# Chapter 1 Rate of chemical reactions
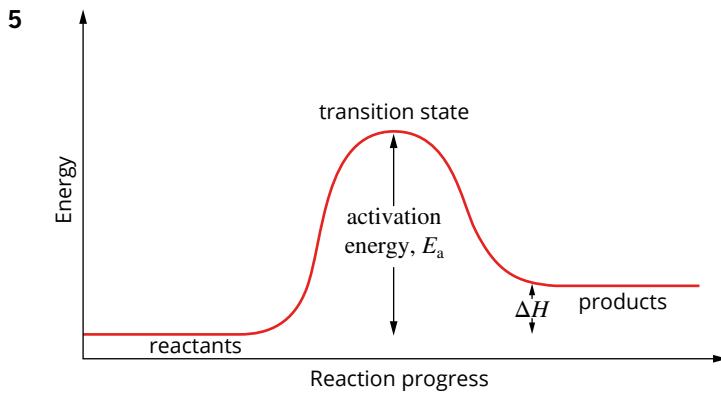
Section 1.1 Rate of chemical reactions

1.1 KEY QUESTIONS

1   C. The concentration of solids is constant and not dependent on the mass of the solid present.
2   Correct orientation and sufficient energy (to meet the required activation energy).
3

4   Activation energy is the minimum energy required to break existing chemical bonds in a collision and allow the formation of products.
5

6   **a** $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
   b   If there are remaining solid marble chips in the conical flask, the hydrochloric acid must be the limiting reagent. If the marble chips have completely dissolved, the marble chips must be the limiting reagent.
   c   The mass lost by the reaction vessel is the mass of carbon dioxide gas escaping from the reaction vessel and thus not being weighed.

Section 1.2 Factors that influence reaction rate

1.2 KEY QUESTIONS
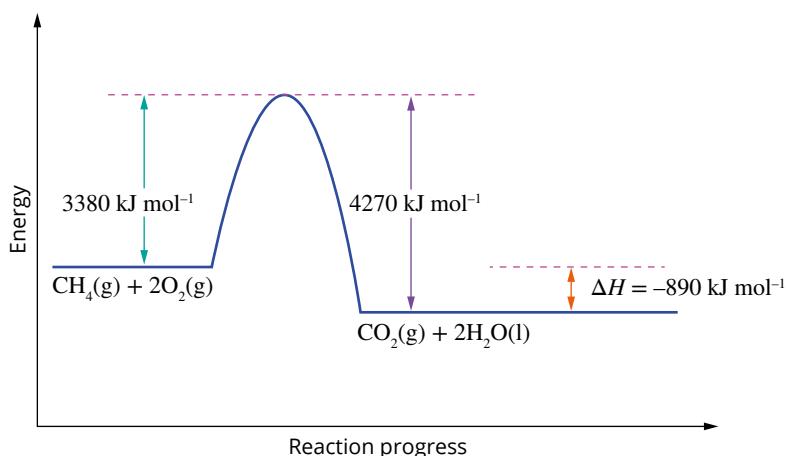
1   D. D is incorrect because reactant particles need to collide with energy equal to or greater than the activation energy for the reaction.
2   A
3   D. An increase in concentration increases collision frequency between reactant particles.

4 **a** The steeper gradient signifies a faster reaction rate as a larger volume of gas (*y*-axis) is produced per unit time (*x*-axis) (due to the concentration of the acid being greatest at the start of the reaction).

   b The reaction has stopped, time is passing and no more volume of gas is produced.

   c This is the maximum amount of carbon dioxide that can be produced for these reagents. Crushing the marble chips into smaller pieces does not increase the mass of marble chips present.

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

   b $-890\,kJ\,mol^{-1}$

   c

Energy diagram showing:
$3380\ kJ\ mol^{-1}$
$4270\ kJ\ mol^{-1}$
$CH_4(g) + 2O_2(g)$
$\Delta H = -890\ kJ\ mol^{-1}$
$CO_2(g) + 2H_2O(l)$
Reaction progress
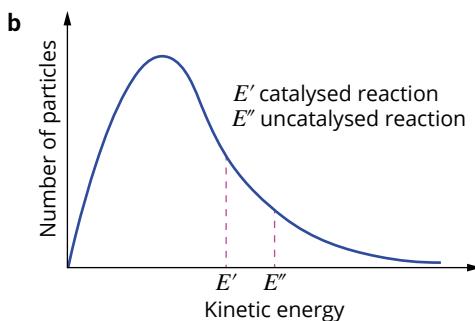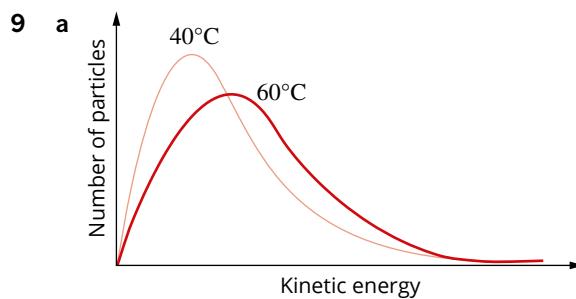
6 $139\,kJ\,mol^{-1}$

7 **a** exothermic

   b activation energy

   **c** change of enthalpy

   d change of enthalpy

   e activation energy

8 They don't differ; they are the same. Adding a catalyst reduces the required activation energy; it does not change the energy distribution of the particles.

Chapter 1 **Review**

1 A reaction only occurs when reacting particles collide with correct orientation and sufficient energy to overcome the activation energy barrier.

2 C. Powder has a higher surface area than chips, and $2\,mol\,L^{-1}$ is a higher concentration than $1\,mol\,L^{-1}$.

3 B. An increase in surface area increases the frequency of collisions between reactant particles.

4 D

5 Reaction rate is measured by how quickly reactants are consumed or products generated over time. The duration, or overall time taken for a reaction, only measures the time taken to consume all of the given reagents; it does not indicate how quickly, i.e. the rate, that those reagents were consumed.

6 As the mixture is heterogeneous and does not have a constant composition throughout, stirring increases the frequency of collisions between reactant particles leading to an increased reaction rate.

7 At the auto ignition temperature, the given temperature is high enough to provide the required activation energy for the combustion of the substance in oxygen provided by the atmosphere.

8 The low temperatures in the freezer slow down the chemical reactions that cause food to rot because fewer of the molecules present have sufficient energy to overcome the activation energy. Lowering the temperature does not stop the reactions; it only slows them significantly. Food will still go rotten eventually.

9 a

b

c When a catalyst is present, the reaction proceeds by an alternative reaction pathway with a lower activation energy (E') than in the uncatalysed reaction (E''). At a given temperature, there will be a greater proportion of reacting particles that have a kinetic energy equal to or greater than the activation energies (E' than E''). As more reactants have sufficient energy to react, the rate of reaction increases.

10 a surface area, concentration, gas pressure, temperature and the presence of catalysts

  b i surface area, concentration and gas pressure (assuming constant T)

    ii temperature and the presence of catalysts

11 A. Reactant is not gaseous, so increasing the pressure of oxygen gas would have no effect on the rate of reaction.
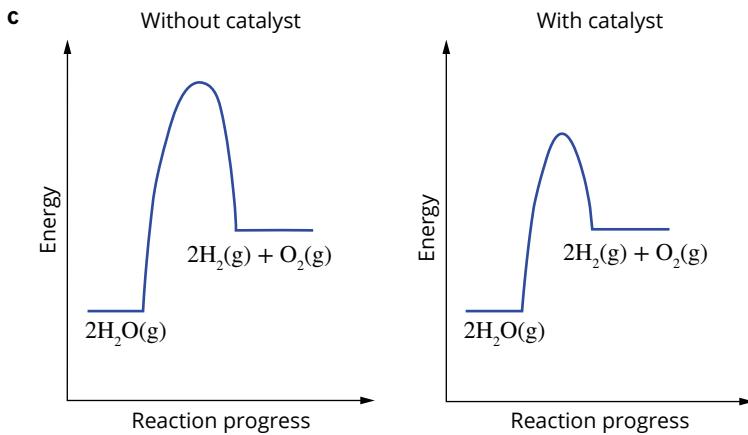
12 The time taken to dissolve the nail is unchanged. Adding a greater volume of acid does not change the concentration of the acid and will not generate a greater number of collisions per unit of time, thus the reaction rate remains the same.

13 To increase the rate of dissolution 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 was dissolving
- stir the sugar and water mixture while the sugar was dissolving.

14 C
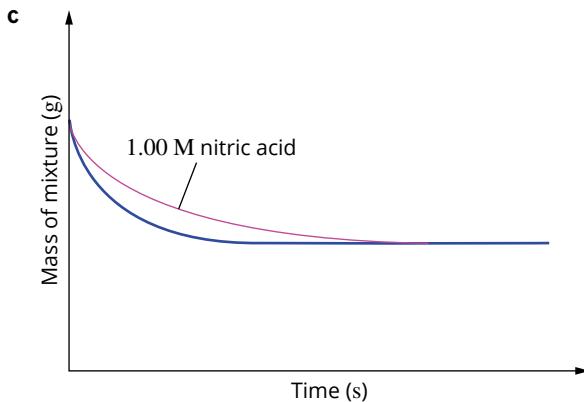
15 a $1370 \, \text{kJ mol}^{-1}$

  b $-572 \, \text{kJ mol}^{-1}$

  c

  d $+572 \, \text{kJ mol}^{-1}$
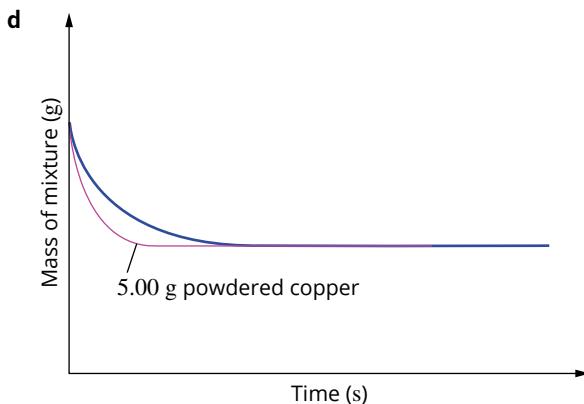
16 a Initially the rate was high due to the highest concentration of nitric acid present. Over time, as the nitric acid was consumed, its concentration began to decrease; this is associated with a gradually decreasing reaction rate. Once all the limiting reagent has been consumed, the reaction stops and there is no more mass change.

**b** The copper is all used up so the reaction stops.

c

Decreased rate of mass loss due to lower nitric acid concentration.
Copper is still limiting, so final mass remains the same.

d

Increased rate of mass loss due to increased copper surface area.
Copper is still limiting, so final mass remains the same.

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

b $n(CaCO_3) = 10.0\,g/100.1\,g\,mol^{-1} = 0.0999\,mol$
$n(HCl) = 0.1\,mol\,L^{-1} \times 0.1\,L = 0.01\,mol$
∴ $CaCO_3$ is in excess because only 0.005 mol of $CaCO_3$ is required to react with 0.01 mol of HCl.
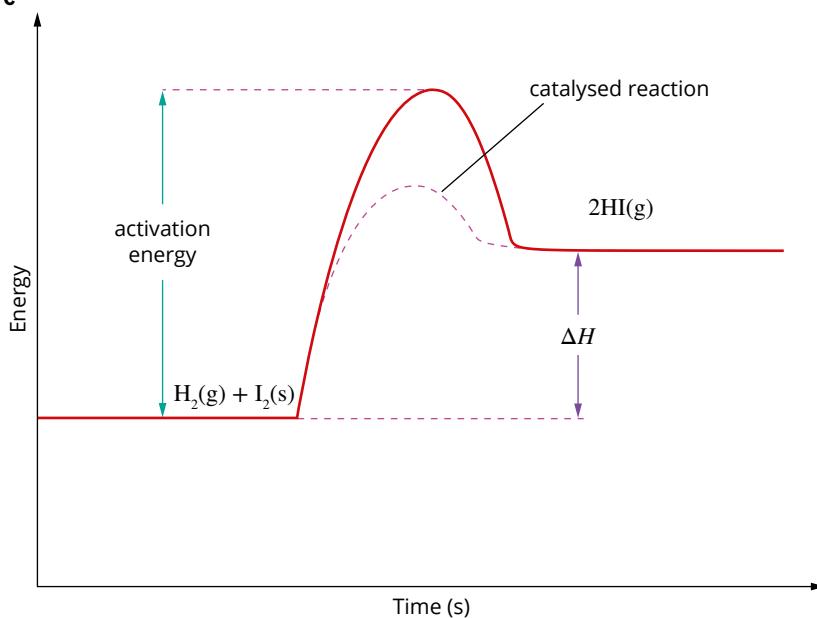
c The rate of reaction can be measured by:
   • a decrease in mass of reaction mixture as $CO_2(g)$ escapes to the atmosphere
   • an increase in pH with a pH probe as acid is consumed.

d The reaction with the smaller lumps will be faster. The smaller lumps have a larger surface area so more collisions can occur per second.

e Increase temperature to increase the proportion of successful collisions; increase the concentration of hydrochloric acid so more collisions can occur per second.

18 a, c

b The reaction is endothermic.

19 a The temperature of the new process (550°C) is much lower than the temperature of 1800°C in the blast furnace.

b $2Fe(s) + O_2(g) \rightarrow 2FeO(s)$
$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

c No. The reaction of iron with water is different from the reaction of iron with dry oxygen and proceeds at a different rate.

d exothermic

e High surface area of iron pellets, 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. 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 was then used to unload the iron into piles less than 1 m deep so the heat could escape.

Chapter 2 **Equilibrium**

Section 2.1 **Chemical systems**

2.1 KEY QUESTIONS

1 B. In a closed system, the reactant and product particles cannot escape. This does not necessarily mean the reaction system must be sealed, unless a gas is involved. A reaction occurring in solution in a beaker might be an example of a closed system.

2 **a** Closed
   b Open
   c Closed
   d Open

An open system exchanges matter and energy with the surroundings. Whereas in closed systems none of the reactant or product particles escape to the surroundings, only energy can be exchanged. The second example is an open system because gaseous NH_3 escapes. Similarly, when toast burns, gaseous CO_2 and H_2O are produced and escape to the surroundings. In the other examples, none of the reactant or product particles escape to the surroundings, so these are closed systems.

