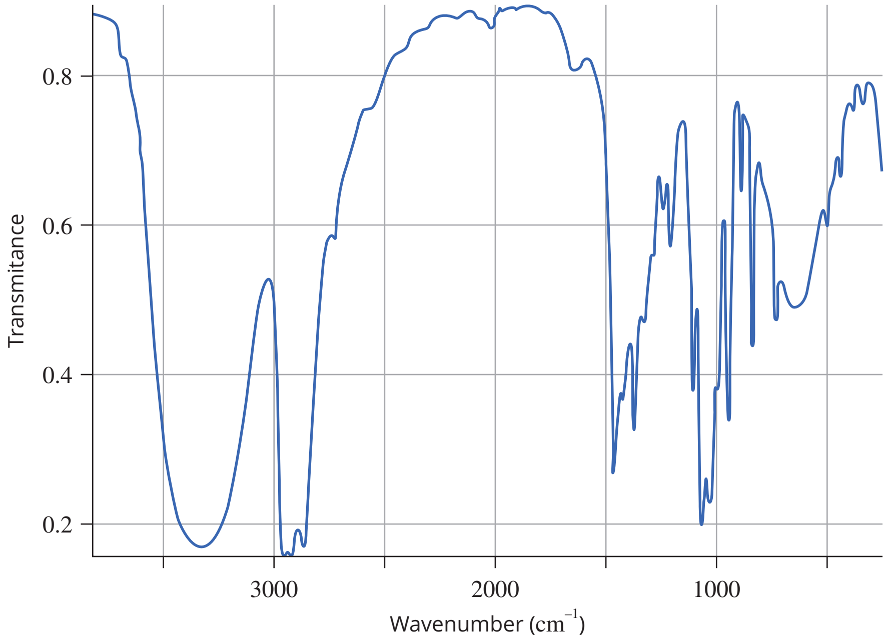
5. a 43
   b $C_6H_{13}^+$
   c Octane, C_8H_{18}
6. a $CH_3CH_2CH_2Br$
   b The peaks at $m/z = 122$ and $m/z = 124$ are due to the molecular ion containing Br, as both the ^{79}Br or ^{81}Br isotopes are present.
   c The two isotopes of bromine, ^{79}Br and ^{81}Br, are found in almost equal abundances, so the peaks are almost equivalent in height.
   d $CH_3CH_2CH_2^+$

14.2 Infrared spectroscopy

Worked example: Try yourself 14.2.1

INTERPRETING THE IR SPECTRUM OF AN UNIDENTIFIED COMPOUND

Use the infrared spectrum of the unidentified compound to identify the functional groups present. The molecular formula of the compound is $C_4H_{10}O$. You will need to refer to the IR absorption data in Table 14.2.4 (page 512).



Thinking	Working
Identify the absorption bands that correspond to the absorption bands of bonds in the IR absorption data table.	There is a strong, wide band at approximately 3300 cm^{-1}, indicating an O–H group. There is a strong, narrow band at approximately 2900 cm^{-1}, which corresponds to the absorption by a C–H group. There are no strong bands between 1670–1750 cm^{-1}, which signifies absence of a carbonyl, C=O, group. No strong bands between 1610–1680 cm^{-1}, which signifies the absence of a C=C group.
Identify the functional group or groups that are present.	The spectrum shows absorption bands corresponding to the presence of O–H alcohol group and C–H groups. This suggests the molecule is an isomer of butanol.

KEY QUESTIONS

Knowledge and understanding

1 B. Frequency is inversely proportional to wavelength. Referring to Figure 14.2.1, frequency decreases as wavelength increases from gamma rays to radio waves. Option A is incorrect because wavelength does not decrease as frequency decreases. Option C is incorrect because frequency is not a logarithmic scale of wavelength. For example, a wavelength of 10^{-9} metres is approximately 3×10^{17} Hz. Option D is incorrect because frequency is related to wavelength.

2 vibrational energy

3 **a** C–C, C=C, C≡C (see Table 14.2.2)

As bond strength increases, infrared absorption frequency increases.

b S–H, O–H, N–H, C–H, H–H (see Table 14.2.3)

As atomic mass (of the atom bonded to hydrogen) increases, the infrared absorption frequency decreases.

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4 **a** O–H at 3200–3550 cm^{-1} and C–O at 1000–1300 cm^{-1}
- **b** C=O at 1660–1745 cm^{-1}
- **c** N–H at 3350–3500 cm^{-1}
- **d** O–H at 2500–3300 cm^{-1}, C=O at 1670–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
- **e** C=O at 1670–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
- **f** C=C at 1610–1680 cm^{-1}

Analysis

5 The absorption bands from C–O and C–C bonds are located in the fingerprint region below 1400 cm^{-1}. Many molecules contain these bonds in various functional groups, so they give few clues to the structure of a compound. The exact wavenumber of C–O and C–C absorption bands are highly specific to an individual molecule, and can be used to compare the molecule to a reference standard for positive identification.

6 **a** O–H acids at approximately 3000 cm^{-1} and C=O at approximately 1700 cm^{-1}
- **b** O–H alcohols at approximately 3300 cm^{-1} and C–H at approximately 2800 cm^{-1}
- **c** N–H at approximately 3400 cm^{-1} and C–H at approximately 2900 cm^{-1}

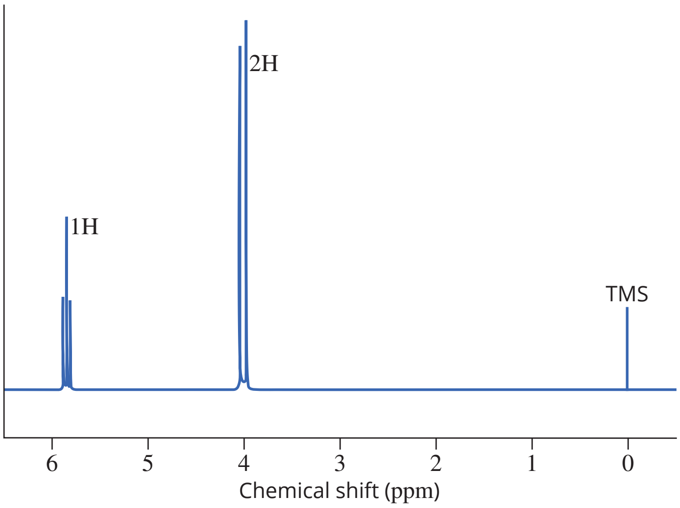
7 **a** B. The correct answer is propan-2-ol because of the very strong absorbance at 3200–3600 cm^{-1} (O–H alcohols), absence of absorbance around 1700 cm^{-1} (carboxyl group) and absence of absorbance around 1620–1680 cm^{-1} (alkene). Note that the strong absorbance just below 3000 cm^{-1} is due to C–H.
- **b** D. The correct answer is butanoic acid because of the very strong broad absorbance around 2600–3300 cm^{-1} (a combination of O–H acids and C–H) and the presence of absorbance around 1680–1740 cm^{-1} (C=O acids).
- **c** B. The correct answer is hexane because of the very strong absorbance at 3000 cm^{-1} (C–H) and absence of absorbance around 1700 cm^{-1} (carboxyl group), absence of absorbance around 1620–1680 cm^{-1} (alkene) and absence of absorbance around 3200–3600 cm^{-1} (alcohols).

14.3 Nuclear magnetic resonance spectroscopy

Worked example: Try yourself 14.3.1

INTERPRETATION OF A PROTON NMR SPECTRUM

The proton NMR spectrum of a compound with a molecular formula of $C_2H_3Cl_3$ is shown below. Relative peak areas are shown on the spectrum.



Identify this compound using the information provided in the NMR spectrum.

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Thinking	**Working**
What information does the molecular formula provide about the compound?	Two molecules are possible from the formula: either 1,1,1-trichloroethane or 1,1,2-trichloroethane.
Summarise the information provided in the NMR spectrum in a table.	**Chemical shift** | **Peak splitting** | **Relative peak area** 4.0 | doublet (2-line pattern) | 2 5.8 | triplet (3-line pattern) | 1
Identify the number of different hydrogen environments.	There are two signals, so there must be two different hydrogen environments.
Use the relative peak area to deduce the number of hydrogen atoms in each environment.	The relative area peak areas of the signals at 5.8 and 4.0 ppm are 1 : 2, so the relative number of hydrogen atoms must be 1 : 2. The sum of hydrogen atoms in the formula is 3, which means that the peak areas are directly equal to the number of hydrogen atoms in each environment. This also supports the splitting information, confirming that the molecule contains one –CH– group and one –CH_2– group.
Use the peak splitting of the signals to identify the types of hydrogen environments.	The signal at 4.0 ppm is a doublet (2-peak pattern). The number of peaks in the pattern given by $n + 1$, so this signal must be generated by an environment that has one neighbouring hydrogen atom, i.e. a –CH group. The signal at 5.8 ppm is a triplet (3-peak pattern). The number of peaks in the pattern is given by $n + 1$, so this signal must be generated by an environment that has two neighbouring hydrogen atoms, i.e. a –CH_2– group.
If possible, use the chemical shifts in Table 14.3.1 (page 523) to identify the types of protons. Remember the ranges are broad.	The table does not give information about compounds containing two chloro groups, so continue on to the next step.
Use the information you gathered to identify the compound.	The molecular formula of the compound is $C_2H_3Cl_3$. On the basis of the formula, the compound is either 1,1,1-trichloroethane or 1,1,2-trichloroethane. The splitting patterns and peak area indicate that the molecule contains a –CH_2– group adjacent to a –CH– group. The molecule must be 1,1,2-trichloroethane because the structure fits the evidence from the spectrum.

KEY QUESTIONS

Knowledge and understanding

1 **a** 1 hydrogen environment. Each hydrogen is bonded directly to the only carbon present.

b 2 hydrogen environments. One chemical environment represents the three hydrogens bonded to the carbon and the other chemical environment represents the two hydrogens bonded to the nitrogen.

c 3 hydrogen environments. One chemical environment represents the –CH_3 group, another chemical environment represents the –CH_2– group, and the third chemical environment represents the –OH group.

d 3 hydrogen environments. One chemical environment represents the two equivalent –CH_3 groups, another chemical environment represents the –CH– group and the third chemical environment represents the –OH group.

2 **a** The number of signals indicates the number of non-equivalent hydrogen environments.

b The relative peak areas indicate the relative number of hydrogen atoms in each proton environment.

c The splitting pattern of a signal indicates the number of hydrogen atoms adjacent to a specific proton environment.

d The chemical shift of a signal indicates the type of hydrogen environment.

3 **a** There will be four proton NMR peaks.

b 6H (–CH_3), 4H (–CH_2), 1H (proton attached to the carbon on the –CHOH– group), 1H (–OH)

c The –CH_3 peak will be split into three.
The –CH_2– peak will be split into five.
The proton attached to the carbon on the –CHOH– group's peak will be split into five.
The –OH peak will not be split as the hydroxyl group does not count as a neighbour for the neighbouring carbon atoms.

d There will be three ^{13}C NMR peaks.

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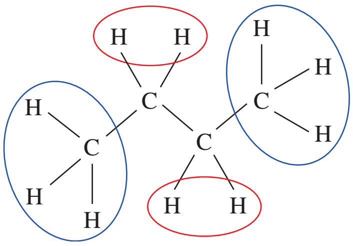
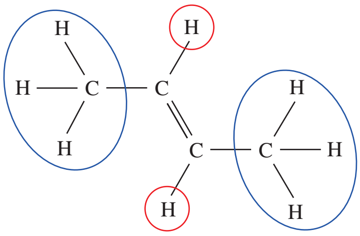
Analysis

4 **a** **i** There are two hydrogen environments.