3 reversible, energy, matter, rates, remains constant

4 $130 \, kJ \, mol^{-1}$
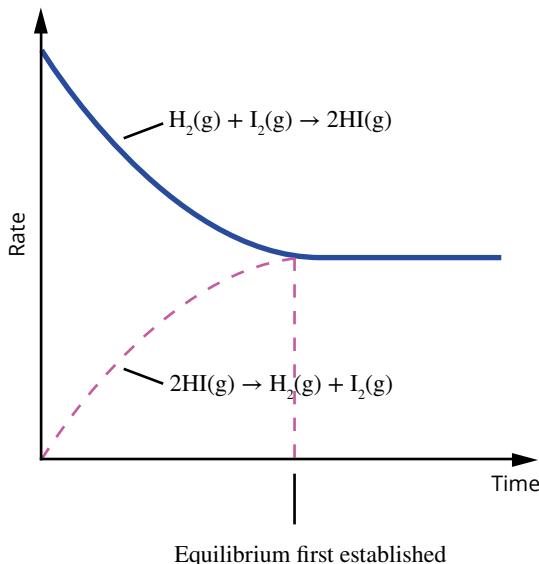
The reverse reaction is exothermic, and the activation energy is the difference between $390 \, kJ \, mol^{-1}$ and $260 \, kJ \, mol^{-1}$, which is $130 \, kJ \, mol^{-1}$.

Section 2.2 **Dynamic equilibrium**

2.2 KEY QUESTIONS

1 C. Options A and D are false because the extent of reaction gives no indication of the rate of reaction. Option B is 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 an equal amount of reactants and products when equilibrium is achieved.

2

Graph: Rate vs Time. Solid curve labelled $H_2(g) + I_2(g) \rightarrow 2HI(g)$ decreasing; dashed curve labelled $2HI(g) \rightarrow H_2(g) + I_2(g)$ increasing. Vertical dashed line at "Equilibrium first established".
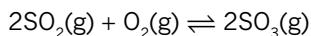
3 closed, decreases, less, reverse, increases, equal

4
- **a** $0.07\,mol\,L^{-1}$
- **b** $0\,mol\,L^{-1}$
- **c** $0.03\,mol\,L^{-1}$
- **d** $0.08\,mol\,L^{-1}$
- **e** $0.04\,mol$
- **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.

Section 2.3 **The equilibrium law**

Worked example: Try yourself 2.3.1

DETERMINING THE EXPRESSION FOR THE EQUILIBRIUM CONSTANT FOR AN EQUILIBRIUM SYSTEM

Write the expression for K_c for the reversible reaction: $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$	
Thinking	**Working**
Identify the reactants and products. The reactants appear in the denominator of the expression and the products in the numerator.	$SO_2(g)$ and $O_2(g)$ are reactants so they appear in the denominator of the expression. $SO_3(g)$ is a product so it appears in the numerator of the expression.
Write the expression for K_c. $$\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$$ Remember that the index of each component concentration is the same as its coefficient in the balanced chemical equation.	$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

2.3 KEY QUESTIONS

1 $K_c = \dfrac{[HCl]^2}{[H_2][Cl_2]}$

2
- **a** Homogeneous system: 3: a system where all the species are in the same state
- **b** Heterogeneous system: 1: a system where some of the species are in different states
- **c** Reaction quotient: 4: is equal to K_c at equilibrium
- **d** Equilibrium constant: 2: is always equal to K_c

3
- **a** $[NH_3][H_2S]$
- **b** $[Ag^+][Cl^-]$
- **c** $\dfrac{1}{[Ag^+]^2[CO_3^{2-}]}$
- **d** $\dfrac{[H_2O]^2[Cl_2]}{[HCl]^4[O_2]}$

4 D. Given the form of the expression for K_c, H_2 and CO must be products and CH_3OH must be the reactant. The expression for K_c also indicates that only H_2 has a coefficient of 2 in the equation.

Section 2.4 **Working with equilibrium constants**

2.4 KEY QUESTIONS
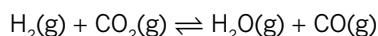
1 equal to, both the reactants and products, negligible

2 **a** $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

b This is the reverse of the reaction in the question, where the equilibrium constant of 100 indicates a high concentration of products compared to reactants. In the reverse reaction, it will be the reactants that will have the relatively high concentration, resulting in a low value for the equilibrium constant.

3 **a** $K_c = \dfrac{[HCl]^2[O_2]^{\frac{1}{2}}}{[H_2O][Cl_2]}$

b $K_c = \dfrac{[H_2O][Cl_2]}{[HCl]^2[O_2]^{\frac{1}{2}}}$

4 B. Reaction 2. The largest value of K_c indicates that the reaction favours the products.

5 **a** Increased
b Decreased
c Increased
d Decreased

Section 2.5 **Le Châtelier's principle**

Worked example: Try yourself 2.5.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

Consider the following equilibrium system:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of CO gas on the equilibrium.

Thinking	Working
Determine the initial effect of the change on the concentration of the particles.	Adding CO molecules increases the concentration (and partial pressure) of these particles.
Use collision theory to determine the initial effect on the rate of the forward (or reverse) reaction.	Collisions between CO and H_2O become more frequent, increasing the rate of the reverse reaction and reducing the concentrations (and partial pressures) of CO and H_2O molecules.
Consider how the rates of the forward and reverse reactions change as the system reaches a new equilibrium.	As more reactant molecules are formed, the rate of the forward reaction increases, until the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Predict the overall effect of the change on the position of equilibrium.	Because of the higher rate of the reverse reaction initially when the CO molecules were added, a net reverse reaction has occurred.

2.5 KEY QUESTIONS

1 **a** Net forward reaction
   b Net reverse reaction
   c Net forward reaction

2 **a** The addition of H_2 gas increases the concentration of H_2 molecules. This causes more frequent collisions between the H_2 molecules and other molecules. So, collisions between H_2 and I_2 mean the forward reaction occurs faster than the reverse reaction. As the forward reactions proceeds, there is a decrease in the rate of the forward reaction and an increase in the rate of the reverse reaction. The rates of the forward and reverse reactions become equal and equilibrium is re-established. Therefore, there is a net forward reaction.

   b The addition of H_2 gas increases the concentration of H_2 molecules. This causes more frequent collisions between H_2 molecules and other molecules. So, collisions between H_2 and N_2 mean the reverse reaction occurs faster than the forward reaction. As the reverse reactions proceeds, there is a decrease in the rate of the reverse reaction and an increase in the rate of the forward reaction. The rates of the forward and revers reactions become equal and equilibrium is re-established. Therefore, there is a net reverse reaction.

3 **a** Net reverse reaction
   b Net forward reaction

4 B. When a reactant is added to an equilibrium, the system will try to oppose the change by consuming some of the reactant and producing more product. The reaction shifts to the right as a consequence.

Section 2.6 Further applications of Le Châtelier's principle
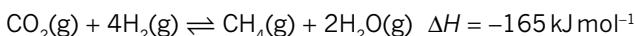
Worked example: Try yourself 2.6.1

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 of all species at equilibrium.
The system will try to partially oppose the change in pressure by reducing or increasing the pressure of the system. (For a volume decrease, the system will shift in the direction of the fewest particles, and vice versa for a volume increase.) 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. This decreases the amount of the product. The Cl_2 concentration and partial pressure will be higher than it was at the initial equilibrium.

Worked example: Try yourself 2.6.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium:

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \quad \Delta H = -165 \, kJ \, mol^{-1}$$

Explain, using collision theory, the effect of an increase in temperature on this reaction.

| Thinking	Working
Decide what effect the temperature change has on the initial rates of reaction. Remember that, for an equilibrium system, an increase in temperature increases the proportion of molecules with the necessary activation energy for the endothermic reaction to a greater extent than for the exothermic reaction, and so the endothermic reaction will be favoured.	With the temperature increase, all reactant and product molecules have more energy and move faster. This reaction has a negative ΔH indicating it is an exothermic reaction. Since the reverse reaction is endothermic, its rate initially increases more than the rate of the forward reaction (because it has a higher activation energy and temperature has a greater effect).
Using collision theory, consider what happens to the rates of the forward and reverse reactions.	As CH_4 and H_2O react and the concentration of products decreases, the rate of the reverse reaction will decrease. As the concentration of CO_2 and H_2 increases, the rate of the forward reaction will increase. Ultimately, the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Determine the overall effect of the change on the equilibrium.	This results in a net reverse reaction, with higher concentrations of CO_2 and H_2 and lower concentrations of CH_4 and H_2O.

2.6 KEY QUESTIONS
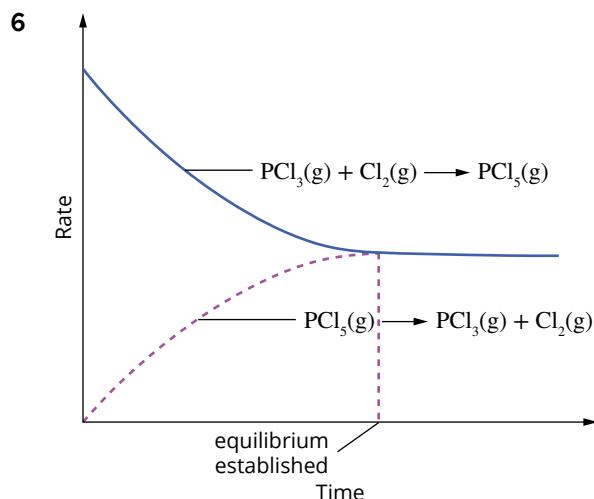
1 B. This gaseous equilibrium contains two particles on both sides of the equation. In such a situation, a volume decrease causes a pressure increase, resulting in an increase in the number of collisions between all molecules. Because there is an equal chance of reactant molecules colliding and forming a product or of product molecules colliding and forming the reactants (2 moles of reactants and 2 moles of products), there is no overall net reaction. The system is unable to oppose the change applied.

2 **a** Shifts to the right
   b No effect
   c Shifts to the right

3 **a** Doubling the pressure causes increased frequency of collisions and an increased rate of both the forward and reverse reactions. However, because there are more particles on the left-hand side, there will be more successful collisions in the forward direction, so a net forward reaction results.
   b Increasing the pressure causes increased frequency of collisions and an increased rate of both the forward and reverse reactions. Because there is an equal chance of reactant molecules colliding and forming a product or of product molecules colliding and forming the reactants (2 moles of reactants and 2 moles of products), there is no overall net reaction.
   c A temperature increase means all reactant and product molecules have more energy and move faster. There will be more collisions and more molecules will have the necessary activation energy. An increased temperature favours an endothermic reaction because a higher proportion of molecules at the higher temperature will have the necessary activation energy than for the exothermic reaction. Hence, there will be a net reaction in the direction of the endothermic reaction—a net forward reaction.

4 **a i** Increase
      ii Increase
      iii Decrease
   b i Cannot cause forward reaction
   **ii** Increase
      iii Cannot cause forward reaction

5 An increase in volume will cause a decrease in pressure. The equilibrium system will respond by favouring the direction that increases pressure, i.e. more NO_2 will be formed in order to re-establish equilibrium.

   a When the volume is increased the partial pressure of NO_2 will decrease. Although, according to Le Châtelier's principle, the reaction will favour the formation of NO_2 the adjustment only partially opposes the change so the corresponding increase in pressure will not reach the initial NO_2 partial pressure.

   b The mass of NO_2 will be higher.

6 **a** Decreasing the temperature would favour the forward exothermic process because there is a net forward reaction.

   b There are five particles on the reactant side and three 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 in order to reduce the overall number of particles.

CHAPTER 2 **REVIEW**

1 C. In an open system, matter and energy can be exchanged with the surroundings.

2 C. In this system, an equilibrium exists between the solid salt and the salt dissolved in solution. This process is reversible. It is a closed system because matter is not exchanged between the system and the surroundings (all the salt stays in the container).

3 **a**

   b If particles of R and S have energies greater than the activation energy of the reverse reaction, when they collide they can react to form P and Q.

4 For a reaction to be homogeneous, the reactants and products must all be in the same state. 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 will be no observable change in concentration of the reactants or the products.

5 **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.

6

7 $K_c = \dfrac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}][Sn^{2+}]}$

8 **a** $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$

b $S_2(g) + 2H_2(g) \rightleftharpoons 2H_2S(g)$

c $NO_2(g) \rightleftharpoons \dfrac{1}{2}N_2O_4(g)$

9 **a** $\dfrac{1}{[Cu^{2+}][CO_3{}^{2-}]}$

b $[Cu^{2+}][CO_3{}^{2-}]$

c $\dfrac{[PCl_5]^4}{[Cl_2]^{10}}$

d $\dfrac{[Cl_2]^{20}}{[PCl_5]^8}$

Remember that pure solids and pure liquids are given the value of 1 in an equilibrium constant expression for K_c.
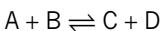
10 The reaction quotient is the ratio of the concentrations of the products to the concentration of the reactants, with the index of each concentration the same as the coefficient of the substance in the reaction equation. The value of the reaction quotient becomes equal to the equilibrium constant at equilibrium.

11 **a** less than

b $\dfrac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$

c moves to the right

12 **a** No; K_c is very small.

b Yes; K_c is very large (provided the rate is sufficiently fast).

13 $K_c = \dfrac{[Br_2][Cl_2]}{[BrCl]^2}$

14 Le Châtelier's principle states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of that change.

For the equilibrium:

$A + B \rightleftharpoons C + D$
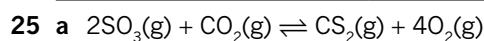
when the products, C and D, are removed, a net forward reaction occurs. Applying Le Châtelier's principle, the system can be regarded as opposing the change and trying to restore equilibrium.

15 The position of an equilibrium system will shift to partially oppose a change.

a The addition of a reactant causes a net forward reaction.

b The removal of a reactant causes a net reverse reaction.

c The removal of a product causes a net forward reaction.

16 **a** More $H_2(g)$ has been added, causing a net forward reaction.

b Some $H_2(g)$ could have been removed, lowering the partial pressure of $H_2(g)$ and causing a net reverse reaction.

17 C. This is because, with an increased pressure, the system will move to decrease the pressure by moving in the direction of the fewest particles. Hence a net forward reaction occurs.

18 **a** A is NO_2. B is N_2O_4.

The graph shows that when the partial pressure of B decreases from 0.10 to 0.05 atm, the pressure of A rises from 0 to 0.10 atm. B must be N_2O_4 and A must be NO_2, because the ratio of N_2O_4 to NO_2 in the equation is 1:2.

b A. The presence of a catalyst will increase the rate of both the forward and reverse reactions equally so equilibrium is established more quickly, but the equilibrium partial pressures of the reactants and products will be the same.

19 D. Although a catalyst increases the rates of the forward and reverse reaction equally, it does this by decreasing the activation energy by providing an alternative pathway for the reaction. It does not change the temperature. Dilution of an aqueous equilibrium system causes the system to oppose the decrease in concentration of dissolved particles by moving in the direction of the most particles.

20 **a** Reaction **i** is exothermic, so an increase in temperature will favour the reverse reaction and K_c will decrease causing the product concentrations to decrease and the reactant concentrations, including H_2 gas, to increase.

Reaction **ii** is endothermic, so an increase in temperature will favour the forward reaction and K_c will increase causing the product concentrations to increase, including H_2 gas, and the reactant concentrations to decrease.

b A temperature increase means all reactant and product molecules have more energy and move faster. An increased temperature favours an endothermic reaction because a higher proportion of molecules will have the required activation energy for the endothermic reaction (at the higher temperature). Since reaction ai is exothermic, the reverse reaction, the endothermic reaction, will be favoured and so the hydrogen gas concentration will increase. Since reaction ii is endothermic, the forward reaction will be favoured. Hence, the reaction moves toward the right and the hydrogen gas concentration will increase.

21 a Net reverse reaction
   b Net forward reaction
   c No effect

22 If Ca^{2+} ions are inefficiently absorbed from food, decreased concentrations of these ions can occur in body fluids. As a consequence, a net forward reaction would occur, raising the concentration of dissolved Ca^{2+} ions and resulting in decreased amounts of calcium phosphate in bones.

23 a i Net forward reaction
      ii No change
      iii Net forward reaction
      iv Net reverse reaction
   b i Increase
      ii No change
      iii No change
      iv No change
   c Likely to be large

24

		Colour change	Explanation using Le Châtelier's principle and collision theory
a	The temperature is increased to 450°C at constant volume.	Lighter	Le Châtelier's principle: The forward reaction is exothermic, so K_c will decrease as temperature increases, so a net reverse reaction occurs. Collision theory: A higher temperature causes all molecules to have more energy and there are more frequent collisions. The increase in temperature affects the rate of the endothermic (reverse) reaction more than the exothermic reaction because this reaction has a higher activation energy to overcome. So the net reaction will be the reverse, endothermic reaction, producing more colourless NO and O_2.
b	The volume of the container is increased at constant temperature.	Lighter	Le Châtelier's principle: An increase in volume causes a decrease in pressure. The system will oppose the change by increasing the pressure, so the equilibrium position moves in the direction of the most particles, producing more NO and O_2. Collision theory: Decreased pressure means there will be less frequent collisions. The rate of the reaction involving the smaller number of particles (the reverse reaction) will be less affected by the change and so it won't be slowed down as much as the forward reaction. Therefore the equilibrium shifts to the left.
c	A catalyst is added at constant volume and temperature.	No change	Le Châtelier's principle: The system cannot adjust to oppose the addition of a catalyst. There is therefore no net reaction. Collision theory: Addition of a catalyst increases the rate of the forward and back reactions equally. There is no net reaction because the change in the number of collisions is equal in both directions.
d	More oxygen is added at constant volume and temperature.	Darker	Le Châtelier's principle: The reaction opposes the change by consuming the added O_2 and shifts toward the right to produce more brown NO_2. Collision theory: Addition of O_2 increases its concentration and causes the number of collisions with NO to increase. As O_2 is consumed, the rate of the forward reaction decreases and the rate of the reverse reaction increases until a new equilibrium is established. Overall, there is a net forward reaction.

25 a $2SO_3(g) + CO_2(g) \rightleftharpoons CS_2(g) + 4O_2(g)$

   b $K_c = \dfrac{[CS_2][O_2]^4}{[SO_3]^2[CO_2]}$

   c i Increase
      ii Increase
      iii No effect
      iv Decrease
      v No effect

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

b 15–20 minutes; 25–30 minutes, 35–40 minutes.

c 10 minutes; before 10 minutes the concentrations were changing slowly but the catalyst caused equilibrium to be reached more rapidly.

d Increased pressure by reducing volume. This results in a net forward reaction, increasing the concentration of SO_3 and reducing the concentrations of SO_2 and O_2.

e Addition of O_2. This results in a net forward reaction, increasing the concentration of SO_3 and reducing the concentrations of SO_2 and O_2.

Chapter 3 Equilibrium systems in the environment

Section 3.1 Carbon dioxide in the atmosphere

3.1 KEY QUESTIONS

1 Carbon dioxide

2 $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

3 A greenhouse gas is a gas in the atmosphere that absorbs and emits radiation within the infrared range. Examples of greenhouse gases are water vapour, carbon dioxide, methane, nitrous oxide and ozone.

4 The enhanced greenhouse effect, or global warming, is caused by additional heat being retained due to the increased amounts of carbon dioxide and other greenhouse gases that have been released into the Earth's atmosphere in the last 200 years. The impact on the Earth's climate is shifting weather patterns and more extreme weather events.

Section 3.2 Carbon dioxide in the oceans

3.2 KEY QUESTIONS

1 $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

or:

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

2 increase, decrease, decrease, increase

3 $CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$

or:

$CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$

hydrogen/hydronium ions react with carbonate ions forming hydrogencarbonate ions.

4 Calcium carbonate. It is formed through a process called calcification.

5 a Krill eggs will not hatch at lower pH, therefore there will be a lower number of krill.

   b Krill are a food source for many marine animals. If the number of krill cannot sustain organisms that feed directly on them, such as seals, penguins and small fish, then organisms such as killer whales and larger fish would also die off. This would lead to an overall decrease in the number of large species that live within specific ecosystems.

Section 3.3 Modelling and responding to climate change

3.3 KEY QUESTIONS

1 • The average global temperature is expected to rise by 0.3–4.8°C over the next century.
   • The amount of rainfall is expected to increase.
   • Tropical storms are likely to increase in wind strength and amount of rainfall.
   • Sea levels are expected to rise by 0.3–1.2 metres in the next century.
   • Sea ice and snow are expected to decrease.

2 B. Countries are hoping to reduce emissions so that the maximum temperature rise is 2 degrees.

3 • The stimulation of many national policies
   • The creation of an international market for carbon
   • The development of emissions trading schemes

4　**a**　Intergovernmental Panel for Climate Change

　　b　To stabilise greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous human-induced effects on the global climate.

5　Kyoto Protocol, reduce, greenhouse gas, stabilised, greenhouse emissions, 26–28%, 2030, solar energy.

6　**a**　Burning coal to generate electricity produces greenhouse gas emissions, which would not help Australia meet its Paris Agreement obligations. However, the cost of electricity could rise if other energy sources are required to replace coal, which is relatively abundant and cheap.

　　b　The use of biofuels (if harvested and produced using renewable energy) could potentially reduce carbon dioxide emissions. The carbon dioxide produced from the combustion of the fuels is offset by the carbon dioxide absorbed to grow the crops, which are used to make the fuels. This would help Australia meet its Paris Agreement obligations.

CHAPTER 3 REVIEW

1　Combustion of fossil fuels and plant decay

2　**a**　A number of atmospheric gases, including carbon dioxide, are capable of absorbing some of the infrared radiation re-radiated from the surface of the Earth. This warms the air nearer the Earth to a higher temperature than it would be without the atmosphere. This has meant that, over millions of years, life on Earth has been able to evolve at temperatures much warmer than would otherwise have been the case.

　　b　Carbon dioxide, methane, water vapour, nitrogen oxides and ozone

3　$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

4　The enhanced greenhouse effect is an increase in the temperature of the Earth's surface due to an increased concentration of greenhouse gases, resulting from human activities. Because of the higher concentration of greenhouse gases, less heat is radiated back into space, which results in an increase in the temperature of the Earth—global warming. This affects the weather patterns, creating more extreme weather events.

5　D. As $[CO_2]$ increases, the oceans become more acidic and there is a reduction in $[CO_3^{2-}]$.

　　Increased concentrations of CO_2 cause the oceans to become more acidic. The H^+ ions combine with CO_3^{2-} ions to produce higher concentrations of HCO_3^- ions, reducing the CO_3^{2-} concentration, and causing $CaCO_3$ to be more soluble. As a consequence, marine animals and corals have difficulty producing exoskeletons, which are made from $CaCO_3$.

6　D. Most dissolved carbon dioxide remains in solution. Only a small proportion of the carbon dioxide that dissolves produces carbonic acid.

7　D. This reaction is not part of the equilibria in sea water involving $CaCO_3$.

　　All of the other equations occur in the Earth's oceans.

8　Carbon dioxide combines with water to produce carbonic acid, as shown in reaction 2. This weak acid produces hydrogen ions in water, as shown by equation 3, hence increasing the concentration of hydrogen ions and reducing the pH.

9　Calcification: b, c.

　　Acidification: a, d, e

　　Calcification involves the precipitation of dissolved ions as calcium carbonate in the form of shells and corals. Once they are formed, such structures are vulnerable to dissolution if concentrations of ions in the water change. High acidity levels limit the formation of corals and shells.

　　Ocean acidification is the continuing decrease in pH that is occurring due to the absorption of carbon dioxide from the atmosphere. The consequence is the destruction of calcium carbonate structures such as coral reefs.

10　C. As more carbon dioxide gas dissolves in the oceans, the acidity of the oceans will increase. This will lead to calcium carbonate dissolving and increasing concentrations of hydrogen carbonate ions.

11　absorbed, reduces, decreases, right, lower, dissolve, left, decreasing

12　**a**　Decalcification

　　b　As the concentration of dissolved carbon dioxide in sea water increases, the concentration of H_3O^+ increases. Applying Le Châtelier's principle, this affects the position of the equilibrium:

　　$H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq)$

　　or:

　　$H_3O^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$

　　The free carbonate ion concentration decreases, causing a net forward reaction in the equilibrium:

　　$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

　　As a consequence, solid calcium carbonate dissolves. The rate of growth of corals can reduce, since they are composed of calcium carbonate.

13 C. It is unlikely that the greenhouse gas concentrations can be reduced in the foreseeable future. The IPCC aims to reduce the level of greenhouse gas emissions in order to stabilise their concentrations in the atmosphere.

14 C. The other statements have not been achieved.

15 The United Nations Framework Convention on Climate Change is supported by reports from the IPCC (Intergovernmental Panel on Climate Change). The ultimate objective is 'to stabilise greenhouse gas concentrations in the atmosphere at a level which prevents human-induced interference with the climate'.

16 a An increase in the average temperature of the Earth, causing a change in the rainfall patterns, a rise in the sea levels flooding of low-lying countries and coastal land.

    b Use alternative energy sources, reduce the amount of energy generated by fossil fuels, use more efficient technologies.

17 $CO_2(g) \rightleftharpoons CO_2(aq)$

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

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

$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$
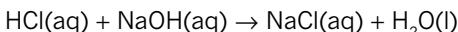
Chapter 4 Acids and bases
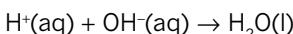
Section 4.1 Introducing acids and bases

4.1 KEY QUESTIONS

1   $HBr(g) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$

2   H_2SO_4/HSO_4^- and $H_2NO_3^+/HNO_3$

3   **a** H_2O
    b H_3O^+
    c CH_3NH_2

4   **a** NH_4^+
    b CH_3COOH
    c $H_2PO_4^-$
    d HCO_3^-

5   Brønsted–Lowry acid–base reactions are those involving the exchange of a proton (H^+ ion). The acid donates the proton to the base. In the reaction below, the HCl loses a proton to the base.

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

    The ionic equation provides a clearer way (by eliminating spectator ions) of noting the reaction between the H^+ and OH^- ions neutralising to form water.

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

6   Acting as an acid, whereby the reactant donates one proton:
    a $HCO_3^- + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
    b $HPO_4^{2-} + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)$
    c $HSO_4^- + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$
    d $H_2O(l) + H_2O(l) \rightarrow OH^-(aq) + H_3O^+(aq)$

    Acting as a base, whereby the reactant accepts one proton:
    a $HCO_3^- + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$
    b $HPO_4^{2-} + H_2O(l) \rightarrow H_2PO_4^-(aq) + OH^-(aq)$
    c $HSO_4^- + H_2O(l) \rightarrow H_2SO_4(aq) + OH^-(aq)$
    d $H_2O + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

Section 4.2 Strength of acids and bases

4.2 KEY QUESTIONS

1   **a** $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$
    b $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$
    c $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

2   Stage 1: $H_3AsO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + H_2AsO_4^-(aq)$
    Stage 2: $H_2AsO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HAsO_4^{2-}(aq)$
    Stage 3: $HAsO_4^{2-}(aq) + H_2O(l) \rightarrow H_3O^+(aq) + AsO_4^{3-}(aq)$

3   A. A strong acid readily donates a proton to a water molecule to form the hydronium ion. The complete ionisation of the acid molecule is indicated by the use of a single arrow, $\rightarrow$.

4   Stronger acids ionise more readily, forming ions in solution. As perchloric acid is a stronger acid, more hydronium ions would be present in solution than in a solution of ethanoic acid, making it a better conductor of electricity.