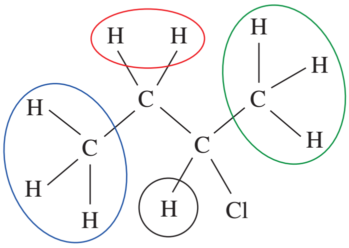


ii There are two hydrogen environments.

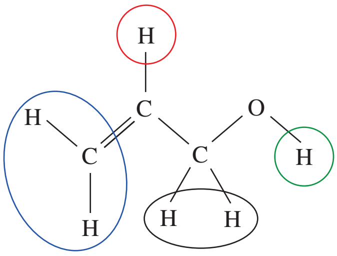


but–2–ene

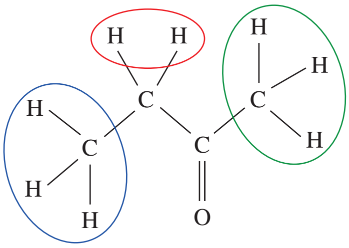
iii There are four hydrogen environments.



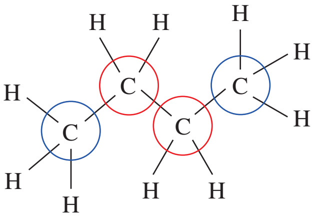
iv There are four hydrogen environments.



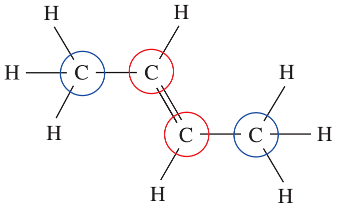
v There are three hydrogen environments.



b **i** There are two carbon environments.

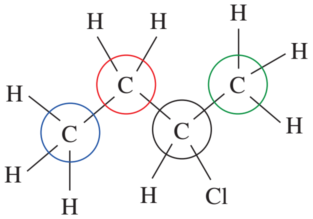


ii There are two carbon environments.

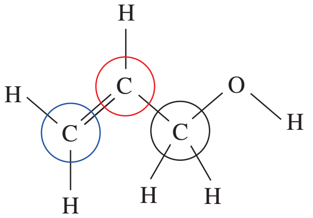


but–2–ene

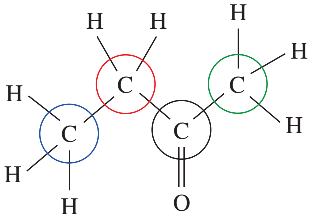
iii There are four carbon environments.



iv There are three carbon environments.



v There are four carbon environments.



c a doublet (two-peak pattern) and a quartet (four-peak pattern)

d 3 : 2

5 **a** There are three peak sets, each representing a different hydrogen environment.

b From Table 14.3.1, the expected chemical shifts are:

–$COCH_3$	2.1–2.7 ppm
RCH_3	0.8–1.0 ppm
–OCH_2R	3.3 ppm

c The relative number of protons for the peak sets is:

A : B : C = 2 : 3 : 3

d Proton NMR peaks are split because of interaction of the magnetic fields on adjacent atom. The number of peaks associated with each proton environment is shown in the proton NMR spectrum. Using the *n* + 1 rule:

i The quartet peaks at A indicate that there are three hydrogen atoms attached to an adjacent atom.

ii The single peak at B indicates that there are no hydrogen atoms attached to the adjacent atom.

iii The triplet at B indicates that there are two hydrogen atoms attached to the adjacent atom.

e A is the CH_2 group.

B is the methyl group of ester.

C is the methyl group of CH_3CH_2.

f You would expect to see four peaks in the carbon-13 NMR spectrum because there are four different carbon environments in the ethyl ethanoate molecule.

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6 **a** proton NMR:

Peak number	Chemical shift	Relative peak area	Splitting pattern	Possible hydrogen environment	Position on structure
1	1.2 ppm	3	triplet (3)	R–CH_3	next to –CH_2–
2	2.2 ppm	2	quartet (4)	R–CH_2– where R is a carbonyl group	next to –CH_3
3	7.0 ppm	2	singlet (1)	no neighbouring H to cause splitting –NH_2	amide

b carbon-13 NMR:

Peak number	Chemical shift	Possible carbon environment	Position on structure
1	10 ppm	R–CH_3	next to –CH_2–
2	30 ppm	R–CH_2	next to –CH_3
3	175 ppm	C=O	

c propanamide

14.4 High-performance liquid chromatography

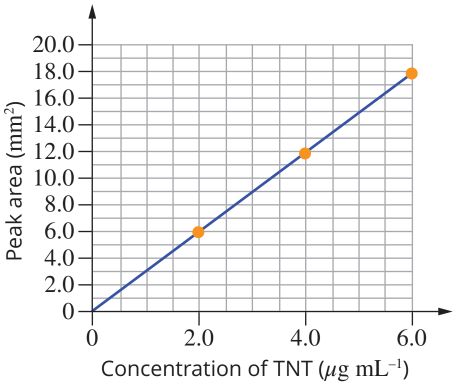
Worked example: Try yourself 14.4.1

CONCENTRATION OF A COMPONENT IN A MIXTURE

Trinitrotoluene (TNT) is often blended with other explosives to suit particular applications. A sample from a solution of an explosive mixture was injected onto an HPLC column using a water/methanol mobile phase. The peak corresponding to TNT had an area of 14.5 mm^2. The peak areas for three standard solutions were also measured, as shown in the table below.

Determine the concentration of TNT in the sample solution in μg mL^{-1}.

TNT standards (μg mL^{-1})	Peak area (mm^2)
0.0	0.0
2.0	6.0
4.0	11.5
6.0	17.5

Thinking	Working
Construct a calibration curve by plotting peak area versus concentration.	 Calibration curve for TNT sample.

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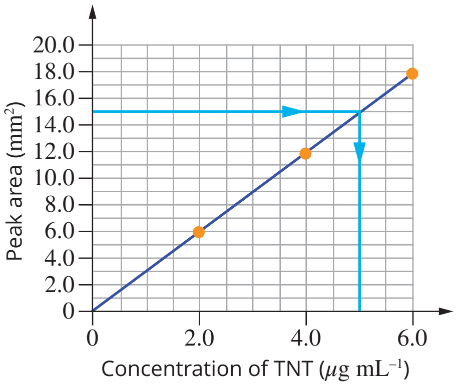
<table>
<tr>
<td>Use the calibration curve to find the concentration corresponding to the peak area of the sample.</td>
<td>
A line can be drawn on the calibration curve from the peak area of the sample to find the corresponding concentration on the graph.



The concentration of TNT in the sample solution is 5.0 μg mL^{-1}.
</td>
</tr>
</table>

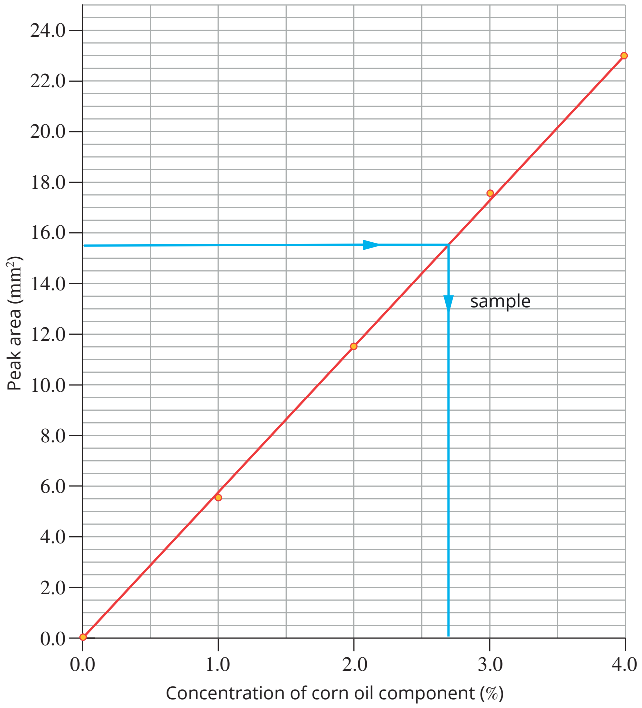
CASE STUDY: ANALYSIS

Making the grade

1 Since the large peaks at about 15 and 18 minutes in the pure olive oil can are also present in the suspect shipment, it is likely there is some olive oil, as well as other substances, present in the shipment.

2 Oil is insoluble in water. An eluent which is non-polar, such as hexane, or partially polar is required.

3



A line can be drawn on the calibration curve from the peak area of the sample (15.5 mm^2) to find the corresponding concentration on the graph: 2.7%.

KEY QUESTIONS

Knowledge and understanding

1 The mobile phase and the stationary phase. Temperature, flow rate and pressure will also affect R_t.

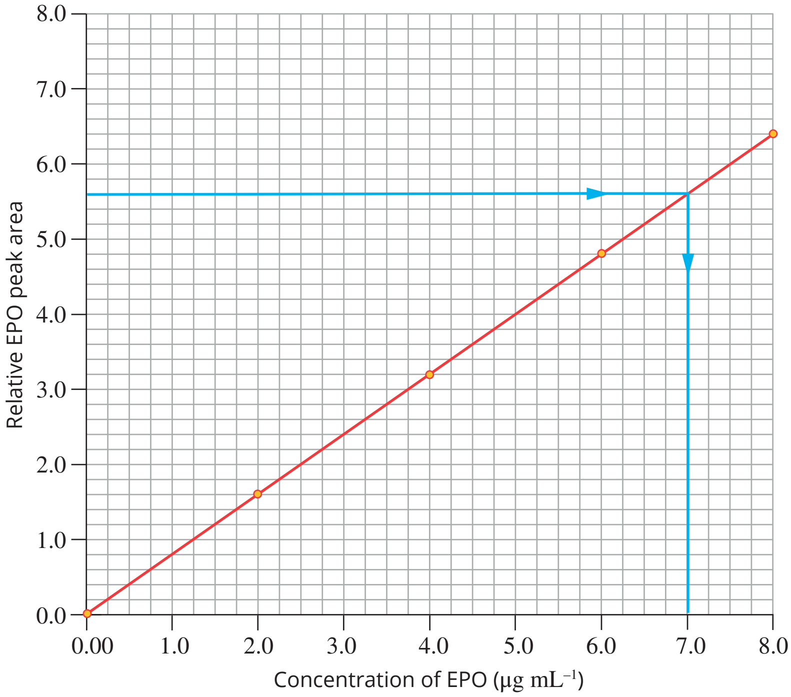
2 **a** retention time
  b retention time
  c peak area

3 An HPLC instrument does not directly produce measurements of concentration. R_t indicates the identity of components in a mixture. A calibration curve can then be used to determine the concentration of the component.

Analysis

4 C, A, B. Compound B is likely to move more slowly through the column than compound A, because it is more strongly absorbed. Since compound C is least strongly adsorbed on the stationary phase and most soluble in the mobile phase, it should pass through the column most rapidly.

5 **a**



b 7.0 μg mL^{-1}

6 A, B, C, D. The water/methanol solvent used as the mobile phase in this analysis is polar. The more polar an alcohol, the more soluble it will be in this solvent, and the more rapidly it will move through the column. In this case, A has the smallest retention time and will be the most polar.

As the length of the non-polar hydrocarbon group in an alcohol increases, the molecule becomes less polar overall. A must therefore be the smallest molecule, with the lowest molar mass, followed by B, and so on.