5   **a** $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$; $K_a = \dfrac{[H_3O][F^-]}{[HF]}$

    b $HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$; $K_a = \dfrac{[H_3O^+][ClO^-]}{[HClO]}$

    c $H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$; $K_a = \dfrac{[H_3O^+][HS^-]}{[H_2S]}$

    d $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$; $K_a = \dfrac{[H_3O^+][NH_3]}{[NH_4^+]}$

Section 4.3 **Acidity of solutions**

Worked example: Try yourself 4.3.1

CALCULATING CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 5.6×10^{-6} mol L^{-1} HNO$_3$ solution at 25°C, calculate [H$_3$O$^+$] and [OH$^-$].	
Thinking	**Working**
Find the concentration of hydronium (H$_3$O$^+$) ions.	HNO$_3$ is a strong acid, so it will ionise completely in solution. Each molecule of HNO$_3$ donates one proton to water to form one H$_3$O$^+$ ion: HNO$_3$(aq) + H$_2$O(l) → H$_3$O$^+$(aq) + NO$_3^-$(aq) Because HNO$_3$ is completely ionised in water, 5.6×10^{-6} mol L^{-1} will produce a solution with a concentration of H$_3$O$^+$ ions of 5.6×10^{-6} mol L^{-1}: i.e [H$_3$O$^+$] = 5.6×10^{-6} mol L^{-1}
Use the expression for the ionisation constant of water to calculate the concentration of OH$^-$ ions.	K_w = [H$_3$O$^+$][OH$^-$] = 1.00×10^{-14} $[OH^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]}$ Since [H$_3$O$^+$] = 5.6×10^{-6} mol L^{-1} $[OH^-] = \frac{1.00 \times 10^{-14}}{5.6 \times 10^{-6}}$ $= 1.8 \times 10^{-9}$ mol L^{-1}

Worked example: Try yourself 4.3.2

CALCULATING pH OF AN AQUEOUS SOLUTION FROM [H$_3$O$^+$]

What is the pH of a solution in which [H$_3$O$^+$] is 6.0×10^{-9} mol L^{-1}? Express your answer to two significant figures.	
Thinking	**Working**
Write down [H$_3$O$^+$] in the solution.	[H$_3$O$^+$] = 6.0×10^{-9} mol L^{-1}
Substitute the value of [H$_3$O$^+$] into: pH = $-\log_{10}$[H$_3$O$^+$] Use the logarithm function on your calculator to calculate the answer.	pH = $-\log_{10}$[H$_3$O$^+$] $= -\log_{10}(6 \times 10^{-9})$ (use your calculator) $= 8.2$

Worked example: Try yourself 4.3.3

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a 0.01 mol L^{-1} solution of Ba(OH)$_2$ at 25°C?	
Thinking	**Working**
Write down the reaction in which Ba(OH)$_2$ dissociates.	In water, each mole of Ba(OH)$_2$ completely dissociates to release 2 moles of OH$^-$ ions. Ba(OH)$_2$(aq) → Ba^{2+}(aq) + 2OH$^-$(aq)
Determine [OH$^-$].	[OH$^-$] = 2 × [Ba(OH)$_2$] $= 2 \times 0.01$ mol L^{-1} $= 0.02$ mol L^{-1}

Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \dfrac{K_w}{[OH^-]}$ $= \dfrac{1.00 \times 10^{-14}}{0.02}$ $= 5 \times 10^{-13}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(5 \times 10^{-13})$ (use your calculator) $= 12.3$

Worked example: Try yourself 4.3.4

CALCULATING pH IN A SOLUTION WHEN SOLUTE CONCENTRATION IS NOT GIVEN

What is the pH of a solution at 25°C that contains 0.50 g KOH in 500 mL of solution?	
Thinking	**Working**
Determine the number of moles of KOH.	$n(KOH) = \dfrac{m}{M}$ $= \dfrac{0.50}{56.0}$ $= 8.9 \times 10^{-3}\,mol$
Write the equation for dissocation of KOH.	$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$ KOH is completely dissociated in water.
Determine the number of moles of OH^- based on the dissociation equation.	$n(OH^-) = n(KOH)$ $= 8.9 \times 10^{-3}\,mol$
Use the formula for determining concentration given the number of moles and volume: $c = \dfrac{n}{V}$	$n = 8.9 \times 10^{-3}\,mol$ $V = 0.500\,L$ $c = \dfrac{8.9 \times 10^{-3}}{0.500}$ $= 0.0179\,mol\,L^{-1}$
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \dfrac{K_w}{[OH^-]}$ $= \dfrac{1.00 \times 10^{-14}}{0.0179}$ $= 5.6 \times 10^{-13}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(5.6 \times 10^{-13})$ (use your calculator) $= 12.3$

Worked example: Try yourself 4.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 10.4 at 25°C.	
Thinking	**Working**
Decide which form of the relationship between pH and $[H_3O^+]$ should be used: $pH = -\log_{10}[H_3O^+]$ or $[H_3O^+] = 10^{-pH}$	As you have the pH and are calculating $[H_3O^+]$, use: $[H_3O^+] = 10^{-pH}$

Substitute the value of pH into the relationship expression and use a calculator to determine the answer.	$[H_3O^+] = 10^{-pH}$ $= 10^{-10.4}$ $= 3.98 \times 10^{-11} \, mol \, L^{-1}$

Worked example: Try yourself 4.3.6

CALCULATING pH OF A SOLUTION AFTER PARTIAL NEUTRALISATION

43.0 mL of 0.200 mol L⁻¹ nitric acid is added to 15.0 mL of 0.300 mol L⁻¹ barium hydroxide (at 25°C). Calculate the pH of the final solution.

Thinking	Working
Identify the type of reaction and write an equation for the reaction.	acid + base → salt + water $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$
Identify the values for the concentrations and volumes of the reactants.	HNO_3 $Ba(OH)_2$ $c = 0.200 \, mol \, L^{-1}$ $c = 0.300 \, mol \, L^{-1}$ $V = 43.0 \, mL$ $V = 15.0 \, mL$
Calculate the number of moles of H⁺ and OH⁻.	$n(HNO_3) = \dfrac{43}{1000} \times 0.2 = 8.6 \times 10^{-3} \, mol$ $n(Ba(OH)_2) = \dfrac{15}{1000} \times 0.3 = 4.5 \times 10^{-3} \, mol$ Total $n(OH^-) = 2 \times 4.5 \times 10^{-3} = 9 \times 10^{-3} \, mol$
Identify the relationship between the number of moles of H⁺ and OH⁻. (This will always be 1:1.)	1 mol of H⁺ reacts with 1 mol of OH⁻.
Identify which of H⁺ and OH⁻ is in excess.	OH⁻ is in excess.
Calculate the number of moles of reactant in excess.	$n(OH^-)$ left $= 9 - 8.6 \times 10^{-3} = 4 \times 10^{-4} \, mol$
Calculate the concentration of the excess OH⁻.	$[OH^-] = \dfrac{4 \times 10^{-4}}{0.058} = 6.897 \times 10^{-3} \, mol \, L^{-1}$
Calculate the concentration of H⁺ (H₃O⁺).	$[H^+] = \dfrac{K_w}{OH^-}$ $[H^+] = \dfrac{1 \times 10^{-14}}{6.897 \times 10^{-3}} = 1.45 \times 10^{-12} \, mol \, L^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$pH = -\log_{10}[H_3O^+]$ $pH = -\log_{10}(1.45 \times 10^{-12}) = 11.8$

4.3 KEY QUESTIONS

1   $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

     $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

     $[OH^-] = \dfrac{1.00 \times 10^{-14}}{0.001} = 1.00 \times 10^{-11} \, mol \, L^{-1}$

2   $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

     $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

     $[OH^-] = \dfrac{1.00 \times 10^{-14}}{5.70 \times 10^{-9}} = 1.75 \times 10^{-6} \, mol \, L^{-1}$

3   $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

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

     $[OH^-] = \dfrac{1.00 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9} \, mol \, L^{-1}$

4 $pH = -\log_{10}[H_3O^+]$

$= -\log_{10}0.01$

$= 2$

5 As nitric acid is a strong acid, the concentration of H_3O^+ ions is $0.0010\,mol\,L^{-1}$.

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

$= -\log_{10}0.0010$

$= 3$

6 $[H_3O^+] = 10^{-pH}$

$= 10^{-6}$

$= 1.0 \times 10^{-6}$ (or 0.0000010) $mol\,L^{-1}$

7 $M(HCl) = M(H) + M(Cl)$

$= 1.0 + 35.5$

$= 36.5$

As HCl completely dissociates to H_3O^+ and Cl^-, $n(HCl) = n(H_3O^+)$, therefore $n(H_3O^+) = 0.01\,mol$.

$c = \dfrac{n}{V} = \dfrac{0.01}{0.20} = 0.050\,mol\,L^{-1}$

$[H_3O^+] = 0.050\,mol\,L^{-1}$

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

$= -\log_{10}0.050 = 1.3$

$= 1.3$

8 HCl

$[H_3O^+] = 10^{-2} = 0.01\,mol\,L^{-1}$

$n(HCl) = c \times V = 0.01 \times 0.1 = 0.001\,mol$

NaOH
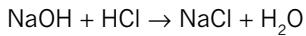
$[H_3O^+] = 10^{-11}\,mol\,L^{-1}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{H_3O^+}$

$[OH^-] = 10^{-3}\,mol\,L^{-1}$

$n(NaOH) = c \times V = 0.001 \times 0.2 = 0.002\,mol$

Neutralisation

$NaOH + HCl \rightarrow NaCl + H_2O$

1 mol of HCl react with 1 mol of NaOH; NaOH is in excess.

$n(OH^-)$ remaining $= 0.002 - 0.001 = 0.001\,mol$

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

$c = \dfrac{0.001}{0.3} = 0.0033\,mol\,L^{-1}$

$[H_3O^+] = \dfrac{K_w}{[OH^-]}$

$[H_3O^+] = \dfrac{10^{-14}}{0.0033} = 3 \times 10^{-12}$

$pH = -\log_{10}[H_3O^+] = 11.5$

Section 4.4 **Dilution of acids and bases**

Worked example: Try yourself 4.4.1

CALCULATING MOLAR CONCENTRATION AFTER DILUTION

Calculate the molar concentration of nitric acid when 80.0 mL of water is added to 20.0 mL of 5.00 mol L^{-1} HNO$_3$.	
Thinking	**Working**
The number of moles of solute does not change during a dilution. So, $c_1V_1 = c_2V_2$, where c is the concentration in mol L^{-1} and V is the volume of the solution. (Each of the volume units must be the same, litres or millilitres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	Remember that 80.0 mL was added to 20.0 mL, so the final volume is 100.0 mL. $c_1 = 5.00$ mol L^{-1} $V_1 = 20.0$ mL $V_2 = 100.0$ mL You are required to calculate c_2, the concentration after dilution.
Transpose the equation and substitute the known values into the equation to find the required value.	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{5.00 \times 20.0}{100.0}$ $= 1.00$ mol L^{-1}

Worked example: Try yourself 4.4.2

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 15.0 mL of 10.0 mol L^{-1} NaOH to dilute the solution to 2.00 mol L^{-1}?	
Thinking	**Working**
The number of moles of solute does not change during a dilution. So, $c_1V_1 = c_2V_2$, where c is the concentration in mol L^{-1} and V is the volume of the solution. (Each of the volume units must be the same, although not necessarily litres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	$c_1 = 10.0$ mol L^{-1} $V_1 = 15.0$ mL $c_2 = 2.00$ mol L^{-1} You are required to calculate V_2, the volume of the diluted solution.
Transpose the equation and substitute the known values into the equation to find the required value.	$V_2 = \frac{c_1 \times V_1}{c_2}$ $= \frac{10.0 \times 15.0}{2.00}$ $= 75.0$ mL
Calculate the volume of water to be added.	Volume of dilute solution = 75.0 mL Initial volume of NaOH = 15.0 mL So 75.0 − 15.0 = 60.0 mL of water must be added.

Worked example: Try yourself 4.4.3

CALCULATING pH OF A DILUTED ACID

10.0 mL of 0.10 mol L⁻¹ HCl is diluted to 30.0 mL. Calculate the pH of the diluted solution.	
Thinking	**Working**
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.10 \, \text{mol L}^{-1}$ $V_1 = 10.0 \, \text{mL}$ $V_2 = 30.0 \, \text{mL}$ $c_2 = ?$
Calculate c_2, which is the concentration of H_3O^+ after dilution, by transposing the formula: $c_1 V_1 = c_2 V_2$	$c_2 = \dfrac{c_1 \times V_1}{V_2}$ $= \dfrac{0.10 \times 10.0}{30.0}$ $= 0.03 \, \text{mol L}^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.03)$ $= 1.5$

Worked example: Try yourself 4.4.4

CALCULATING pH OF A DILUTED BASE

15.0 mL of 0.020 mol L⁻¹ KOH is diluted to 60.0 mL. Calculate the pH of the diluted solution.	
Thinking	**Working**
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.020 \, \text{mol L}^{-1}$ $V_1 = 15.0 \, \text{mL}$ $V_2 = 60.0 \, \text{mL}$ $c_2 = ?$
Calculate c_2, which is the concentration of $[OH^-]$ after dilution, by transposing the formula: $c_1 V_1 = c_2 V_2$	$c_2 = \dfrac{c_1 \times V_1}{V_2}$ $= \dfrac{0.020 \times 15.0}{60.0}$ $= 0.005 \, \text{mol L}^{-1}$
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \dfrac{K_w}{[OH^-]}$ $= \dfrac{1.00 \times 10^{-14}}{0.005}$ $= 2 \times 10^{-12} \, \text{mol L}^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to calculate pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(2 \times 10^{-12})$ $= 11.7$

4.4 KEY QUESTIONS

1 $c_1V_1 = c_2V_2$, $c_1 = 0.10\,\text{mol L}^{-1}$, $V_1 = 3.0\,\text{L}$, $V_2 = 4.0\,\text{L}$, $c_2 = ?$

$0.10 \times 3.0 = c_2 \times 4.0$

$c_2 = \dfrac{0.10 \times 3.0}{4.0} = 0.075\,\text{mol L}^{-1}$

2 $c_1V_1 = c_2V_2$, $c_1 = 2.0\,\text{mol L}^{-1}$, $V_1 = 10\,\text{mL}$, $V_2 = ?$, $c_2 = 0.50\,\text{mol L}^{-1}$

$2.0 \times 10 = 0.50 \times V_2$

$V_2 = \dfrac{2.0 \times 10}{0.50} = 40\,\text{mL}$

Final volume – initial volume = 40 – 10 = 30 mL, so 30 mL of water needs to be added.

3 $c_1V_1 = c_2V_2$, $c_1 = 0.60\,\text{mol L}^{-1}$, $V_1 = 20\,\text{mL}$, $V_2 = ?$, $c_2 = 0.10\,\text{mol L}^{-1}$

$0.60 \times 20 = 0.10 \times V_2$

$V_2 = \dfrac{0.60 \times 20}{0.10} = 120\,\text{mL}$

Final volume – initial volume = 120 – 20 = 100 mL, so 100 mL of water needs to be added.