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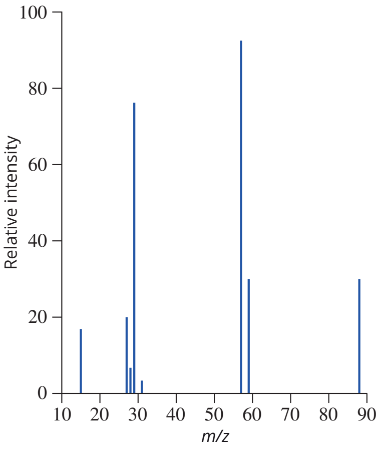
14.5 Determination of molecular structure by spectroscopy

Worked example: Try yourself 14.5.1

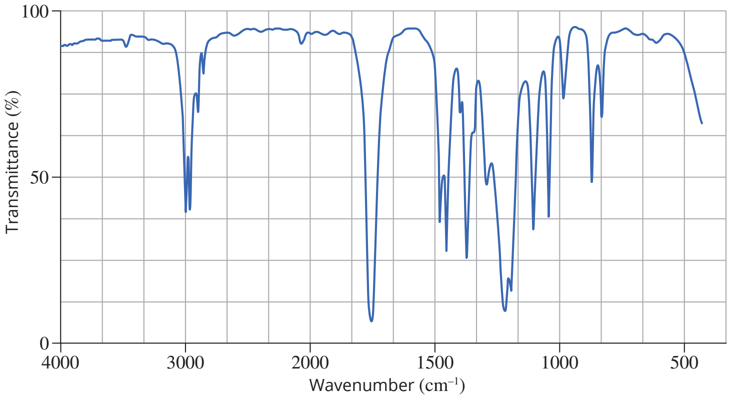
DEDUCING MOLECULAR STRUCTURE FROM SPECTROSCOPIC DATA

A sweet-smelling liquid has an empirical formula of C_2H_4O. Chemical tests show that the compound is not an aldehyde or ketone. Use this information and the mass, IR and NMR spectra provided to deduce the structure and name of the compound.

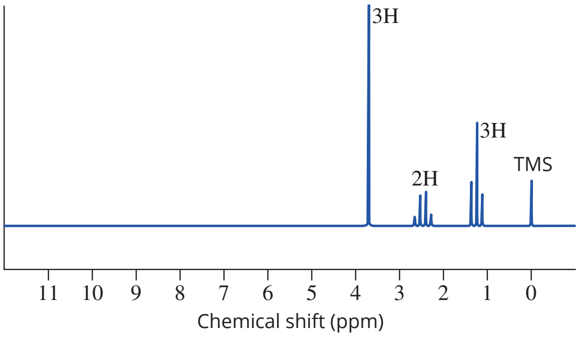
Mass spectrum



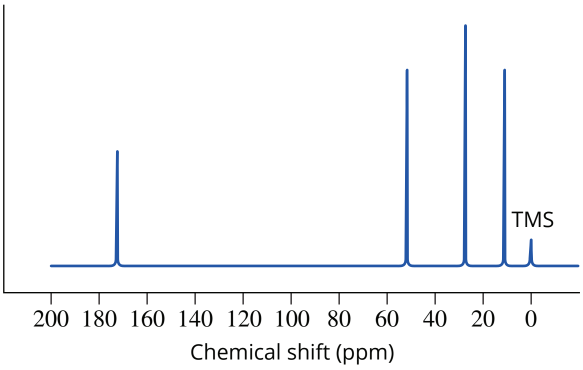
Infrared spectrum



Proton NMR spectrum



Carbon-13 NMR spectrum



Thinking	**Working**
Use the mass spectrum to identify the molecular ion and relative molecular mass.	The mass of the empirical formula C_2H_4O is $(2 \times 12.0) + (4 \times 1.0) + (1 \times 16.0) = 44.0$. The molecular ion *m/z* is 88. Therefore, the molecular formula is twice the empirical formula: $C_4H_8O_2$.
Use the IR spectrum to identify functional groups present in the compound. (Refer to Table 14.2.4 on page 512.)	The IR spectrum shows a strong absorption band at 1700 cm^{-1}, suggesting the presence of a C=O bond and hence a carbonyl group. The IR spectrum does not contain a strong, broad absorption in the range of 2500–3300 cm^{-1}, which shows there is no O–H bond in the molecule.

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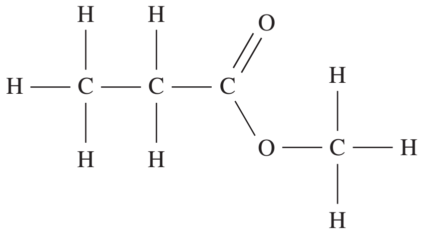
<table>
<tr>
<td>Use the proton NMR spectrum to identify the different hydrogen environments (refer to Table 14.3.1 on page 523).
Note that chemical shifts can be outside the ranges quoted in Table 14.3.1, and so can be slightly higher or lower than the values provided. Use the relative peak area and splitting pattern first to identify hydrogen environments.</td>
<td>The proton NMR data is summarised in the following table.
<table>
<tr><th>Chemical shift (ppm)</th><th>Splitting pattern</th><th>Relative peak area</th></tr>
<tr><td>1.1</td><td>triplet (3-line pattern)</td><td>3</td></tr>
<tr><td>2.3</td><td>quartet (4-line pattern)</td><td>2</td></tr>
<tr><td>3.7</td><td>singlet (1-line pattern)</td><td>3</td></tr>
</table>
The spectrum contains three signals, so there are three different hydrogen environments.
The sum of the relative peak areas is 8, which is consistent with the molecular formula, as each unit of peak area corresponds to one hydrogen atom.
The signal at 1.1 ppm is consistent with the signal produced by a $–CH_3$ group with two hydrogens in a neighbouring environment.
The signal at 2.3 is consistent with the signal produced by a $–CH_2–$ group bonded to the carbon of an ester group, with three hydrogens in a neighbouring environment.
The signal at 3.7 ppm is a singlet, indicating that there are no hydrogen atoms attached to adjacent atoms. The chemical shift is consistent with a methyl group singly bonded to an oxygen atom.</td>
</tr>
<tr>
<td>Use the carbon-13 NMR spectrum to identify the different carbon environments (refer to Table 14.3.2 on page 526).</td>
<td>There are four signals in the carbon-13 NMR spectrum and so the molecule contains four different carbon environments.
The number of carbon environments corresponds to the number of carbons in the molecular formula, so each environment represents one carbon atom.
The signal at 175 ppm is consistent with a carbon atom in a carbonyl group.
The signal at 51 ppm is consistent with a carbon atom attached to an oxygen atom by a single bond to an oxygen atom.
The signal at 27 ppm is consistent with a $R–CH_2–R$ group.
The signal at 9 ppm is consistent with a methyl group, $R–CH_3$.</td>
</tr>
<tr>
<td>Use the data from the spectra to deduce the structure of the compound.</td>
<td>The data provided by the spectra shows that:

the molecular formula of the compound is $C_4H_8O_2$
the compound has a carbonyl group, but no hydroxyl group
it is an ester
the compound has a $CH_3CH_2^-$ group attached to the carbon of a carbonyl group
the compound has a methyl group attached by a single bond to an oxygen atom.

A structure consistent with this data is:
</td>
</tr>
<tr>
<td>Name the compound.</td>
<td>methyl propanoate</td>
</tr>
</table>

KEY QUESTIONS

Knowledge and understanding

1 The spectrum of a reference sample is compared to the spectrum of the unknown organic compound. If the spectra match, the unknown organic compound is pure. If there are any additional or missing peaks, the unknown organic compound is not pure.

2 **a** IR spectroscopy would not provide sufficient information, as both gases have the same functional groups.

b Proton NMR spectra would identify the gas, as there is one hydrogen environment for ethane and two hydrogen environments for propane.

c Carbon NMR spectra would identify the gas, as ethane has one carbon environment and propane has two carbon environments.

3 Petrol is a mix of many different organic compounds, so the proton NMR spectrum will be very complex to analyse. A proton NMR database will compare and match the petrol spectrum with individual organic compounds using chemical shift, splitting and integration values.

Analysis

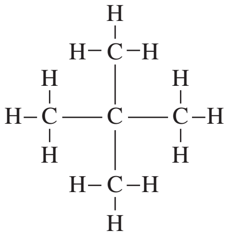
4 Step 1: Determine the molecular formula: Molecular ion peak on mass spectrum was at $m/z = 72$. The mass of the empirical formula is $(12.0 \times 5) + (1.0 \times 12) = 72$ g mol^{-1}. Therefore, the molecular formula is C_5H_{12}.

Step 2: No IR spectrum is provided.

Step 3: There is only one singlet peak at 0.9 ppm. Therefore, all the hydrogens are in the same environment as 4 equivalent R–CH_3.

Step 4: There are two carbon environments. As all the hydrogens are in the same environment, the carbon-13 peak at 28 ppm will be 4 equivalent R–CH_3. The peak at 36 ppm would be R_4C.

Step 5: Combining all the above information, the name of this compound is 2,2-dimethylpropane.



5 Strong absorption around 1750 cm^{-1} is consistent with the presence of C=O. A strong peak at 3000 cm^{-1} corresponds to the absorption of a –CH bond (it cannot be due to the OH of a carboxylic acid because the formula only contains one oxygen).

The proton NMR spectrum indicates:

Chemical shift	Peak splitting	Relative peak area
1.0	triplet	3
2.1	singlet	3
2.4	quartet	2

There are three signals so there must be three hydrogen environments.

The chemical shift of 1.0 indicates R–CH_3.

The chemical shift of 2.1 indicates a C=O environment.

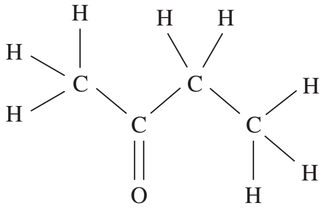
The chemical shift of 2.4 indicates $RCOCH_3$.

The signal at 1.0 is a triplet, so the neighbouring environment must be CH_2.

The signal at 2.1 is a singlet, so there are no neighbouring protons.

The signal at 2.4 is a quartet, so it has a CH_3 neighbour.

The carbon NMR spectrum indicates four peaks and therefore four different carbon environments, so the formula is C_4H_8O. The structural formula is for butan-2-one.



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6 **a** The peak at 910 cm^{-1} is present in sunflower oil, but not in olive oil.

b If the olive oil was adulterated with sunflower oil, there would be a 910 cm^{-1} peak on the IR spectrum. If it is pure olive oil, there would be no peak at 910 cm^{-1}.

Chapter 14 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 B. Infrared radiation is absorbed by the molecule, causing the molecule to bend and stretch. The energy required for the molecule to bend and stretch is known as vibrational energy. Option A is incorrect because IR spectroscopy does not directly determine molecular mass. Option C is incorrect because electronic energy is measured in the UV–visible region of the electromagnetic spectrum. Option D is incorrect because nuclear spin is measured in the radio wave region of the electromagnetic spectrum.

2 B. Refer to Table 14.2.4 for the list of functional groups and their infrared absorption bands. The C=O bond absorbs between 1630–1840 cm^{-1}. Option A is incorrect because the C–O bond absorbs between 1050–1410 cm^{-1}. Option C is incorrect because the O–H bond absorbs between 2500–3300 cm^{-1}. Option D is incorrect because the N–H bond absorbs between 3300–3500 cm^{-1}.

3 A. The ‘$n + 1$ rule’ applies to proton (^1H) NMR. Option B is incorrect because the ‘$n + 1$ rule’ does not apply to carbon NMR. Option C and D are incorrect because oxygen and cations are not measured using proton NMR.

4 D. Hydrogen environments is the incorrect answer. Molecular mass is the molecular ion *m/z* value. Isotopic ratios are determined on a mass spectrum by the relative intensities of each isotope. Mass-to-charge ratios (*m/z*) is what mass spectrometers measure.

5 C. There are three peaks in the carbon-13 NMR spectrum, which means there are three carbon environments. The TMS peak is not counted in the total of peaks. The other options are incorrect.

6 D. $R_2C{=}CR_2$. Referring to Table 14.2.2, option A is incorrect because the chemical shift of R–CH is 8–25 ppm; option B is incorrect because the chemical shift of $R{-}CH_2{-}X$ (X = F, Cl, Br or I) is 15–80 ppm; and option C is incorrect because the chemical shift of $RC{\equiv}CR$ is 75–95 ppm. Option D is correct because the chemical shift of $R_2C{=}CR_2$ is 110–150 ppm, which is in the range of 115 ppm.

7 **a** alkane C_nH_{2n+2}

The molecular mass of carbon is 12 and hydrogen is 1, then:

$12n + 1\,(2n + 2) = 58$

$14n = 56,\ n = 4$

alkane = C_4H_{10}

b alkane + one oxygen = $C_nH_{2n}O$

$12n + 1\,(2n) + 16 = 58$

$14n = 42,\ n = 3$

alkane + one oxygen = C_3H_6O

c alkane + two nitrogen = $C_nH_{2n+2}N_2$

$12n + 1\,(2n + 2) + 2 \times 14 = 58$

$14n = 28,\ n = 2$

alkane + two nitrogen = $C_2H_6N_2$

8 **a** Base ion has *m/z* of 29

b Molecular ion has *m/z* of 44

c alkane C_nH_{2n+2}

$12n + 1\,(2n + 2) = 44$

$14n = 42,\ n = 3$

alkane = C_3H_8 = propane

9 *m/z* $COH^+ = 29$

10 **a** **i** 98 corresponds to the molecular ion, which includes two ^{35}Cl isotopes. It has the formula $C_2H_4{}^{35}Cl_2$.

ii 100 corresponds to the molecular ion with one ^{35}Cl and one ^{37}Cl isotope. It has the formula $C_2H_4{}^{35}Cl^{37}Cl$.

iii 102 corresponds to the molecular ion with two ^{37}Cl isotopes with the formula $C_2H_4{}^{37}Cl_2$.

b The most abundant Cl isotope is ^{35}Cl, therefore the molecule with two ^{35}Cl isotopes has a higher peak.

c *M*(base peak) = 62 $^{35}ClCCH_3$

11 **a** C–H

b O–H

12 from lowest to highest: C–Br, C–O, C–H, O–H

13 **a** C=O has a sharp absorption band between 1680–1740 cm^{-1}; O–H has a broad absorption at 2500–3300 cm^{-1}.

b N–H has an absorption band at 3300–3500 cm^{-1}.

c C–O has an absorption band at 1050–1410 cm^{-1} and C=O has an absorption band at 1720–1840 cm^{-1}.

d C=O has an absorption band at 1680–1850 cm^{-1}.

14 TMS, tetramethyl silane ($Si(CH_3)_4$), is used as a reference in NMR spectroscopy. The location of a signal in the spectrum of a sample is compared to the TMS signal and is called the chemical shift. The chemical shift is measured in units of ppm.

15 **a** 4
b 1
c 4
d 5

16 Compared with conventional column chromatography, HPLC is more sensitive, faster, resolves components better and it is able to detect colourless components readily.

Application and analysis

17 **a** Four components. There are two distinct peaks and one peak which is made up of two peaks that are very close to one another, and have slightly merged.

b Solid samples are dissolved in a suitable solvent. The liquid sample is injected into the top of an HPLC column. The stationary and mobile phases are chosen to achieve a good separation of the components in the sample. The sample components alternately adsorb onto the stationary phase and then desorb into the solvent as they are swept forward. The time taken to exit the column increases if the component strongly absorbs onto the stationary phase and has a low solubility in the mobile phase.

18 **a** Retention time for peak 1 = 3.5 min
Retention time for peak 2 = 4.8 min
Retention time for peak 3 = 8.0 min
Retention time for peak 4 = 10.5 min

b Caffeine molecular ion peak will be $m/z = 194$.
Mass spectrum for peak 1 is caffeine as it has a molecular ion peak at $m/z = 194$.
The mass spectrum for peak 2 has a molecular ion peak at $m/z = 295$, so it cannot be caffeine.
The mass spectrum for peak 3 has a molecular ion peak at $m/z = 121$, so it cannot be caffeine.
The mass spectrum for peak 4 has a molecular ion peak at $m/z = 113$, so it cannot be caffeine.

c Soft drinks are a complex mixture, therefore, it is possible another molecule with similar polarity as caffeine has the same retention time of 3.5 min. There are two common methods to determine whether the component in the eluent is pure caffeine or not:
Method 1: The scientist can analyse the eluent on an IR, mass or NMR spectrometer and compare the spectra with a pure caffeine standard. Any additional or missing peaks on the IR, mass or NMR spectra will confirm the eluent is not 100% caffeine.
Method 2: The scientist can change the mobile phase of the HPLC to alter the polarity sufficiently to separate the components at 3.5 min and compare their spectra with the spectra of pure caffeine standard.

19 **a**

Group	Shift (ppm)	Splitting	Peak area
$-CH_3$	0.9	triplet	3
$-CH_2-$	1.3	septet	1

b

Group	Shift (ppm)	Splitting	Peak area
$-CH_3$	0.9	triplet	3
$-CH_2-$	1.5	quartet	2

c

Group	Shift (ppm)	Splitting	Peak area
$-CH_3COO$	2.0	singlet	3
$-\mathbf{CH}_2\text{OH}$	3.3	quartet	2
$-CH_2O\mathbf{H}$	9	singlet	1

20 **a** Both spectra contain broad absorption bands at 3200–3600 cm^{-1}, which correspond to the expected absorbance by O–H bonds, together with the C–H absorbance around 2850–3090 cm^{-1}. The spectra also contain peaks at 1700–1750 cm^{-1}, which correspond to the absorbance by C=O bonds.

b The two spectra have different peaks in the fingerprint region, so cannot be of the same molecule.

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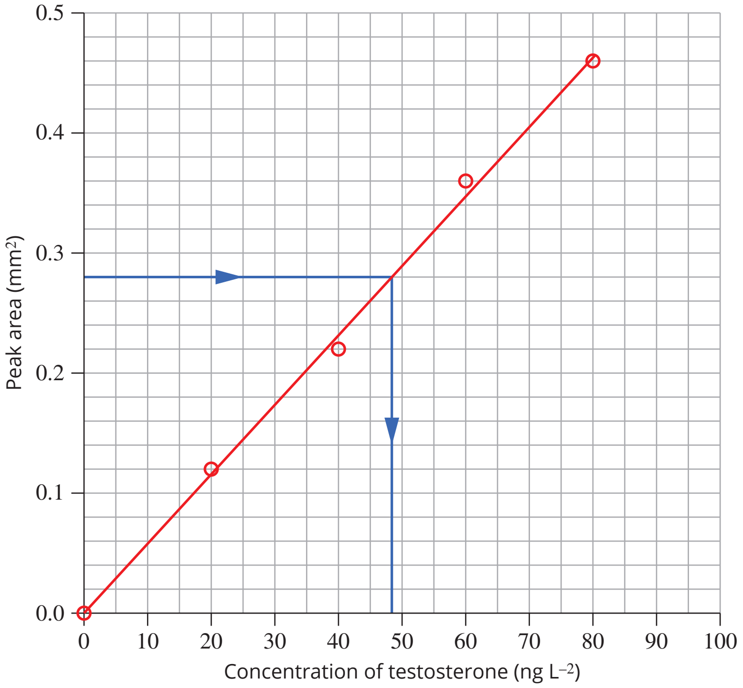
21 Serine, threonine, valine. Molecules of serine and threonine are more polar than valine. They will therefore dissolve more readily in the polar liquid used in this technique. Valine will move most slowly through the column. Because threonine has an extra methyl group in its side group, it will be less polar and move more slowly than serine.

22 **a** Obtain chromatograms of the blood sample and of standard solutions of testosterone. Use R_t values to identify the testosterone peak on the chromatogram of blood. Measure the testosterone peak areas. Construct a calibration curve and mark the blood testosterone peak area on it. Determine the testosterone concentration in the blood sample.

b 48.0 ng L^{-1}



23 The computer would look for specific functional group and fingerprint region peaks that would match reference samples stored in a database. The reference samples must include explosives and illegal drugs, so that the computer can check for the presence of these compounds.

24 **a** methyl ethanoate

b ethyl methanoate

c propanoic acid

25 $n(\text{C}) = \dfrac{48.6}{12} = 4.05$

$n(\text{H}) = \dfrac{8.2}{1.0} = 8.2$

$n(\text{O}) = \dfrac{43.2}{16} = 2.7$

Ratio of C : H : O = 1.5 : 3 : 1 = 3 : 6 : 2

The empirical formula is $C_3H_6O_2$.

In the mass spectrum, the largest molecular ion has a m/z value of 74. This is equal to the molecular mass of an element with the empirical formula of $C_3H_6O_2$.

In the IR spectrum, there is a narrow band at 1700 cm^{-1}, which indicates a C=O bond. There is a broad band at 3000 cm^{-1}, which indicates an –OH group of a carboxylic acid. This slightly masks the peak at 3000 cm^{-1} due to C–H bonds.

The proton NMR spectrum indicates three different hydrogen environments.

A chemical shift of 1.0 ppm is a triplet. A chemical shift of 2.0 ppm is quartet.

A chemical shift of 9 ppm is a singlet, indicating no neighbours and therefore a hydrogen of a carboxylic acid.

The carbon NMR spectrum shows that there are three different carbon environments.

The compound is a carboxylic acid with three carbons. Therefore, this is propanoic acid.

26 The molecular formula is $C_5H_{11}Cl$.

In the IR spectrum, there are only C–H bands observed above the fingerprint region.

The proton NMR spectrum indicates two different hydrogen environments. The total number of hydrogen atoms from the relative peak areas is equal to the molecular formula.

- 0.9 ppm: a singlet, hence it has no neighbouring hydrogen atoms. It has a relative peak area of 9, so the peak represents nine hydrogen atoms ($R–(CH_3)_3$).
- 3.2 ppm: a singlet, hence it has no neighbouring hydrogen atoms. It has relative peak area of 2, so the peak represents two hydrogen atoms ($Cl–CH_2^–$).

There are three carbon environments:

- 27 ppm = $R–CH_3$
- 33 ppm = $C–R_4$
- 58 ppm = C–Cl

The hydrogen and carbon environments show three methyl groups bonded to a central carbon. The central carbon is bonded to $–CH_2Cl$.

The molecule is 1-chloro, 2,2-dimethylpropane, $CH_2ClC(CH_3)_2CH_3$.

27 **a** The scientists must analyse a reference sample of the organic compound on the HPLC-MS to determine the retention time and obtain a mass spectrum.

b The food sample contains hundreds of different compounds in a complex mixture. Each of these different compounds will form fragment ions. It will be difficult for the scientist to determine whether compound X is present in the mass spectrum due to hundreds of fragment ion peaks.

28 The unknown substance has the molecular formula $C_4H_7NO_4$.

In the IR spectrum, there is a peak around 1690 cm^{-1}, indicating at least one oxygen is a carbonyl group. It can be a carboxylic acid or amide. The broad band around 3000 cm^{-1} could be –OH or –NH functional groups. Typically, –OH bands from carboxylic acid do not absorb in the IR region due to loss of hydrogen.

The proton NMR spectrum indicates five different hydrogen environments. The total number of hydrogens from the relative peak areas is equal to the molecular formula. Each peak area represents the number of hydrogens.