4 This increases the pH by one unit.

5 $c_1V_1 = c_2V_2$, $c_1 = 0.100\,\text{mol L}^{-1}$, $V_1 = 20.0\,\text{mL}$, $V_2 = 50.0\,\text{mL}$, $c_2 = ?$

$0.100 \times 20.0 = c_2 \times 50.0$

$c_2 = \dfrac{0.100 \times 20.0}{50.0} = 0.040\,\text{mol L}^{-1}$

As NaOH dissociates completely to Na^+ and OH^-, $[NaOH] = [OH^-]$, therefore $[OH^-] = 0.040\,\text{mol L}^{-1}$

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$

$1.00 \times 10^{-14} = [H_3O^+] \times 0.040$

$[H_3O^+] = \dfrac{1.0 \times 10^{-14}}{0.040} = 2.5 \times 10^{-13}$

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

$pH = -\log_{10}2.5 \times 10^{-13} = 12.6$

6 a i The concentration of H_3O^+ ions equals the concentration of a monoprotic acid = $0.001\,\text{mol L}^{-1}$

   ii $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]} = \dfrac{1.00 \times 10^{-14}}{0.001\,\text{mol L}^{-1}} = 1 \times 10^{-11}\,\text{mol L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(10^{-3}\,\text{mol L}^{-1}) = 3$

 b i $[H_3O^+] = 0.03\,\text{mol L}^{-1}$

   ii $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]} = \dfrac{1.00 \times 10^{-14}}{0.003\,\text{mol L}^{-1}} = 3.33 \times 10^{-13}\,\text{mol L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(0.030\,\text{mol L}^{-1}) = 1.5$

 c i NaOH dissociates completely to Na^+ and OH^-, $[NaOH] = [OH^-]$, therefore $[OH^-] = 0.010\,\text{mol L}^{-1}$.

    $[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{0.010\,\text{mol L}^{-1}} = 1.0 \times 10^{-12}\,\text{mol L}^{-1}$

   ii From part **i**, $[OH^-] = 0.010\,\text{mol L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(10^{-12}\,\text{mol L}^{-1}) = 12$

 d i $10^{-4.5}\,\text{mol L}^{-1}$ HCl = $[H_3O^+] = 3.16 \times 10^{-5}\,\text{mol L}^{-1}$

   ii $[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]} = \dfrac{1.00 \times 10^{-14}}{3.16 \times 10^{-5}\,\text{mol L}^{-1}} = 3.16 \times 10^{-10}\,\text{mol L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(3.16 \times 10^{-5}\,\text{mol L}^{-1}) = 4.5$

 e i $[OH^-] = 2 \times [Ba(OH)_2] = 2 \times 0.005\,\text{mol L}^{-1} = 0.01\,\text{mol L}^{-1}$

    $[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{0.010\,\text{mol L}^{-1}} = 1.0 \times 10^{-12}\,\text{mol L}^{-1}$

   ii From part **i**, $[OH^-] = 0.01\,\text{mol L}^{-1}$

   iii $pH = -\log_{10}[H_3O^+] = -\log(1.0 \times 10^{-12}\,\text{mol L}^{-1}) = 12$

Section 4.5 **pH of salt solutions**

Worked example: Try yourself 4.5.1

DETERMINING THE ACIDITY OF A SALT PRODUCED IN A NEUTRALISATION REACTION

Determine the acidity of the salt produced by the reaction of calcium hydroxide ($Ca(OH)_2$) and oxalic acid ($H_2C_2O_4$).	
Thinking	**Working**
Write the equation for the neutralisation reaction.	$Ca(OH)_2(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4 (aq) + 2H_2O(l)$
Identify the anion and cation in the salt.	Ca^{2+} and $C_2O_4{}^{2-}$
Determine whether the ions will react with water in a hydrolysis reaction. (Are the ions neutral, acidic or basic?)	Ca^{2+} cannot accept a proton from water (Ca^{2+} is a neutral ion) $C_2O_4{}^{2-}(aq) + H_2O(l) \rightleftharpoons HC_2O_4{}^-(aq) + OH^-(aq)$ ($C_2O_4{}^{2-}$ is a basic ion)
If an ion accepts a proton from water, it is basic. If an ion donates a proton to water, it is acidic.	The salt is basic.

4.5 KEY QUESTIONS

1

Reactants	Name of salt formed	Formulae of ions present in the salt solution
Hydrochloric acid + magnesium hydroxide	Magnesium chloride	$Mg^{2+}(aq) + Cl^-(aq)$
Sulfurous acid + zinc hydroxide	Zinc sulfite	$Zn^{2+}(aq) + SO_3{}^{2-}(aq)$
Phosphoric acid + potassium hydroxide	Potassium phosphate	$K^+(aq) + PO_4{}^{3-}(aq)$
Ethanoic acid + calcium hydroxide	Calcium ethanoate	$Ca^{2+}(aq) + CH_3COO^-(aq)$
Ammonia + nitric acid	Ammonium nitrate	$NH_4{}^+(aq) + NO_3{}^-(aq)$
Phosphoric acid + sodium hydroxide	Sodium dihydrogenphosphate	$Na^+(aq) + H_2PO_4{}^-(aq)$

2   **a** $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^- (aq) + OH^-(aq)$
     b $ClO_2{}^-(aq) + H_2O(l) \rightleftharpoons HClO_2 (aq) + OH^-(aq)$
     c $PH_4{}^+(aq) + H_2O(l) \rightleftharpoons PH_3(aq) + H_3O^+(aq)$
     d $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$

3   **a**   Neutral: KNO_3 is the salt of a strong acid and a strong base (KOH and HNO_3). Neither ion can hydrolyse in aqueous solution.
     b   Acidic: NH_4NO_3 is the salt of a strong acid and a weak base (HNO_3 and NH_3). The nitrate ion cannot hydrolyse but the ammonium ion can.
        $NH_4{}^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
     c   Basic: $Ca(H_3COO)_2$ is the salt of a weak acid (CH_3COOH) and a strong base ($Ca(OH)_2$). The calcium ion cannot hydrolyse but the ethanoate ion can.
        $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
     d   Neutral: $MgBr_2$ is the salt of a strong acid (HBr) and a strong base ($Mg(OH)_2$). Neither ion can hydrolyse in aqueous solution.

CHAPTER 4 REVIEW

1 B

NH$_4$Cl dissolves, producing NH$_4^+$ and Cl$^-$.

NH$_4^+$ hydrolyses, producing NH$_3$ and H$_3$O$^+$.

Cl$^-$ does not hydrolyse in water, therefore is most abundant.

2 D. A base is a proton acceptor. CH$_3$NH$_2$ accepts a proton to produce CH$_3$NH$_3^+$.

3 **a** NH$_4^+$
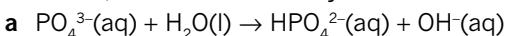
b HCl

c HCO$_3^-$
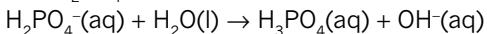
d H$_3$O$^+$

e CH$_3$COOH(aq)
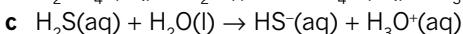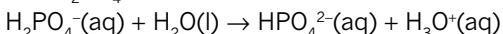
4 Remember that if a chemical acts as a base, it will accept a proton. In this question, the proton comes from a water molecule, but this is not always the case. If a chemical acts as an acid, it must be able to donate one or more protons.

a PO$_4^{3-}$(aq) + H$_2$O(l) → HPO$_4^{2-}$(aq) + OH$^-$(aq)

b The H$_2$PO$_4^-$ accepts a proton from water, and acts as a base:

H$_2$PO$_4^-$(aq) + H$_2$O(l) → H$_3$PO$_4$(aq) + OH$^-$(aq)

The H$_2$PO$_4^-$ donates a proton to the water, and acts as an acid:

H$_2$PO$_4^-$(aq) + H$_2$O(l) → HPO$_4^{2-}$(aq) + H$_3$O$^+$(aq)

c H$_2$S(aq) + H$_2$O(l) → HS$^-$(aq) + H$_3$O$^+$(aq)
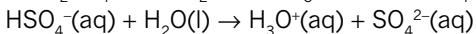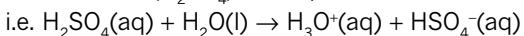
5 **a** Cl$^-$

b H$_2$O
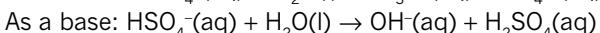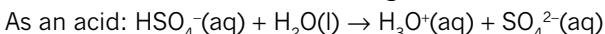
c OH$^-$

d SO$_4^{2-}$

6 **a** Sulfuric acid (H$_2$SO$_4$) is a diprotic acid because each molecule can donate two protons to a base:

i.e. H$_2$SO$_4$(aq) + H$_2$O(l) → H$_3$O$^+$(aq) + HSO$_4^-$(aq)

HSO$_4^-$(aq) + H$_2$O(l) → H$_3$O$^+$(aq) + SO$_4^{2-}$(aq)
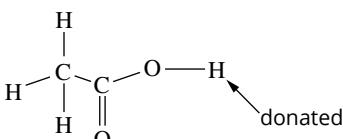
The HSO$_4^-$ ion, however, is amphiprotic because it can act as either an acid or a base, depending on the environment. In water it will undergo both acid and base reactions. For example:

As an acid: HSO$_4^-$(aq) + H$_2$O(l) → H$_3$O$^+$(aq) + SO$_4^{2-}$(aq)

As a base: HSO$_4^-$(aq) + H$_2$O(l) → OH$^-$(aq) + H$_2$SO$_4$(aq)
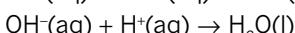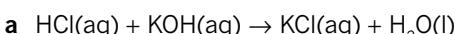
b A strong acid is one that ionises completely in solution (e.g. HCl). A concentrated acid is one in which there is a large amount of acid dissolved in a given volume of solution; for example, 5 mol L^{-1} HCl and 5 mol L^{-1} CH$_3$COOH are concentrated acids.
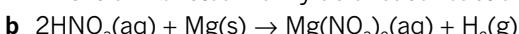
7
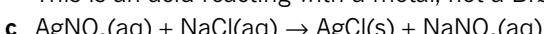
8 The first step, as in the development of any equation, is to write the correct chemical formulas for each of the chemicals involved.

a HCl(aq) + KOH(aq) → KCl(aq) + H$_2$O(l)

OH$^-$(aq) + H$^+$(aq) → H$_2$O(l)

This is a Brønsted–Lowry acid–base reaction. H$^+$ donated to OH$^-$.

b 2HNO$_3$(aq) + Mg(s) → Mg(NO$_3$)$_2$(aq) + H$_2$(g)
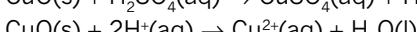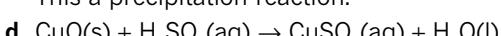
This is an acid reacting with a metal, not a Brønsted–Lowry acid–base reaction.

c AgNO$_3$(aq) + NaCl(aq) → AgCl(s) + NaNO$_3$(aq)

This a precipitation reaction.

d CuO(s) + H$_2$SO$_4$(aq) → CuSO$_4$(aq) + H$_2$O(l)

CuO(s) + 2H$^+$(aq) → Cu^{2+}(aq) + H$_2$O(l)

This is a Brønsted–Lowry acid–base reaction. H$^+$ donated to O^{2-}.

9 D

K_a is a measure of the extent to which a reaction occurs
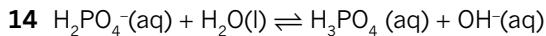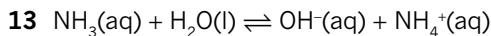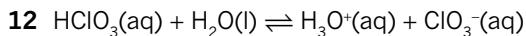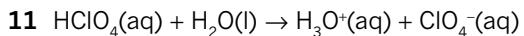
K_a for accepting a proton > K_a for donating a proton. This means that H$_2$PO$_4^-$ more readily accepts a proton than donates a proton in water.

10 C

pH of $0.00001\,mol\,L^{-1}$ H^+ is 5

A monoprotic strong acid (HA) hydrolyses so that $[H^+] = [HA] = 0.00001\,mol\,L^{-1}$

I, II and IV must be diprotic or triprotic and may be strong or weak

11 $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$

12 $HClO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_3^-(aq)$

13 $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

14 $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$

15 At 25°C, $[OH^-] \times [H_3O^+] = 1 \times 10^{-14}$

(Note: [ ] denotes concentration in molar units.)

$\therefore [OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

a $10^{-11}\,mol\,L^{-1}$

b $10^{-9}\,mol\,L^{-1}$

c $1.8 \times 10^{-6}\,mol\,L^{-1}$

d $2.9 \times 10^{-3}\,mol\,L^{-1}$

e $1.5 \times 10^{-13}\,mol\,L^{-1}$

f $4.48 \times 10^{-2}\,mol\,L^{-1}$

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

$[H_3O^+] = 10^{-pH}$ (or 10 to the power of pH)

$= 10^{-1}$

$= 0.1\,mol\,L^{-1}$

At 25°C, $[OH^-] \times [H_3O^+] = 1 \times 10^{-14}$

$\therefore [OH^-] = \dfrac{1.00 \times 10^{-14}}{[H_3O^+]}$

$= \dfrac{1.00 \times 10^{-14}}{0.10\,mol\,L^{-1}} = 1.0 \times 10^{-13}\,mol\,L^{-1}$

b $[H_3O^+] = 10^{-3}\,mol\,L^{-1}$

$[OH^-] = 10^{-11}\,mol\,L^{-1}$

c $[H_3O^+] = 10^{-7}\,mol\,L^{-1}$

$[OH^-] = 10^{-7}\,mol\,L^{-1}$

d $[H_3O^+] = 2 \times 10^{-12}\,mol\,L^{-1}$

$[OH^-] = 5 \times 10^{-3}\,mol\,L^{-1}$

17 A solution with a pH of 7.4 is basic.

The concentration of hydroxide ions will be greater than the concentration of hydronium ions.

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

pH = 3

$\therefore [H_3O^+] = 10^{-3}\,mol\,L^{-1}$

pH = 5

$\therefore [H_3O^+] = 10^{-5}\,mol\,L^{-1}$

$\therefore$ the difference is a factor of 100.