- 2.7 ppm: a doublet, hence it has one neighbouring hydrogen. It has a relative peak area of 2, so the peak area represents two hydrogen atoms ($–\underline{CH_2}–CH–$).
- 3.8 ppm: a triplet, hence it has two neighbouring hydrogens. It has a relative peak area of 1, so peak represents one hydrogen atom ($–CH_2\underline{–CH–}$).
- 8.8 ppm: a singlet, hence it has no neighbouring hydrogens. It has a relative peak area of 2, so peak area represents two hydrogen atoms ($–RH_2$).
- 12.6 ppm: a singlet, hence it has no neighbouring hydrogens. It has a relative peak area of 2, so the peak area represents one hydrogen atom (–OH on carboxylic acid).
- 13.9 ppm: a singlet, hence it has no neighbouring hydrogens. It has relative peak area of 1, so the peak area represents one hydrogen atom (–OH on carboxylic acid).

There are four carbon environments.

- 38 ppm = $–CH_2–$
- 51 ppm = $R_3–CH–$
- 178 ppm: C=O (carboxylic acid)
- 179 ppm: C=O (carboxylic acid)

The hydrogen and carbon environments show that there are no methyl groups. The two carbonyl groups are carboxylic acids, based on the proton NMR singlets at 12.6 and 13.9 ppm. Thus, all four oxygen atoms are accounted for.

One carbon atom is $–CH_2–$ and the other carbon atom is –CH–. The two hydrogen atoms at 8.8 ppm must be bonded to the nitrogen.

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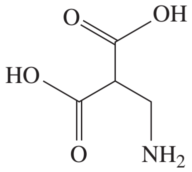
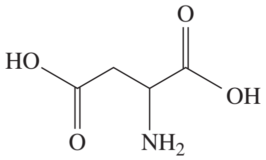
Using all this information, two possible structures can exist.

Option 1:



Option 2:



To decide which structure is the correct one, consider the carbon atom bonded to the $-NH_2$ group. In structure 1, it is $-CH_2-$. In structure 2, it is $-CH-$. For both the proton and carbon NMR spectra, the chemical shifts of the hydrogen and carbon in $-CH_2-$ are lower than $-CH-$. The $-NH_2$ would pull electrons away from the carbon and hydrogen more than the carboxylic acid group because of the stronger electronegativity of nitrogen.

The unknown compound is structure 2, aspartic acid.

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Chapter 15 Medicinal chemistry

15.1 Medicinal ingredients from plants

CASE STUDY: ANALYSIS

INVESTIGATING THE UNCHA PLANT

1. Any three of: hydroxyl, OH; carboxyl, COOH; ester, R-COO-R'; carbon–carbon double bond, C=C; phenyl ring, C_6H_5 or ether, –O–.
2. The structure is very complex. It is easier to continue extracting it from plants than to try and find a pathway to build the molecule.
3. The ingredients need to be extracted, then separated, then identified and then tested.
4. The climate and vegetation in different parts of Australia varies. Different plants are available to different peoples.

KEY QUESTIONS

Knowledge and understanding

1. Methods such as: blending, which breaks down the cell structure of the plants, and heat, which also helps break down plant structures.
2. Plant extracts are never pure substances. Each active ingredient needs to be isolated so that its properties can be studied without interference from other substances. Chromatography is likely to be the most successful technique that can be used to separate the components.
3. The structure of the active ingredient usually needs to be determined to decide on the best ways of producing it commercially. The molecule would need to be tested to establish its efficacy and how it might be administered. The storage life and handling procedures are relevant concerns. It would need to be determined if there are any negative side-effects to the medication.

Analysis

4. The polarity of the solvent used should match that of the molecule extracted. Therefore, both molecules need to be inspected to judge their degree of polarity. The presence of highly electronegative atoms such as oxygen and nitrogen will make the molecule polar. On large molecules, such as digitoxin, several oxygen atoms are needed to compensate for the size of the molecule. Both molecules contain some oxygen, but will not be highly polar as the number of oxygen atoms is limited.
5. **a** Steam distillation involves prolonged heating at temperatures of at least 100°C. For this method to be successful, the extracts need to be relatively stable at these temperatures.
   b Oil and water do not mix, making them easy to separate. A piece of equipment called a separating funnel can be used for this purpose.
6. **a** The *m/z* ratio of the molecular ion peak will be 176, matching a molecular formula of $C_6H_8O_6$.
   b Likely absorptions include: a broad peak around 3400 cm^{-1} due to –OH (alcohol), broad band around 3000 cm^{-1} due to –OH (acid) and a peak around 1750 cm^{-1} for C=O.
   c Vitamin C has several hydroxyl groups. When protons are part of a hydroxyl group they rarely produce splitting of peaks in proton-NMR.
7. **a** The *m/z* ratio of the molecular ion peak will be 151, matching the molecular formula of $C_8H_9NO_2$.
   b 3300 cm^{-1} broad band for –OH (alcohol), 1700 cm^{-1} for C=O bond and 3500 cm^{-1} for N-H bond.
   c Ethanol is a polar solvent due to the presence of the –OH group, but not as polar as water. The functional groups in paracetamol will similarly make it relatively polar. The molecules will be soluble in each other due to similar polarity.

15.2 Proteins

KEY QUESTIONS

Knowledge and understanding

1. **a** tertiary
   b secondary
   c primary
   d quaternary

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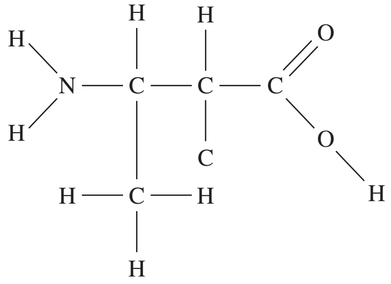
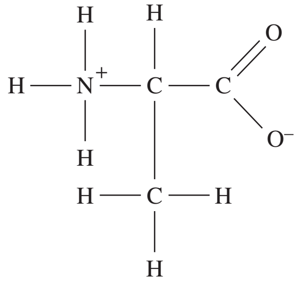
2 The primary structure bonding involves covalent bonds in the peptide linkages, i.e. bonds between carbon and the nitrogen atoms. The secondary structure is caused by hydrogen bonds between different parts of the peptide linkages (amide) in the protein chain.

3 **a** The tertiary structure is related to the overall three-dimensional shape of the protein. The shape of the protein needs to be appropriate for its function.

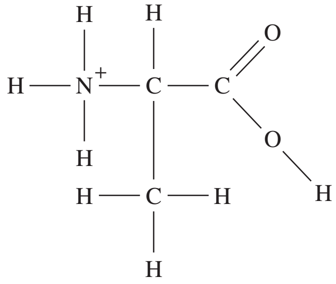
b the R groups

4 **a**

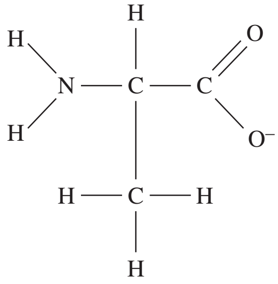




b i



ii



Analysis

5 **a** α-helix

b α-helices result from hydrogen bonding in different regions of the amino acid sequence. In this case, the hydrogen bonds arise due to attraction between the partial positive charge on the H of a –N–H bond in a peptide link, with the partial negative charge on the O of a –C=O bond of a peptide, link four amino acid units along the chain.

6 B, C and D. Hydrogen bonds between the polar –NH group in one peptide link, and the polar –C=O group in another peptide link, can form at regular intervals to form the alpha helix and beta pleated sheets that make up the secondary structure. Hydrogen bonds can also form between R groups that contain –O–H, –N–H or –C=O functional groups that make up the tertiary structure. The quaternary structure involves two or more polypeptides bonded together through a variety of bonds, some of which could be hydrogen bonds. Therefore, B, C and D are all correct. A is incorrect because only covalent bonds are responsible for the primary structure.

7

Structure of R group	Is the R group polar or non-polar?	Is the R group acidic, basic or neutral?
$-CH(CH_3)_2$	**non-polar**	**neutral**
$-CH_2COOH$	**polar**	**acidic**
$-CH_2C_6H_5$	**non-polar**	**neutral**
$-(CH_2)_4NH_2$	**polar**	**basic**

15.3 Enzymes

CASE STUDY: ANALYSIS

Burke and Wills and thiaminase

1 **a** Like most enzymes, the rate of reaction is low at low temperatures. It rises as the temperature rises until it reaches an optimum, and then the rate falls away quickly if the temperature continues to increase.

b As the temperature rises towards its optimum, the rate increases as the frequency of collisions is increasing. Above the optimum temperature the rate drops due to denaturation.

2 The optimum temperature for many enzymes is around body temperature of 37°C. The optimum temperature for thiaminase is significantly higher than 37°C (between 60 and 80°C).

3 The human body requires thiamine (vitamin B1) for digestion of carbohydrates. The presence of thiaminase causes the level of thiamine to drop. Therefore, digestion will be better if there is no thiaminase.

KEY QUESTIONS

Knowledge and understanding

1 Part of the structure of an enzyme is a region known as the active site. It is at this position that the substrate (reacting species) bonds to the enzyme, weakening the bonds in the substrate. The reaction can now occur with a lower activation energy.

2 At lower temperatures (20°C to 37°C), the rate of reaction would be slow, but it would gradually increase as the temperature increased. The rate would be greatest at 37°C. Above 37°C the rate would decrease rapidly because the enzyme would be denatured by the higher temperatures.

3 A change in pH can reduce enzyme activity because the different pH affects the structure of the protein and changes its intermolecular forces. In comparison, a change in pH is likely to have less (or no) effect on the ability of an inorganic catalyst to operate as it is unlikely to change the structure.

4 When an enzyme is denatured it loses its unique shape, but it retains its structure as a protein. The primary structure is not affected, but the quaternary, tertiary and secondary structures are disrupted.

Analysis

5 **a** At high temperatures, the enzyme is denatured. This means that the structure of the protein is changed, with bonds between different parts of the molecule being broken by the increased energy present. As a result, the shape of the active site is changed and the enzyme is unable to catalyse the reaction.

b Once the enzyme has been denatured, the effect often cannot be reversed. Once the bonds between different parts of the molecule have been broken, the same bonds do not form when the temperature is lowered. So, even though the temperature was returned to the optimum temperature, the shape of the active site had already been changed and the enzyme was no longer able to catalyse the reaction.

c The enzyme is deactivated when it is cooled, but this effect can be reversible as bonds are unlikely to be broken. So when the enzyme is returned to 37°C, the enzyme’s activity is no different to an enzyme that had never been cooled.

6 The enzyme activity starts off at a very low (almost zero) value at pH 5 and below. At a low pH, the enzyme is completely denatured and cannot catalyse the reaction. At a higher pH, the enzyme is denatured, but it retains some activity, and this increases as the pH increases, until the activity reaches a maximum value at the optimum pH of 7. The activity then decreases again rapidly above pH 7, because it is once again denatured at a higher pH.

7 Bonds that hold together the secondary and tertiary structure of insulin are sensitive to excessive heat. An increase in temperature can cause these bonds to break, causing the insulin to lose its shape. When a protein loses its shape, it loses its function.