19 a $[H^+] = 10^{-pH} = 0.001\,mol\,L^{-1}$

$[OH^-] = \dfrac{1.00 \times 10^{-14}}{[H^+]} = \dfrac{1.00 \times 10^{-14}}{10^{-3}\,mol\,L^{-1}} = 1.0 \times 10^{-11}\,mol\,L^{-1}$

b $[H^+] = 10^{-10}\,mol\,L^{-1}$, $[OH^-] = 10^{-4}$

c $[H^+] = 3.16 \times 10^{-9}\,mol\,L^{-1}$, $[OH^-] = 3.16 \times 10^{-6}\,mol\,L^{-1}$

d $[H^+] = 1.58 \times 10^{-6}\,mol\,L^{-1}$, $[OH^-] = 6.3 \times 10^{-9}\,mol\,L^{-1}$

e $[H^+] = 2.5 \times 10^{-10}\,mol\,L^{-1}$, $[OH^-] = 4.0 \times 10^{-5}\,mol\,L^{-1}$

f $[H^+] = 3.16 \times 10^{-14}\,mol\,L^{-1}$, $[OH^-] = 0.316\,mol\,L^{-1}$

20 $pH = -\log_{10}[H_3O^+] = -\log_{10}5.3$

$[H_3O^+] = 10^{-5.3}$, $[OH^-] = \dfrac{1.00 \times 10^{-14}}{10^{-5.3}\,\text{mol L}^{-1}} = 2.0 \times 10^{-9}\,\text{mol L}^{-1}$

21 Remember to use $[OH^-] \times [H_3O^+] = 1 \times 10^{-14}$ at 25°C and $pH = -\log_{10}[H_3O^+]$.

   a $pH = 2$, $\therefore$ $[H_3O^+] = 10^{-2}$ or $0.01\,\text{mol L}^{-1}$

   b The formula for amounts of substance in solution is $n = c \times V$ (where n is the amount in moles, c the concentration in mol L^{-1} and V the volume of the solution in litres).

   $n = 0.01 \times 0.500 = 0.005\,\text{mol}$

22 These three questions have two steps.

   Step 1. Dilution questions are best answered using the formula $c_1V_1 = c_2V_2$, where c is the concentration in mol L^{-1} and V is the volume of the solution. Each of the volume units needs to be the same, although not necessarily litres.

   Step 2. Also remember, $pH = pH = -\log_{10}[H_3O^+]$

   a $c_2 = 0.25 \times \dfrac{10}{50} = 0.05\,\text{mol L}^{-1}$

   $\therefore [H_3O^+] = 0.05\,\text{mol L}^{-1}$

   $pH = -\log_{10}(0.05\,\text{mol L}^{-1}) = 1.3$

   b $c_2 = 0.0050 \times \dfrac{20}{500} = 2 \times 10^{-4}\,\text{mol L}^{-1}$

   $\therefore [OH^-] = 2.0 \times 10^{-4}\,\text{mol L}^{-1}$

   $[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{[OH^-]} = \dfrac{1.00 \times 10^{-14}}{2 \times 10^{-4}\,\text{mol L}^{-1}} = 5.0 \times 10^{-11}\,\text{mol L}^{-1}$

   $pH = -\log_{10}(5.0 \times 10^{-11}\,\text{mol L}^{-1}) = 10.3$

   c $c_2 = 0.15 \times \dfrac{10}{1500}$ (1.5 L has been converted to mL to maintain identical units)

   $= 0.001\,\text{mol L}^{-1}$

   $\therefore [H_3O^+] = 0.001\,\text{mol L}^{-1} = 10^{-3}\,\text{mol L}^{-1}$

   $\therefore pH = 3$

23 $c_1V_1 = c_2V_2$, $c_1 = 18.0\,\text{mol L}^{-1}$, $V_1 = ?$, $c_2 = 2.00\,\text{mol L}^{-1}$, $V_2 = 1.00\,\text{L}$

   $V_1 = \dfrac{2.00 \times 1.00}{18.0} = 0.111\,\text{L} = 111\,\text{mL}$

24 Initial $pH = 2$. $[H_3O^+] = 10^{-pH} = 10^{-2} = 0.010\,\text{mol L}^{-1}$

   Final $pH = 4$. $[H_3O^+] = 10^{-pH} = 10^{-4} = 1.00 \times 10^{-4}\,\text{mol L}^{-1}$

   $c_1V_1 = c_2V_2$, $c_1 = 0.010\,\text{mol L}^{-1}$, $V_1 = 10.0\,\text{mL}$, $c_2 = 1.00 \times 10^{-4}\,\text{mol L}^{-1}$, $V_2 = ?$

   $V_2 = \dfrac{0.010 \times 1.00}{1.00 \times 10^{-4}} = 1000\,\text{mL}$

25 $pH(\text{initial}) = -\log_{10}[H_3O^+] = 1.0$

   $c_1V_1 = c_2V_2$, $c_1 = 0.10\,\text{mol L}^{-1}$, $V_1 = 40.0\,\text{mL}$, $c_2 = ?$, $V_2 = 500\,\text{mL}$

   $c_2 = \dfrac{0.10 \times 40.0}{500} = 8.0 \times 10^{-3}\,\text{mol L}^{-1}$

   $pH(\text{final}) = -\log_{10}(8 \times 10^{-3}) = 2.10$

   Therefore the pH will increase.

26 B

   In A, the ammonium ion hydrolyses to produce an acid and the ethanoate ion hydrolyses to produce a base. The pH of the salt will be close to neutral (pH = 7)
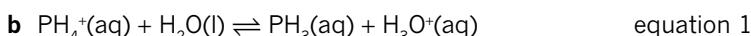
   In B, the ammonium ion hydrolyses to produce an acid. The chloride ion cannot accept a proton because it is the conjugate base of a strong acid. The solution will be acidic with pH < 7.

   In C, the ammonium ion hydrolyses to produce an acid and the phosphate ion hydrolyses to produce a base. The pH of the salt will be close to neutral (pH = 7).

   In D, the sodium ion cannot accept or donate a proton and the bromide is the conjugate base of a strong acid. The solution will be neutral (pH = 7).

27 a

Salt dissolved	Approximate pH (5, 7 or 9)
Potassium nitrate	7
Ammonium chloride	5
Sodium phosphate	9
Potassium hydrogensulfate	5

b $PH_4^+(aq) + H_2O(l) \rightleftharpoons PH_3(aq) + H_3O^+(aq)$ equation 1
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ equation 2
Since pH < 7, $[H^+]$ must be greater than $[OH^-]$
And so, the position of equilibrium in equation 1 must be further over to the right-hand side than in equation 2.

28 Solution A: weaker base, few freely moving charged particles—ammonia

Solution B: neutral, no freely moving charged particles—glucose

Solution C: strong base, many freely moving charged particles—sodium hydroxide

Solution D: strong acid, many freely moving charged particles—hydrochloric acid

Solution E: weaker acid, few freely moving charged particles—ethanoic acid
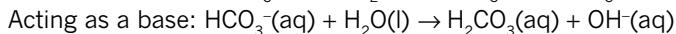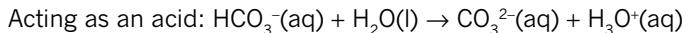
29 a i A Brønsted–Lowry acid is a proton donor.

   **ii** A strong base is a substance that readily accepts hydrogen ions.
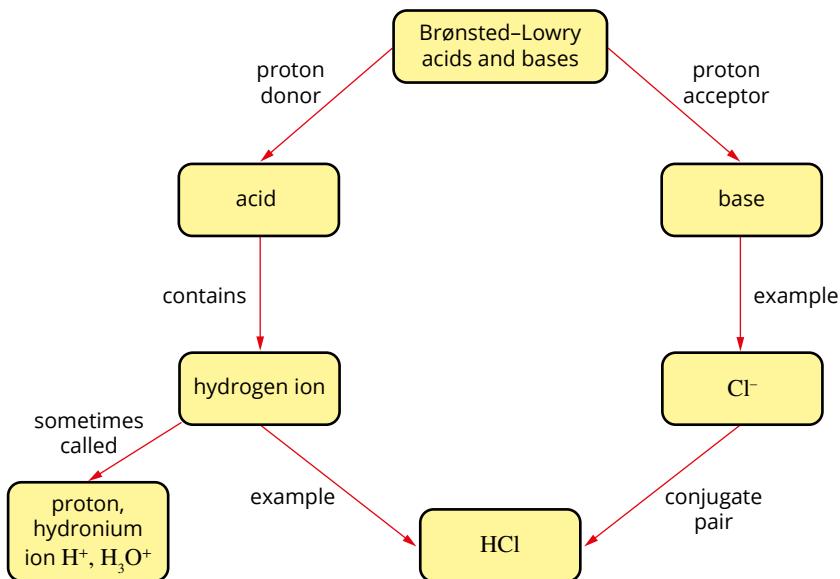
   iii Molarity is a measure of concentration of a solution expressed in $mol\,L^{-1}$.

   iv The conjugate acid of a base contains one more hydrogen ion (proton) than the base.

b An amphiprotic substance can act as an acid (proton donor) or a base (proton acceptor).

Acting as an acid: $HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$

Acting as a base: $HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$

30

31 a $NH_3(l) + NH_3(l) \rightleftharpoons NH_4^+(am) + NH_2^-(am)$
   acid 1   base 2   acid 2   base 1

b As the value of K increases, the concentration of ions increases. Heating a reaction in equilibrium favours the endothermic reaction. Thus the forward for the ionisation of ammonia is endothermic.

Chapter 5 **Buffers**

Section 5.1 **Introducing buffers**

5.1 KEY QUESTIONS

1 D. An appropriate buffer made from a weak acid and its conjugate base.

2 $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

3 $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

4 $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

5 Alkaline, acidic, acidic

Section 5.2 **How buffers work**

5.2 KEY QUESTIONS

1 C. The additional OH^- ions react with NH_4^+ which are converted to NH_3. The pH of the solution does not change significantly.

2 CH_3COO^-, left, H_3O^+, small, CH_3COOH, H_3O^+.

3 C. This solution has the greatest concentration of lactic acid and its conjugate. Therefore, it can accept the most hydronium or hydroxide ions before reaching buffer capacity.

Section 5.3 **Applications of buffers**

5.3 KEY QUESTIONS

1 $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq)$
   $H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq)$
   $H_6C_8O_7(aq) \rightleftharpoons H_5C_8O_7^-(aq)$

2 **a** $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
   b When acid is added the concentration of H_3O^+ increases and the equilibrium is disturbed. In accordance with Le Châtelier's principle, the equilibrium moves to the left to re-establish equilibrium.

3 A more alkaline environment disturbs the equilibrium. The equilibrium moves to the right as the $H_2PO_4^-$ reacts with the additional base; therefore, the concentration of $H_2PO_4^-$ will decrease.

4 $H_6C_8O_7(aq) + H_2O(l) \rightleftharpoons H_5C_8O_7^-(aq) + H_3O^+(aq)$

CHAPTER 5 **REVIEW**

1 A near equimolar solution of either a weak acid and its conjugate or a weak base and its conjugate.

2 A conjugate acid is a species formed when a base accepts a proton; a conjugate base is a species formed when a proton is removed from an acid.

3 $CH_3COOH(aq)/CH_3COO^-(aq)$, $NH_3(aq)/NH_4^+(aq)$

4 A cannot be a buffer because the NaOH is a strong base. Hence, the reverse reaction cannot occur. In B, the acetate ion readily accepts a proton to form acetic acid.

5 $H_2PO_4^-(aq)$ (acid) $\rightleftharpoons HPO_4^{2-}(aq)$ (base)

6 HPO_4^{2-}, left, H_3O^+, small, $H_2PO_4^-$, H_3O^+

7 The number of moles of acid or base that can be added to a buffer before a significant change in pH is observed (usually one pH unit).

8 D

9 **a** Carbonic acid/hydrogencarbonate, dihydrogen phosphate/monohydrogen phosphate

b Carbonic acid/hydrogencarbonate, citric acid/citrate

10 E numbers are a system of labelling used to classify food additives. E numbers between E330 and E340 represent a group of antioxidants, food additives that can also act as buffers.

11 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. Increases, decreases, returns to almost the original value

12 The phosphate buffer system ($H_2PO_4^-/HPO_4^{2-}$) is described by the chemical equation: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$. If the hydronium ion concentration rises the equilibrium is disturbed. In accordance with Le Châtelier's principle, the equilibrium moves to the left to re-establish equilibrium. In a more alkaline environment, the equilibrium is disturbed and moves to the right.

13 The buffer can be summarised as: $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

Because both species are present, the equation can move to the RHS (right-hand side) or the LHS (left-hand side) depending on the $[H_3O^+(aq)]$. Thus it is a buffer.

14 Lactic acid $C_3H_6O_3$ is a monoprotic acid. It ionises: $C_3H_6O_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_3H_5O_3^-(aq)$. This causes a drop in pH with a rise in $[H_3O^+]$ in the blood, which affects the hydrogen carbonate/bicarbonate buffer. $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. In accordance with Le Châtelier's principle, the rise in $[H_3O^+(aq)]$ causes the buffer to move to the LHS and absorb the excess H_3O^+.

15 **a** With no removal of carbon dioxide the blood pH will fall.

b $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. The basic HCO_3^- reacts with the additional hydronium ions to raise the pH.

16 **a** $C_6H_8O_7(aq) + H_2O(l) \rightleftharpoons C_6H_7O_7^-(aq) + H_3O^+(aq)$

b $C_6H_7O_7^-(aq)$

c $C_6H_8O_7(aq) + H_2O(l) \rightleftharpoons C_6H_7O_7^-(aq) + H_3O^+(aq)$

If the hydronium ion concentration rises the equilibrium is disturbed. In accordance with Le Châtelier's principle, the equilibrium moves to the LHS to re-establish equilibrium. In a more alkaline environment, the equilibrium is disturbed and the equilibrium moves to the right.