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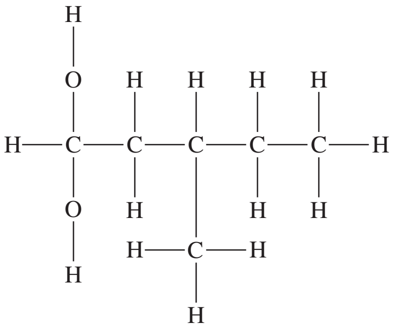
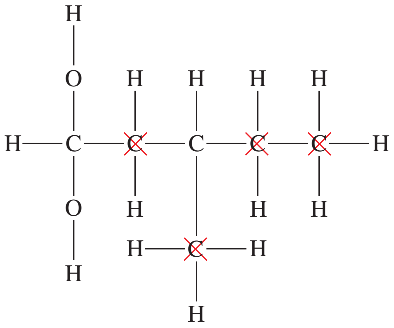
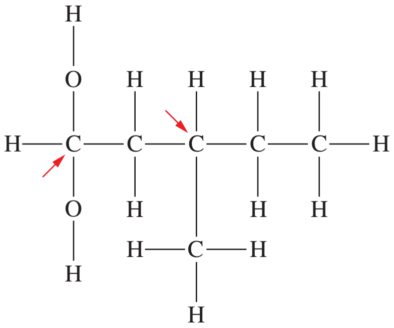
15.4 Optical isomers and inhibition of enzymes

Worked example: Try yourself 15.4.1

IDENTIFYING CHIRAL CENTRES IN ORGANIC MOLECULES

Identify any chiral centres in the following molecule.



Thinking	Working
Eliminate the carbon atoms that cannot be chiral centres. This includes all $-CH_3$ and $-CH_2-$ groups and any atom that is part of a double or triple bond, because these carbon atoms cannot be bonded to four different groups.	 This leaves two carbon atoms that may or may not be chiral centres.
For each remaining carbon atom, examine the groups attached to the atom. If there are four different groups, the atom is a chiral centre.	 The first carbon atom from the left has the following groups attached: $-H$ $-OH$ $-OH$ $-CH_2-$ The four groups are not all different, so this carbon atom is not a chiral centre. The third carbon atom from the left has the following groups attached: $-H$ $-CH_2CH_3$ $-CH_2CH(OH)_2$ $-CH_3$ The two $-CH_2-$ groups are different, as one is attached to $-CH_3$ and the other is attached to $-C(OH)_2H$. This means the four groups are all different, so this carbon atom is a chiral centre.

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KEY QUESTIONS

Knowledge and understanding

1 A carbon atom that is attached to four different groups is a chiral centre.

2 Options **b** and **d** can have optical isomers as they contain chiral carbons.

3 **a** true

b False – in most cases, enantiomers will have a different impact on the body.

c False – enantiomers cannot be superimposed. If they could be superimposed, they would not be enantiomers.

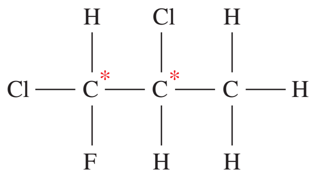
4 **a** The active site of the enzyme.

b Some part of the enzyme other than the active site

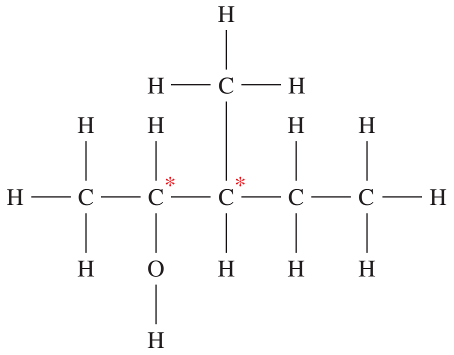
Analysis

5 **a** 0

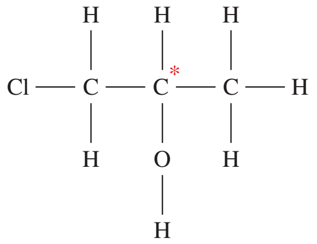
b 2



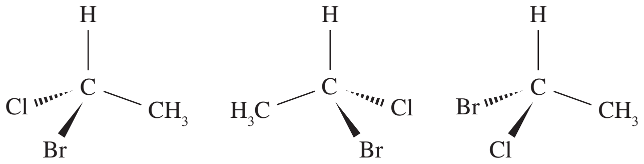
c 2



d 1



6 The enantiomer is shown as a mirror image of the original molecule. The enantiomer is rotated to put the hydrogen and methyl groups in the same arrangement, and the bromine and chlorine atoms are inverted, showing it is not superimposable.

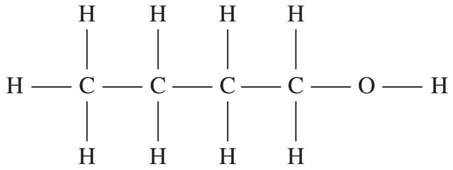


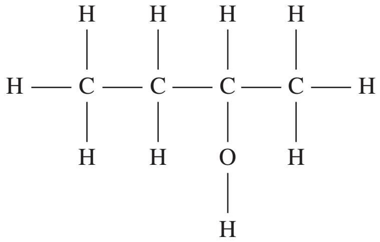
original

enantiomer as mirror image

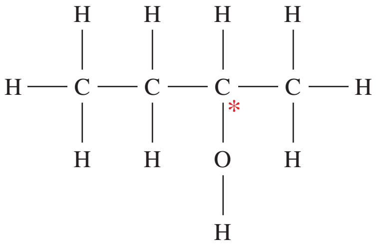
rotated enantiomer

7 The two molecules below are structural isomers (butan-1-ol and butan-2-ol). They have the same molecular formula but the functional group is in a different position.





The only form of butanol that can have enantiomers is butan-2-ol, where the third carbon shown below is a chiral carbon. The two enantiomers are optical isomers of each other.



8 *R*-ketamine might:
- be safe but less effective
- effective at treating something else
- harmful
- be equally effective
- be more effective.

Chapter 15 **Review**

REVIEW QUESTIONS

Knowledge and understanding

1 D. Naphthalene is a hydrocarbon. It will be non-polar and best extracted with a non-polar solvent such as hexane. The other options contain solvents with some degree of polarity.

2 C. The secondary structure in a protein is the result of hydrogen bonding between the polar peptide bonds on different parts of the molecule. Option A is incorrect as it refers to covalent bonds and options B and D are incorrect as they are not related to the peptide bonds.

3 B. Temperatures above 40°C will lead to denaturation of most enzymes. In denaturation it is the tertiary and secondary structures that are disrupted. Option A is incorrect as the frequency of collision should increase, option C is incorrect as the primary structure remains intact, and option D is incorrect as enzymes are usually specific to one reaction only.

4 D. Glucokinase is acting as an enzyme and the main component of enzymes are proteins. Options A and C are incorrect as enzymes are specific to one reaction or type of reaction only, and option B is incorrect as catalysts lower the activation energy.

5 A. Alternative A is correct because under highly acidic conditions, an amino acid is protonated at the amino group ($–NH_3^+$) and protonated at the carboxyl group (–COOH). Options B and D are incorrect as the amine group is not protonated, and option C is incorrect as it has a COO^- group without the proton.

6 **a** In steam distillation, the plant leaves are placed in a flow of steam. The heat of the steam breaks the leaves down and carries the active ingredients from the leaves. The active ingredients will usually condense with the steam.
b Molecules should be thermally stable and volatile to be extracted by steam and it is also helpful if they are non-polar, so they form a separate layer to the water.

7 **a** both inorganic catalysts and enzymes
b enzymes
c enzymes
d both inorganic catalysts and enzymes
e both inorganic catalysts and enzymes

8 **a** Enantiomers are optical isomers. They are mirror images of each other and cannot be superimposed.
b Competitive enzyme inhibitor: a molecule with a similar structure to a substrate that allows it to compete with the substrate for the active site of an enzyme.
c Substrate: a reactant in a reaction catalysed by enzymes.
d Lock-and-key model: a model proposing that an enzyme has an active site to suit the shape of a particular substrate, allowing the enzyme to catalyse a reaction of the substrate.
e Zwitterion: a dipolar ion formed when the amino and carboxyl groups in an amino acid or polypeptide are both charged.
f Active site: the location on an enzyme where a substrate can attach. It is usually a hollow or cavity in the protein structure.

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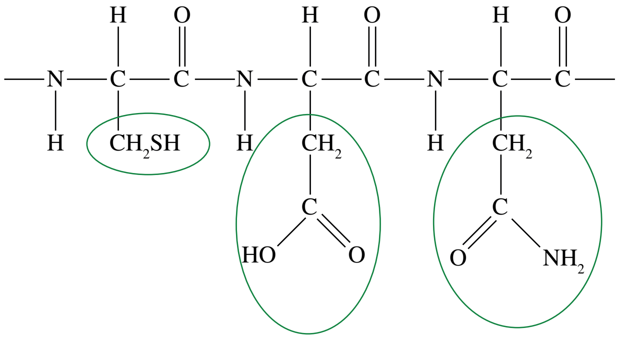
9 **a** covalent bond/peptide bond/amide bond
  b hydrogen bond
  c α-helix

10 **a** true
  b true
  c False. Enzymes are not changed by the reaction they catalyse.
  d False. Enzymes decrease the activation energy of the reaction they catalyse.
  e true
  f true
  g true

11 High pH will favour the formation of a negatively charged ion.

12



13 **a** Enzymes in the body include:

- pepsin, which hydrolyses peptide bonds of certain amino acids
- lactase, which breaks down the sugar lactose in the small intestine
- salivary amylase, which breaks down polysaccharides in the mouth.

Many other answers are possible.

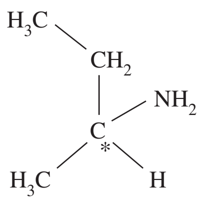
b Almost all the chemical reactions occurring in living organisms are controlled by enzymes. Enzymes speed up the reactions that are essential for life processes by as much as 10^{10} times; reactions that do not contribute to the functioning of a creature are not catalysed and occur at much slower rates.

c The shape and functional groups in the active site of the enzyme allow it to bind only with certain substrates, so that only a specific reaction is catalysed. In a similar way, a lock will only open using a key of a certain shape.

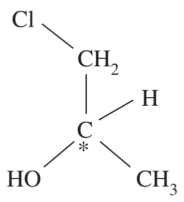
Application and analysis

14 The second molecule containing sulfur atoms in place of oxygen atoms will be much less polar and suited to extraction by the non-polar solvent, hexane.

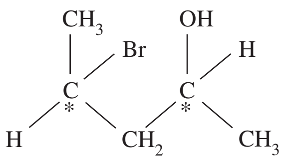
15 **a**



b

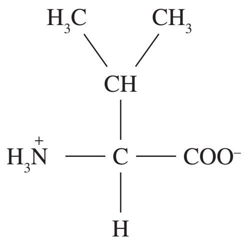


c



16 Four. The four middle carbon atoms with a hydrogen and a hydroxyl group attached are all chiral.

17



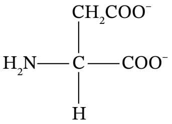
18 The catalytic property of the enzyme can be destroyed by changing its shape—in a process called denaturation. This can be done by heating the pineapple. Alternatively, canned pineapple can be used to make this dessert because the fruit is heated during the canning process.

19 **a** **i** carboxyl

ii amine

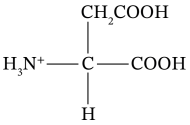
b A zwitterion is a molecule that contains positive and negative charges, but has no charge overall.

c **i**



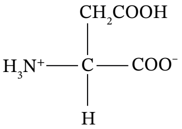
$$H_2N-\overset{CH_2COO^-}{\underset{H}{C}}-COO^-$$

ii



$$H_3N^+-\overset{CH_2COOH}{\underset{H}{C}}-COOH$$

iii



$$H_3N^+-\overset{CH_2COOH}{\underset{H}{C}}-COO^-$$

Either carboxyl protons may be lost.

20 **a** Competitive enzyme inhibitors are molecules with a similar shape to the substrate. They can bond to the active site of the enzyme, blocking the normal substrate. The rate of reaction of the substrate drops as the percentage of active sites blocked increases. The shape of the substrate is evident on the diagram – the inhibitor needs to be a similar shape to this.

b Non-competitive enzyme inhibitors attach themselves to the enzyme, but not on the active site. Their attachment causes enough of a change to the active site to cause it to no longer catalyse the substrate reaction.

21

Bond type	Required components in R group	Amino acid examples
hydrogen bonds	contains –O–H, –N–H and –C=O	serine, threonine, histidine
dipole−dipole interactions	any polar group, such as those containing –S–H, –O–H or –N–H	cysteine, asparagine
ionic interactions	contains $-NH_3^+$ and another group that contains –COO−	aspartic acid, glutamic acid, lysine, arginine
covalent cross-links	cysteine side groups react to form a disulfide bridge (–S–S–)	cysteine
dispersion forces	any non-polar group	alanine, leucine, phenylalanine

22 **a** Procaine contains an amine group, an ester group and a phenyl $-C_6H_4$ ring.

b Possible answers include: 1700 cm^{-1} due to C=O bond, 3400 cm^{-1} due to N–H bond, 3000 cm^{-1} C–H bond.

c Procaine has no chiral carbon atoms, so will not have enantiomers.

23 **a** One method chemists use to distinguish between optical isomers is to subject them to polarised light. The enantiomers will rotate the light in the opposite direction to each other.

b It cannot be assumed that both enantiomers will have the same impact and be as effective in the body. Many enantiomers need to be separated before they are sold commercially.

24 **a** The protein in milk is denatured.

b The R groups with carboxyl or amine groups can form salt bridges in the protein. This is an important aspect of their tertiary structure. The addition of acid or base will disrupt these salt bridges and consequently the shape of the enzyme.

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25 **a** Denaturation occurs when there is a change to the structure and shape of an enzyme, which prevents it from functioning. The enzyme is said to be ‘denatured’.

b Denaturation usually involves disruption of the bonds that hold the enzyme’s protein chain in a particular shape, followed by unfolding of the chain. The unfolded chains will often clump together. It is the tertiary and secondary structures that are disrupted.

c No, the covalent bonds are not broken by a slight increase in temperature.

d The overall three-dimensional shape of an enzyme is known as its tertiary structure. Since enzyme action depends upon the existence of a suitable hollow or cavity within the molecule, the tertiary structure is crucial to the enzyme’s operations.

26 A: optimum temperature, with the fastest reaction rate or enzyme activity; B: There are less frequent collisions, lower energy reactants, the enzyme has been deactivated; C: enzyme has been denatured. The tertiary structure has changed and the three-dimensional shape of the active site has altered.

27 Methotrexate is a competitive enzyme inhibitor. Its effectiveness depends upon its concentration. At high concentrations it will occupy most active sites, preventing any other reactions. At lower concentrations, the normal substrates will occupy most active sites and be catalysed. The substrate reaction must be helpful to prevent cancers in some way. The main point is that the relative concentrations of inhibitor and substrate are important.

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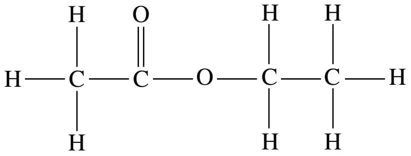
Unit 4 Area of Study 2

How are organic compounds analysed and used?

Multiple-choice questions

1 C. The peak corresponding to the unfragmented molecule is called the molecular ion (or parent ion) peak. The base peak in a mass spectrum corresponds to the strongest signal, and therefore is due to the most abundant fragment.

2 A. Ethyl ethanoate has the structure:



Each set of hydrogens has a different environment, so there are three hydrogen environments and thus three peaks (at low resolution, i.e. with no signal splitting). Each carbon has a different environment, so there are four carbon environments and hence four peaks.

3 C. More surface area means more frequent adsorption–desorption and leads to better separation.

4 B. Peak height may give a reasonable estimate, provided the peaks are very sharp, but peak area is the true measure of quantity. Retention time can be used to determine the identity of the component of the mixture, and R_f value is not relevant to HPLC.

5 B. An increase in temperature (and corresponding increase in heat energy) will break the weak intermolecular forces which hold the tertiary structure of the enzyme together, and this is called denaturation. The peptide links in the primary structure are held by covalent bonds, which are not broken by changes in temperature. The increase in temperature is not so specific that only hydrogen bonds in the secondary structure will be affected. The increase in temperature decreases the enzyme activity.

6 A. The hydrogen bond between C=O and N–H groups on nearby, regularly spaced peptide links causes the helical shape. The other types of intermolecular bonds listed are involved in holding the tertiary structure of the enzyme together.

$$n(\text{cervonic acid}) = \frac{4.928}{328.5} = 0.0150 \text{ mol}$$

7 D. $n(I_2) = \dfrac{22.842}{(2 \times 126.9)} = 0.0900 \text{ mol}$

$$\frac{n(I_2)}{n(\text{cervonic acid})} = \frac{0.0900}{0.0150} = 6$$

Because each C=C double bond reacts with one molecule of iodine, I_2, the number of C=C double bonds is 6.

8 D. The fingerprint region of the IR spectrum is typically unique to a particular compound. Small differences between structural isomers affect the energies of bond vibration. All the other alternatives are correct.

9 C. The retention time results from the interactions of individual component molecules with the stationary and mobile phases. It depends on the nature of the particles, not on how many of them there are.

10 A. Acid disrupts the weaker intermolecular forces which maintain the secondary and tertiary structure of the protein. The addition of heat to the acidic conditions results in the acid hydrolysis of the peptide links, destroying the primary structure. Alternative B is not correct because amino acids are not broken down by heat to carbon dioxide and water. Alternative C is wrong because the white gelatinous substance in egg white is a protein, not glucose, and alternative D is incorrect because the egg white is not composed of free amino acids.

11 B. There are two hydroxyl (–OH) groups on the phenyl ring, there is an amine (–NH_2) group on the second carbon and there is a carboxyl (–COOH) group on the first carbon. The alternatives that refer to amide groups have confused the amide (–CONH–) functional group with amine, and those that refer to ester have possibly confused the ester (–COO–) functional group the carboxyl group.

12 B. When water is in the pipette before use, the concentration of sodium thiosulfate that will be in the pipette after it has been filled will be less that it should be. This will mean that there are fewer moles of sodium thiosulfate that are required to completely react with the iodine than there should be, so the volume of the titre of iodine solution will be less than the first titre.

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13 A. A competitive inhibitor binds to the active site of an enzyme, thus preventing the substrate from binding to the active site. Alternative B is describing the action of a non-competitive inhibitor, and alternatives C and D are not referring to inhibitors at all.

14 C. Spectrum B is not a ketone, as it is not possible to have a ketone with the molecular formula $C_3H_8O_2$. While spectrum B does not have an O–H bond, this is not because it is a ketone. It is actually an ester. The other three statements are all correct.

15 D. $n(Cr_2O_7^{2-}) = cV = 0.0512 \times 0.021\,44$

$$= 1.0977 \times 10^{-3} \text{ mol}$$

$$\text{mole ratio} = \frac{n(C_2H_5OH)}{n(Cr_2O_7^{2-})} = \frac{3}{2}$$

$$\text{So, } n(C_2H_5OH) = \frac{3}{2} \times n(Cr_2O_7^{2-})$$

$$= \frac{3}{2} \times 1.0977 \times 10^{-3} = 1.6465 \times 10^{-3} \text{ mol}$$

$$c(\text{diluted } C_2H_5OH) = \frac{n}{V} = \frac{1.6465 \times 10^{-3}}{0.0200} = 0.0823 \text{ M}$$

10.0 mL was diluted to 250 mL, so c(ethanol in wine) = $0.0823 \times \frac{250}{10.0} = 2.06 \text{ mol L}^{-1}$

Short-answer questions

16 **a** Add an aqueous solution of Br_2 to both compounds and shake the mixture. The orange colour due to Br_2 will disappear almost immediately in the hex-1-ene, while the orange colour will take a longer time to fade in the case of hexane and requires the presence of UV light.

b Add an acidified solution of potassium permanganate or potassium dichromate to both liquids. The hexan-1-ol will react with the potassium permanganate and the colour of the solution will change from purple to colourless. If potassium dichromate is used, the colour change will be from yellow-orange to green. There will be no reaction with hexane.

c Add a solution of sodium carbonate. With the propanoic acid, a reaction should occur to produce bubbles of a colourless gas (CO_2). There should be no reaction with the propanone.

17 **a** Spectrum A: ~3000 cm^{-1} is due to C–H, ~1700 cm^{-1} is due to C=O
Spectrum B: ~3000 cm^{-1} is due to C–H, ~3400 cm^{-1} is due to O–H

b Spectrum A is propanone; spectrum B is propan-2-ol.

c Because of the symmetry of the molecule, all six hydrogens are in the same chemical environment and are 'equivalent'.

d Again, because of the symmetry of the molecule the two terminal carbon atoms are in identical environments and hence absorb and emit the same frequency.

e ^1H NMR: three peaks as there are three different H environments ($-C\underline{H}_3$, $-C\underline{H}(OH)-$ and $-CH(O\underline{H})-$)
^{13}C NMR: two peaks as there are two different C environments ($-\underline{C}H_3$, $-\underline{C}H(OH)-$)

f **i** 58. The molecular mass of propan-2-one (C_3H_6O) = (3 × 12) + 6 + 16 = 58. The peak at 59 would be due to molecules with one ^{13}C isotope.

ii It provides the molecular mass from which the molecular formula can be deduced. The fragmentation pattern can be used to obtain further information about the structure of the molecule.

iii $[CH_3CO]^+$

18 **a** The vitamin C tablets have a large amount of vitamin C in them, so one tablet would react with too much iodine solution to make a reasonable titration. When the vitamin C tablet is dissolved in 250 mL of water, the aliquots of solution have a smaller amount of vitamin C in them and only require around 20 mL of iodine solution to react.

b Titrations are repeated to ensure that the volume of the titre is accurate. If the titrations are repeated until three concordant (within 0.1 mL) titres can be achieved, then we can be confident of both the precision (a very small range of values) and the accuracy.

c **i** Table 1 Titration of 20.00 mL aliquots of vitamin C solution with 0.00995 M iodine solution.

Trial	1	2	3	4
Final volume (mL)	22.70	46.70	22.90	45.55
Initial volume (mL)	0.00	22.70	0.10	22.80
Volume of titre (mL)	22.70	24.00	22.80	22.75

The volumes of titres are calculated in the table by subtracting the initial volume from the final volume. The volume of trial 2 is 24.00 mL. This is not concordant with the other volumes and so should be disregarded.

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ii Average (mean) titre = $\frac{(22.70 + 22.80 + 22.75)}{3} = 22.75\,\text{mL}$

iii $n(I_2) = cV = 0.009\,95 \times 0.022\,75 = 2.26 \times 10^{-4}$ mol

iv From the equation: $C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2I^-(aq) + 2H^+(aq)$

$n(\text{vitamin C}) = n(I_2) = 2.26 \times 10^{-4}$ mol

$c(\text{vitamin C}) = \frac{n}{v} = \frac{2.26 \times 10^{-4}}{0.02000} = 0.0113\,\text{mol}\,\text{L}^{-1}$

v Amount of vitamin C in one tablet = n(vitamin C) in 250 mL solution

$= cV = 0.0113 \times 0.250 = 2.83 \times 10^{-3}$ mol

$m(\text{vitamin C}) = n \times M = 2.83 \times 10^{-3} \times 176.1 = 0.498$ g = 498 mg

19 a

Amino acids	Strongest interaction between side groups
threonine and lysine	hydrogen bonds
cysteine and cysteine	covalent bonds (disulfide bridges)
valine and leucine	dispersion forces
aspartic acid and lysine	ionic interactions

b At high temperatures the kinetic energy of the molecule is sufficient to disrupt the bonding between the side groups of amino acid residues (such as valine and leucine, or threonine and lysine), so the tertiary structure is lost. Extremes of pH affect the charges of amino acid residues with acidic or basic side chains (such as aspartic acid and lysine), thus changing the interactions between those amino acids, and resulting in the loss of some of the tertiary enzyme structure.