17 The buffer can be summarised as: $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. In accordance with Le Châtelier's principle, when acidity is increased the equilibrium moves to the LHS to re-establish equilibrium. In a more alkaline environment the equilibrium is disturbed and the equilibrium moves to the RHS

18 **a** $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

Excess $OH^-(aq)$ would decrease the $[H_3O^+(aq)]$. In accordance with Le Châtelier's principle, this will cause the third equation to move to the right. Thus the $[H_2CO_3(aq)]$ will fall. This decrease will, in accordance with Le Châtelier's principle, cause the second equation to move to the RHS and decrease $[CO_2(aq)]$. There would be less $CO_2(aq)$ than in pure water.

b Atmospheric CO_2 reacts with ocean water, as shown in three equations:

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

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

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

Calcium carbonate is sparing soluble in water. $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$. Coral uses the reverse reaction to make coral reefs. By increasing the $[CO_2(g)]$ in the atmosphere, the first, second and third reactions are moved to the right in accordance with Le Châtelier's principle. Thus the ocean becomes more acidic. This increase in $[H_3O^+(aq)]$ causes a decrease in $[CO_3^{2-}(aq)]$ thus:

$CO_3^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$

and limits the formation of calcium carbonate solid. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$

Chapter 6 Indicators

Section 6.1 Characteristics of indicators

6.1 KEY QUESTIONS

1 C. Indicators are large organic molecules whose colour changes in response to changes in the pH of the solution they are dissolved in. They are either weak acids or weak bases. In solution, the acid form of the indicator is in equilibrium with its conjugate base and the position of equilibrium changes depending on the pH. The colour of the acidic form of an indicator (HIn) and the colour of its conjugate base (In⁻) are different and visible at low concentrations. Hence, option C is the suitable answer.

2   **a** 0–1.7
    b 8.2–14
    c Approximately 4.6

Section 6.2 Common indicators

6.2 KEY QUESTIONS

1 The ammonia and sodium hydroxide solutions change colour because they are both basic. Phenolphthalein is colourless in solutions of pH less than 8.2. Ammonia and sodium hydroxide are strong bases, so the phenolphthalein would appear magenta in colour.

2   **a** HIn, In⁻
    b The concentration of HIn is much greater than the concentration of In⁻, and the colour of the solution is red.

3 B. According to Figure 6.2.2, bromothymol blue is yellow at pH 0–5.4; and in Figure 6.2.4, methyl orange is yellow at pH 4.4–14. The only option that shows this is B.

4   **a** violet
    b violet
    c yellow

Section 6.3 pH range of an indicator

6.3 KEY QUESTIONS

1 The end point is the point in the titration at which the indicator changes colour. The equivalence point is the point in the reaction at which equivalent amounts of acid and base have been mixed according to the ratio given in the chemical equation.

2 C. Alizarin yellow indicator changes colour at pH 11 when the concentrations of the acidic form and its conjugate base are equal. Therefore, it can be used to distinguish between solutions of pH 9 and pH 13 because it will appear a different colour at the two pH values.

3   **a** Cgr^-, H_3O^+
    b **i** purple
       ii red
      iii blue
      iv red

CHAPTER 6 REVIEW
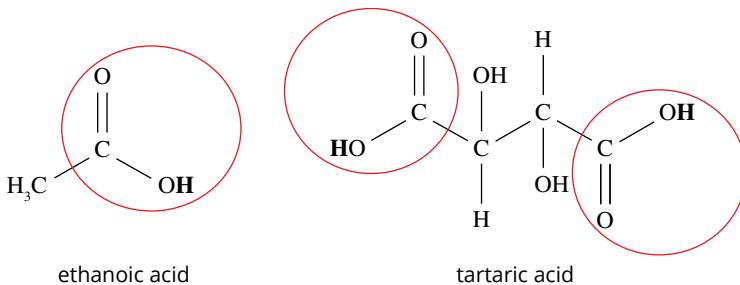
1 $HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$

2 C. Indicators are large organic molecules that change colour in response to changes in the pH of the solution they are dissolved in. They are either weak acids or weak bases. In solution, the acidic form is in equilibrium with its conjugate base and the position of equilibrium changes depending on the pH. The colours of the acidic form (HIn) and its conjugate base (In⁻) are different and visible at low concentrations. Hence, option C is the only correct answer.

3 **a** yellow
  b colourless
  c intermediate between blue and yellow

4 **a** synthetic
  b natural; litmus is derived from lichens
  c synthetic

5 Universal indicator is a mixture of several indicators and so it changes through a range of colours.

6 **a** yellow
  b The addition of an acid solution of pH 5 will shift the equilibrium to the left. The concentration of HBB (acidic form) molecules is now much greater than the concentration of BB⁻ ions (conjugate base) and the solution is yellow.

7 pH 8.3 and very pale pink (practically colourless)

8 The end point (during a titration) is when the indicator changes colour. The equivalence point is the point during a neutralisation reaction when the amounts of acid and base are in the stoichiometric ratio represented by the reaction equation.

9 Near the equivalence point, a very small addition of either the acid or the base in the burette can cause a large change in pH. A sharp end point is one at which the indicator changes colour (due to a large change in pH) with just one additional drop of the solution being added from the burette. Selecting the indicator based on the expected equivalence point enables a sharp end point to be seen.

10 Le Châtelier's principle states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change. Therefore, in reactions with weak acids and their conjugate bases, the addition of the base will cause the system to move the equilibrium position towards the reactants. This causes the colour of the indicator to appear as it would in acidic solution.

Chapter 7 Volumetric analysis

Section 7.1 Acids and bases in water

7.1 KEY QUESTIONS

1 Non-metal oxides are acidic and they lower the pH of the water.

2 Nitrogen oxides produced by the reaction of nitrogen and oxygen from the air in internal combustion engines contribute to the formation of acid rain. Acid rain is more acidic than pure water (pH of 7); therefore, nitrogen oxides lower the pH.

3 $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

4 Ethanoic acid can donate only one proton from its single carboxylic acid group; therefore, it is a monoprotic acid. Tartaric acid can donate two protons from its two carboxylic acid groups; therefore, it is a diprotic acid.

ethanoic acid   tartaric acid

Section 7.2 Calculations involving acids and bases

Worked example: Try yourself 7.2.1

A SOLUTION VOLUME–VOLUME CALCULATION

What volume of $0.500\,mol\,L^{-1}$ hydrochloric acid (HCl) reacts completely with $25.0\,mL$ of $0.100\,mol\,L^{-1}$ calcium hydroxide ($Ca(OH)_2$) solution? The salt formed in this acid–base reaction is calcium chloride.

Thinking	Working
Write a balanced full equation for the reaction.	$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$
Identify the 'known', and calculate the amount, in mol, of the substances with known volume and concentration.	The known is calcium hydroxide (the volume and concentration of calcium hydroxide solution are given) use $n = cV$ (remember that volume must be expressed in litres). $n(Ca(OH)_2) = cV$ $\qquad = 0.100 \times 0.0250$ $\qquad = 0.00250\,mol$
Use the mole ratio from the equation to calculate the amount, in mol, of the required substances.	The balanced equation shows that 2 mol of hydrochloric acid reacts with 1 mol of calcium hydroxide. $\dfrac{n(HCl)}{n(Ca(OH)_2)} = \dfrac{2}{1}$ $n(HCl) = \dfrac{2}{1} \times n(Ca(OH)_2)$ $\qquad = \dfrac{2}{1} \times 0.00250$ $\qquad = 0.00500\,mol$
Calculate the volume required.	The volume of HCl is found by using $n = cV$. $V(HCl) = \dfrac{n}{c}$ $\qquad = \dfrac{0.00500}{0.500}$ $\qquad = 0.0100\,L = 10.0\,mL$

Worked example: Try yourself 7.2.2

A SOLUTION VOLUME–CONCENTRATION CALCULATION

20.5 mL of 0.200 mol L^{-1} hydrochloric acid reacts completely with 18.8 mL of sodium hydroxide solution. Calculate the concentration of the sodium hydroxide.

Thinking	Working
Write a balanced full equation for the reaction.	NaOH(aq) + HCl(aq) → NaCl(aq) + H$_2$O(l)
Identify the 'known', and calculate the amount, in mol, of the substance with known volume and concentration.	The known is hydrochloric acid Use $n = cV$ $n(HCl) = cV$ $ = 0.200 \times 0.0205$ $ = 0.00410$ mol
Use the mole ratio from the equation to calculate the amount, in mol, of the required substances.	The balanced equation shows that 1 mol of hydrochloric acid reacts with 1 mol of sodium hydroxide. $n(NaOH) = \frac{1}{1} \times 0.00410$ $ = 0.00410$ mol
Calculate the concentration required.	The concentration of NaOH is found by using $c = \frac{n}{V}$. (Remember that 18.8 mL = 0.0188 L) $ = \frac{0.00410}{0.0188}$ $ = 0.218$ mol L^{-1}

7.2 KEY QUESTIONS

1 **a** H$_2$SO$_4$(aq) + 2KOH(aq) → K$_2$SO$_4$(aq) + 2H$_2$O(l)
   b $n(KOH) = cV = 0.300 \times 0.0100 = 0.00300$ mol

   $n(H_2SO_4) = 0.00300 \times \frac{1}{2} = 0.00150$

   $V(H_2SO_4) = \frac{0.00150}{0.100} = 0.0150$ L = 15.0 mL

2 **a** 2HNO$_3$(aq) + Ca(OH)$_2$(aq) → Ca(NO$_3$)$_2$(aq) + 2H$_2$O(l)
   b $n(Ca(OH)_2) = cV = 0.100 \times 0.010 = 0.00100$ mol
      $n(HNO_3) = 2 \times 0.00100$ mol $= 0.00200$ mol

   $c(HNO_3) = \frac{n}{V} = \frac{0.00200}{0.0150} = 0.133$ mol L^{-1}

3 **a** HNO$_3$(aq) + KOH(aq) → KNO$_3$(aq) + H$_2$O(l)
   b $n(KOH) = cV = 0.09927 \times 0.02000 = 0.001985$ mol
   c $n(HNO_3) = n(KOH) = 0.001985$ mol
   d $c(HNO_3) = \frac{n}{V} = \frac{0.001985}{0.01826} = 0.1087$ mol L^{-1}

Section 7.3 **Standard solutions**

Worked example: Try yourself 7.3.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 17.0 g of oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) dissolved in a 250.0 mL volumetric flask.	
Thinking	**Working**
Use the chemical formula to determine the molar mass (M) of the compound.	The molar mass (M) of oxalic acid dihydrate ($H_2C_2O_4.2H_2O$) is $(1.008 \times 6) + (12.01 \times 2) + (16.00 \times 6) = 126.068 \, g \, mol^{-1}$
Use the mass (m) and molar mass (M) of the compound and the formula $n = \frac{m}{M}$ to determine the amount, in mol.	$n = \frac{17.0}{126.068}$ $= 0.13485 \, mol$
Use the amount, in mol, to determine the concentration of the solution using the formula $c = \frac{n}{V}$.	$c = \frac{0.13485}{0.250}$ $= 0.539 \, mol \, L^{-1}$

7.3 KEY QUESTIONS

1   Weigh the solid primary standard on an electronic balance.

Transfer the solid into the volumetric flask using a clean, dry funnel.

Rinse any remaining solid particles into the flask using deionised water.

Half fill the flask with deionised water and swirl vigorously to dissolve the solid.

Fill the flask with deionised water to just below the calibration mark.

Add deionised water drop by drop up to the calibration line on the flask until the bottom of the meniscus touches the line.

Stopper and shake the solution to ensure an even concentration throughout.

2   $n = \frac{m}{M} = \frac{2.042}{204.2} = 0.01000 \, mol$

$c = \frac{n}{V} = \frac{0.01000}{0.050000} = 0.2000 \, mol \, L^{-1}$

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

$n = c \times V = 0.500 \times 0.2500 = 0.125 \, mol$

$m = n \times M = 0.125 \times 105.99 = 13.25 \, g = 13.3 \, g$

Section 7.4 **Volumetric analysis**

7.4 KEY QUESTIONS

1   A. The concentration of NaOH doubled. Consequently, the volume of NaOH solution required to react will be halved. A strong acid is reacting with a strong base so the pH will be 7.

2

Indicator	Colour after adding indicator
Alizarin yellow	Yellow
Bromothymol blue	Yellow
Methyl red	Orange
Methyl orange	Yellow
Phenolphthalein	Colourless

3 Trials 2, 3 and 5 provide concordant titres.

Average titre $= \frac{25.46 + 25.38 + 25.42}{3} = 25.42\,\text{mL}$

Section 7.5 Calculations in volumetric analysis

Worked example: Try yourself 7.5.1

SIMPLE TITRATION

The concentration of a solution of barium hydroxide ($Ba(OH)_2$) was determined by titration with a standard solution of hydrochloric acid.

A 10.00 mL aliquot of $Ba(OH)_2$ solution was titrated with a 0.125 M solution of HCl. Titres of 17.23 mL, 17.28 mL and 17.21 mL of HCl were required to reach the end point.

What is the concentration of the barium hydroxide solution?

Thinking	Working
Write a balanced chemical equation for the reaction.	An acid is reacting with a metal hydroxide, or base, so the products will be a salt and water. $2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$
Determine the volume of the average titre.	Average titre $= \frac{17.21 + 17.23 + 17.28}{3}$ $= 17.24\,\text{mL}$
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(HCl) = c \times V$ $= 0.125 \times 0.01724$ $= 0.002155\,\text{mol}$
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that would have reacted with the given amount, in mol, of the standard solution.	mole ratio $= \frac{n(Ba(OH)_2)}{n(HCl)} = \frac{1}{2}$ $n(Ba(OH)_2) = \frac{1}{2} \times n(HCl)$ $= \frac{1}{2} \times 0.002155$ $= 0.001078\,\text{mol}$
Determine the concentration of the unknown substance.	$c(Ba(OH)_2) = \frac{n}{V}$ $= \frac{0.001078}{0.01000}$ $= 0.108\,\text{mol L}^{-1}$
Express your answer to the appropriate number of significant figures.	The final result is rounded off to three significant figures corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of the $Ba(OH)_2 = 0.108\,\text{mol L}^{-1}$

Worked example: Try yourself 7.5.2

TITRATION THAT INVOLVES DILUTION

A commercial concrete cleaner contains hydrochloric acid. A 10.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask.