20 a ethanol

b propanoic acid

c The hydrocarbon chain length in ethanol and propanoic acid molecules are similar, so it is mainly the intermolecular forces, in particular, hydrogen bonding, between the molecules that cause the difference in their boiling points. The hydrogen bonding between carboxyl groups is stronger than those between alcohol groups because dimers form between carboxyl groups (see Chapter 10), but not between hydroxyl groups. The stronger forces result in propanoic acid needing more energy to separate the molecules and so it has a higher boiling point.

d Propanoic acid will react with sodium hydrogen carbonate to produce bubbles of carbon dioxide. This will not occur with ethanol. Ethanol is a primary alcohol and will undergo oxidation with acidified potassium dichromate, $K_2Cr_2O_7$, or with acidified potassium permanganate, $KMnO_4$. If potassium dichromate is used, during the reaction the solution mixture will change from an orange colour to green. If potassium permanganate is used as the oxidising agent, there will be a change from purple to colourless.

e $CH_3CH_2COOCH_2CH_3(l) + H_2O(l) \xrightarrow{H^+} CH_3CH_2COOH(aq) + CH_3CH_2OH(aq)$

21 Samples of pure compounds generally have a sharp melting point. Mixing a pure compound with a different compound will lower its melting point.

Compound B and compound X are the same compound. The original melting point of B was the same as that of compound X and did not change when a mixed melting point was carried out.

Although the mixed melting point of compound A with compound X was 158°C, the same as that of compound X, this was a decrease from the original melting point of compound A, indicating that compounds A and X were different.

The melting point of compound C was the same as that of compound X. However, when a mixed melting point was carried out, the melting point decreased, indicating the compounds C and X were not the same.

22 a radio waves (radio frequencies)

b The change associated with this is that nuclei with spin ‘flip’ between low and high energy states corresponding to alignment with the external magnetic field.

c It is used as a reference for determination of chemical shifts.

d i B. High chemical shift is characteristic of an aldehyde and the quartet results from three adjacent H atoms.

ii D. A singlet suggests there are no neighbouring H atoms. The chemical shift is consistent with an adjacent C=O group.

iii E. A quartet indicates there are three neighbouring H atoms. A moderately high chemical shift is consistent with an adjacent O atom.

iv C. A singlet indicates that all H atoms in the molecule are equivalent so no splitting is observed. The chemical shift is consistent with an adjacent halogen (Cl) atom.

v F. A triplet shows there are two neighbouring H atoms and the low chemical shift is consistent with no adjacent atoms such as O, N or a halogen.

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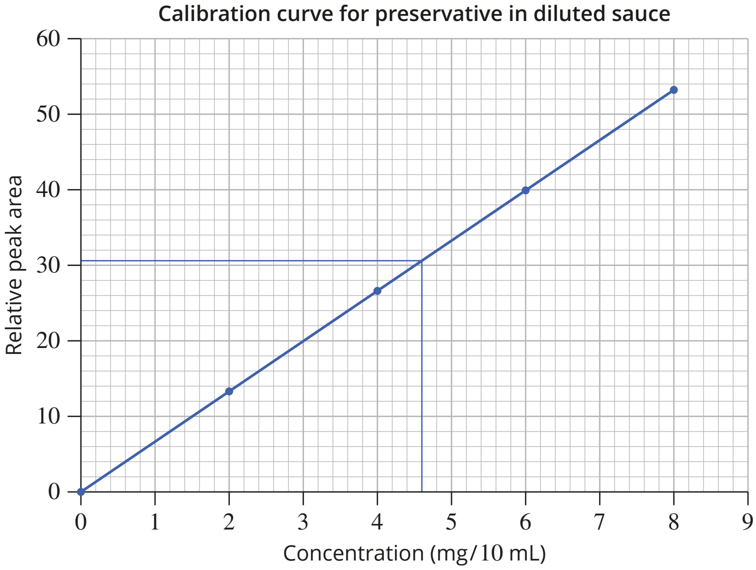
vi A. A doublet suggests there is one neighbouring H atom and the chemical shift is consistent with an adjacent C=O group.

23 **a** Sorbic acid adsorbs most strongly. Its longer retention time indicates that it spends a relatively long time adsorbed onto the stationary phase.

b Only benzoic acid, for which there is a peak in the sample spectrum with the same retention time. There are no peaks in the sample with retention times corresponding to the other two.

c



Concentration of preservative in diluted sauce is 4.58 mg/10 mL

d Mass of preservative in 10.0 mL solution = 4.58 mg

Concentration of preservative in sauce = $\frac{4.58}{1.50} \times 100 = 305$ mg/100 g

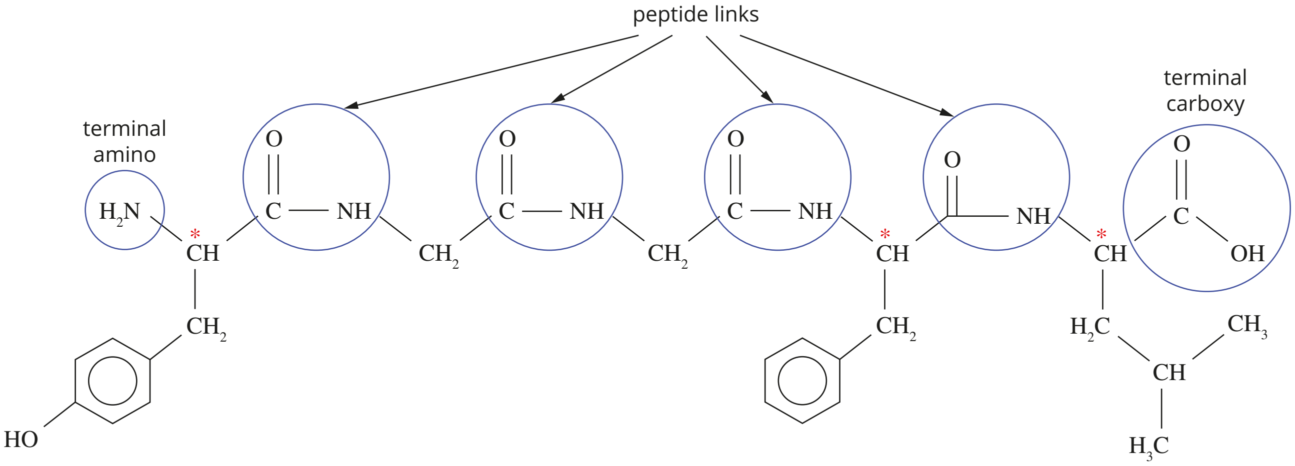
24 **a** The ‘active site’ of an enzyme is the region on its surface responsible for its catalytic activity. This region has the ability to bind to a specific molecule, or part of a molecule. This molecule is called the ‘substrate’ and binding to the active site of the enzyme alters the substrate in a way that lowers the activation energy of a reaction in which the substrate participates.

b Like all catalysts, enzymes increase the rate of reaction, but are unchanged after the reaction is complete, so that a single enzyme molecule can catalyse a reaction many times over. A reactant is changed and consumed in the course of a reaction.

c In the lock-and-key model, the active site has a fixed shape that only the substrate, or a close mimic, can fit into and bind. The substrate reacts when it is bound to the active site, and products are made. When the products leave the enzyme, it is available to catalyse the reaction of another substrate.

d The competitive inhibitor would bind to the active site of the enzyme and it would prevent the substrate from binding to that active site. This would render the enzyme unable to catalyse the reaction. Depending on what proportion of the enzymes were affected by this competitive inhibitor, the person could lose the ability to digest lactose.

25 **a, c, d** See diagram.



b Tyrosine, glycine (× 2), phenylalanine

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26 a The primary structure of a protein relates to the formation of peptide linkages between the amino acids as they are linked together in a specific sequence. Since this is a condensation reaction between carboxyl and amino functional groups, water is a by-product. Secondary and tertiary structures do not involve condensation reactions, but instead involve intermolecular forces.

b The secondary and tertiary structures of proteins are largely maintained by non-covalent bonding interactions such as hydrogen bonding, ionic interactions, ion–dipole attractions and dispersion forces, which are generally weaker than the covalent bonding in the peptide linkages maintaining the primary structure. As a result, the structures held together by these weaker attractions are more easily disrupted.

c The bonding that maintains the tertiary structure of a protein includes types of widely varying strength, including some strong covalent bonding in the form of disulfide bridges. Proteins with higher proportions of the stronger bonding types involved in their tertiary structures will tend to be more stable.

27 a $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

$n(Cr_2O_7^{2-}) = 0.010\,00 \times 0.0525$
$= 5.25 \times 10^{-4}$ mol

$n(Fe^{2+}) = 0.060\,00 \times 0.0360$
$= 2.16 \times 10^{-3}$ mol

From the balanced equation:

$n(Fe^{2+})$ needed to react $= 6 \times n(Cr_2O_7^{2-})$
$= 6 \times (5.25 \times 10^{-4})$
$= 3.15 \times 10^{-3}$ mol

3.15×10^{-3} mol of Fe^{2+} is needed for all of the $Cr_2O_7^{2-}$ to react.

There is only 2.16×10^{-3} of Fe^{2+} present

So, Fe^{2+} is the limiting reactant and $Cr_2O_7^{2-}$ is in excess.

b $n(Cr_2O_7^{2-})$ that reacts $= \dfrac{n(Fe^{2+})}{6} = \dfrac{2.16 \times 10^{-3}}{6} = 3.60 \times 10^{-4}$ mol

$n(Cr_2O_7^{2-})$ in excess $= n(Cr_2O_7^{2-})$present $- n(Cr_2O_7^{2-})$ that reacts
$= 5.25 \times 10^{-4} - 3.60 \times 10^{-4}$
$= 1.65 \times 10^{-4}$ mol

c Since Fe^{2+} is the limiting reactant, the mass of iron(III) sulfate is calculated using the amount of Fe^{2+}.

$n(Fe^{3+}) = n(Fe^{2+}) = 2.16 \times 10^{-3}$ mol

$n(Fe_2(SO_4)_3) = \dfrac{1}{2} \times n(Fe^{3+}) = 1.08 \times 10^{-3}$ mol

$m(Fe_2(SO_4)_3) = n(Fe_2(SO_4)_3) \times M(Fe_2(SO_4)_3)$
$= 1.08 \times 10^{-3} \times (2 \times 55.8 + 3 \times (32.1 + 4 \times 16))$
$= 1.08 \times 10^{-3} \times 399.9$
$= 0.432$ g

28 a i Citric acid would be found in the lower aqueous layer. The many polar hydroxyl groups in citric acid would make it very soluble in water.

a ii Limonene would be found in the upper diethyl ether layer. A limonene molecule contains only non-polar methyl groups, and would readily dissolve in the non-polar diethyl ether solvent.

b If sodium hydrogen carbonate powder is added to the solution from the lower layer in the separating funnel, bubbles of gas would be observed. This is because citric acid would react with sodium bicarbonate to produce carbon dioxide gas.

c High-performance liquid chromatography could be used to separate the compounds in the same layer as limonene.