A 20.00 mL aliquot of 0.2406 mol L^{-1} sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The methyl orange indicator changed permanently from yellow to red when 18.68 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Thinking	Working
Write a balanced chemical equation.	A dilute acid is reacting with a metal carbonate so the products will be a salt, water and carbon dioxide gas. $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
Using the concentration of the standard solution, calculate the amount, in mol, of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(Na_2CO_3) = cV$ $\qquad = 0.2406 \times 0.02000$ $\qquad = 0.004812\,mol$
Use the mole ratio in the equation to calculate the amount, in mol, of the diluted unknown solution that reacted in the titration.	$\dfrac{n(HCl)}{n(Na_2(CO_3))} = \dfrac{2}{1}$ $n(HCl) = \dfrac{2}{1} \times n(Na_2CO_3)$ $\qquad = \dfrac{2}{1} \times 0.004812$ $\qquad = 0.009624\,mol$
Calculate the concentration of diluted unknown solution reacting in the titration.	$V(\text{diluted HCl}) = 0.01868\,L$ $c(HCl) = \dfrac{n}{V}$ $\qquad = \dfrac{0.009624}{0.01868}$ $\qquad = 0.5152\,mol\,L^{-1}$
Multiply by the dilution factor to determine the concentration of undiluted concrete cleaner.	Dilution factor $= \dfrac{250.0}{10.00} = 25.00$ So undiluted $c(HCl) = $ diluted $c(HCl) \times 25.00$ $\qquad = 0.5152 \times 25.00$ $\qquad = 12.88\,mol\,L^{-1}$

Worked example: Try yourself 7.5.3

BACK TITRATION

A student was given a 0.122 g sample of chalk and asked to determine the mass, in grams, of calcium carbonate in the chalk.

The student made the following notes:

- The chalk sample was placed in a 250 mL conical flask.
- Using a 50.00 mL pipette 50.00 mL standardised $0.198\,mol\,L^{-1}$ HCl solution was added to the flask.
- The excess HCl left in the 250 mL conical flask was then titrated using $0.250\,mol\,L^{-1}$ NaOH solution.
- The experiment was repeated three times and volumes of NaOH added: Trial 1: 32.15 mL, Trial 2: 32.05 mL, Trial 3: 32.10 mL
- The average volume NaOH titrated was 32.10 mL

Using the student's results, calculate the mass of calcium carbonate, in grams, present in the chalk sample.

Step 1: From the titration results determine the amount of HCl in excess. This is the HCl that is left over after all the ammonia is used up in the first step.

Thinking	Working
Write the equation for the titration.	Titration reaction: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
Calculate the moles, n, of NaOH(aq) that reacted in the titration: moles = concentration (mol L^{-1}) × volume (L)	$n(NaOH(aq)) = c \times V$ $c(NaOH(aq)) = 0.250\,mol\,L^{-1}$ $V(NaOH(aq)) = 32.10\,mL = 32.10 \times 10^{-3}\,L$ $n(NaOH(aq)) = 0.250 \times 32.10 \times 10^{-3} = 8.025 \times 10^{-3}\,mol$
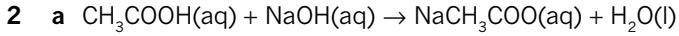
Use the balanced chemical reaction for the titration to determine the moles of excess HCl that reacted in the titration.	From the balanced chemical equation, 1 mole NaOH reacts with 1 mole of HCl, so: $n(HCl)_{excess} = 8.025 \times 10^{-3}$ mol
Step 2: Determine the amount of calcium carbonate in the chalk.	
Calculate the total moles of HCl originally added to the flask: moles = concentration (mol L^{-1}) × volume (L)	$n(HCl) = c \times V$ $c(HCl) = 0.198$ mol L^{-1} $V(HCl) = 50.00$ mL $= 0.0500$ L $n(HCl)_{total\ added} = 0.198 \times 0.0500 = 9.90 \times 10^{-3}$ mol
Calculate the moles of HCl that reacted with the calcium carbonate in the chalk by taking away the amount in excess from the total amount.	$n(HCl)_{titrated} + n(HCl)_{reacted\ with\ chalk} = n(HCl)_{total\ added}$ $n(HCl)_{total\ added} = 9.90 \times 10^{-3}$ mol $n(HCl)_{titrated} = 8.025 \times 10^{-3}$ mol (calculated in Step 1) $n(HCl)_{reacted\ with\ chalk} = n(HCl)_{total\ added} - n(HCl)_{titrated}$ $n(HCl)_{reacted\ with\ chalk} = 9.90 \times 10^{-3} - 8.025 \times 10^{-3} = 1.875 \times 10^{-3}$ mol
Write the balanced chemical equation for the reaction between calcium carbonate in the chalk and the HCl(aq).	Acid–chalk reaction: $2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + 2H_2O(g) + CO_2(g)$
From the balanced chemical equation, calculate the number of moles of $CaCO_3$ that reacted with HCl.	From the equation, 2 mol HCl reacts with 1 mol $CaCO_3$ $n(CaCO_3) = \frac{1}{2} \times n(HCl)$ $\quad = \frac{1}{2} \times 1.875 \times 10^{-3}$ mol $\quad = 9.375 \times 10^{-4}$ mol
Calculate the mass of calcium carbonate in the chalk. State the mass to the correct number of significant figures.	$m(CaCO_3) = n \times M$ $\quad = 9.375 \times 10^{-4} \times 100.09$ $\quad = 0.0938$ g

7.5 KEY QUESTIONS

1 $n(KOH) = cV = 1.34 \times 0.02298 = 0.03079$ mol

$\frac{n(H_2SO_4)}{n(KOH)} = \frac{1}{2}$; therefore, $n(H_2SO_4) = \frac{1}{2} \times n(KOH) = 0.01540$ mol

$\frac{n}{V} = \frac{0.01540}{0.02000} = 0.770$ mol L^{-1}

2 **a** $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$
  b $n(NaOH) = cV = 0.995 \times 0.02156 = 0.02145$ mol
  c $n(NaOH) = n(CH_3COOH) = 0.02145$ mol
  d $c(CH_3COOH) = \frac{n}{V} = \frac{0.02145}{0.02500} = 0.858$ mol L^{-1}

3 $n(Na_2CO_3) = cV = 0.5000 \times 0.02500 = 0.01250$ mol

$\frac{n(HCl)}{n(Na_2CO_3)} = \frac{2}{1}$; therefore, $n(HCl) = n(Na_2CO_3) \times 2 = 0.02500$ mol

$c(HCl) = \frac{n}{V} = \frac{0.02500}{0.02392} = 1.045$ mol L^{-1} of diluted sample

Dilution factor $= \frac{250.0}{25.00} = 10$

Concentration of undiluted $= 1.045 \times 10 = 10.45$ mol L^{-1}

4 $n(Na_2CO_3) = 0.050 \times 0.02150 = 0.001075 \, mol$

$\dfrac{n(HCl)}{n(Na_2CO_3)} = \dfrac{2}{1}$

$n(HCl)_{excess} = \dfrac{2}{1} \times n(Na_2CO_3) = 0.00215 \, mol$

$n(HCl)_{initial} = c \times V = 0.102 \times 0.0500 = 0.0051 \, mol$

$n(HCl)_{reacted} = 0.0051 - 0.00215 = 0.00295 \, mol$

$\dfrac{n(HCl)}{n(NH_3)} = \dfrac{1}{1}$

$n(NH_3) = n(HCl)_{reacted} = 0.00295 \, mol$

Concentration of ammonia $= \dfrac{n}{V} = \dfrac{0.00295}{0.025} = 0.118 \, mol \, L^{-1}$
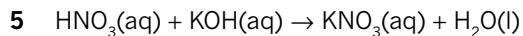
CHAPTER 7 **REVIEW**

1 Acid rain is rainfall made acidic when pollutant gases generated by smelters, the internal combustion engine and the burning of fossil fuels dissolve in rain. These gases contain SO_2, NO_2 and NO and they dissolve in rain to form sulfuric, nitrous and nitric acids respectively.

2 D. Both reactions occur in river water. Carbon dioxide is absorbed from the atmosphere and is produced by decaying plants. A small amount of calcium carbonate reacts with water when a river flows through limestone. Because the pH > 7, there must be an excess of OH^- ions, so the second equation is occurring to a greater extent.

3 Any two of tartaric acid, malic acid, citric acid
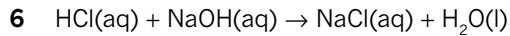
4 If a wine is too acid, it will taste tart and sour, while too little acid will cause the wine to taste flat.

5 $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$

$n(HNO_3) = cV = 0.100 \times 0.0300 = 0.00300 \, mol$

$n(HNO_3) = n(KOH)$; therefore, $n(KOH) = 0.00300 \, mol$

$V(KOH) = \dfrac{n}{c} = \dfrac{0.00300}{0.200} = 0.0150 \, L = 15.0 \, mL$

6 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$n(HCl) = cV = 0.200 \times 0.02000 = 0.00400 \, mol$

$n(HCl) = n(NaOH)$, so $n(NaOH) = 0.00400 \, mol$

$V(NaOH) = \dfrac{n}{c} = \dfrac{0.00400}{0.100} = 0.0400 \, L = 40.0 \, mL$

7 C. The colour of a compound is not usually considered when selecting a primary standard. Primary standards must be soluble because they react with the substance being analysed in solution. A high level of purity minimises errors in calculating the results of the analyses. A high molar mass minimises the percentage error in calculations.

8 $n = \dfrac{m}{M} = \dfrac{25.21}{126.0} = 0.20008 \, mol$

$c = \dfrac{n}{V} = \dfrac{0.20008}{0.2500} = 0.8003 \, mol \, L^{-1}$

9 $c = \dfrac{n}{V}$, $0.400 = \dfrac{n}{0.500}$, $n = 0.400 \times 0.500 = 0.200 \, mol$

$n = \dfrac{m}{M}$, $m = n \times M$, $m = 0.200 \times 106.0 = 21.2 \, g$
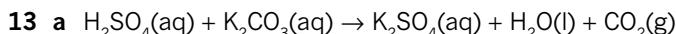
10 **a** A burette delivers a precise variable volume of solution.
  b A pipette delivers a precise known volume of solution.
  c A volumetric flask is used to prepare a solution of known concentration.

11 The equivalence point is the point in the reaction at which equivalent amounts of acid and base have been mixed according to the ratio given in the chemical equation. The end point is the point in the titration at which the indicator changes colour.
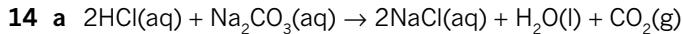
12 Near the equivalence point, a very small addition of either the acid or the base in the burette can cause a large change in pH. A sharp end point is one where the indicator changes colour (due to a large change in pH) with just one additional drop of the solution being added from the burette. Selecting the indicator based on the expected equivalence point enables a sharp end point to be seen.

13 a $H_2SO_4(aq) + K_2CO_3(aq) \rightarrow K_2SO_4(aq) + H_2O(l) + CO_2(g)$

b $c(K_2CO_3) = \dfrac{m}{MV} = \dfrac{1.227\,g}{138.0\,g\,mol^{-1} \times 0.2500\,L}$

$\qquad\qquad = 0.03557\,mol\,L^{-1}$

c From the equation, 1 mol of H_2SO_4 reacts with 1 mol of K_2CO_3 in the titration.

$\dfrac{n(H_2SO_4)}{n(K_2CO_3)} = \dfrac{1}{1}$

$n(K_2CO_3) = cV = 0.03557\,mol\,L^{-1} \times 0.02000\,L = 0.0007114\,mol$

$n(H_2SO_4) = n(K_2CO_3) = 0.0007113\,mol$

$\therefore c(H_2SO_4) = \dfrac{n}{V} = \dfrac{0.0007113\,mol\,L^{-1}}{0.02256\,L} = 0.0315\,mol\,L^{-1}$

14 a $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
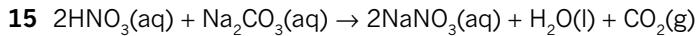
b $n(Na_2CO_3) = \dfrac{m}{M} = \dfrac{1.358}{105.99} = 0.01281\,mol$

$c(Na_2CO_3) = \dfrac{0.01281}{0.250} = 0.05125\,mol\,L^{-1}$

c From the equation, 2 mol of HCl reacts with 1 mol of Na_2CO_3 in the titration.

$\dfrac{n(HCl)}{n(Na_2CO_3)} = \dfrac{2}{1}$

$n(Na_2CO_3) = cV = 0.05125\,mol\,L^{-1} \times 0.02000\,L = 0.001025\,mol$

$n(HCl) = 2 \times n(Na_2CO_3) = 0.002050\,mol$

$\therefore c(HCl) = \dfrac{n}{V} = \dfrac{0.002050}{0.02024} = 0.1013\,mol\,L^{-1}$
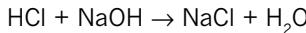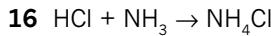
d Sulfuric acid is a diprotic acid so only half as much acid would be required to neutralise an equivalent amount of sodium carbonate. Since the two acids have the same concentration, half the volume of sulfuric acid is required.

15 $2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$

a $n(Na_2CO_3) = \dfrac{m}{M} = \dfrac{1.104}{105.99} = 0.010416\,mol$

$c(Na_2CO_3) = \dfrac{n}{V} = \dfrac{0.010416}{0.250}$

$\qquad\qquad = 0.04166\,mol\,L^{-1}$

b From the equation, 2 mol of HNO_3 reacts with 1 mol of Na_2CO_3 in the titration.

$\dfrac{n(HNO_3)}{n(Na_2CO_3)} = \dfrac{2}{1}$

$n(Na_2CO_3) = cV = 0.04166\,mol\,L^{-1} \times 0.02000\,L = 0.0008332\,mol$

$n(HNO_3) = 2n(Na_2CO_3) = 2 \times 0.0008332 = 0.001666\,mol$

$c(HNO_3) = \dfrac{n}{V} = \dfrac{0.001666\,mol}{0.02347\,L} = 0.007100\,mol\,L^{-1}$

16 $HCl + NH_3 \rightarrow NH_4Cl$

$HCl + NaOH \rightarrow NaCl + H_2O$

$n(NaOH) = 0.100 \times 0.02150 = 0.002150\,mol$

$\dfrac{n(HCl)}{n(NaOH)} = \dfrac{1}{1}$

$n(HCl)_{excess} = \dfrac{1}{1} \times n(NaOH) = 0.002150\,mol$
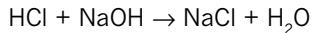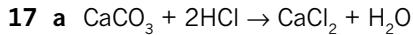
$n(HCl)_{initial} = cV = 0.100 \times 0.0500 = 0.00500\,mol$

$n(HCl)_{reacted} = 0.00500 - 0.00215 = 0.00285\,mol$

$\dfrac{n(HCl)}{n(NH_3)} = \dfrac{1}{1}$

$n(NH_3) = n(HCl)_{reacted} = 0.00285\,mol$

Concentration of ammonia $= \dfrac{n}{V} = \dfrac{0.00285}{0.025} = 0.114\,mol\,L^{-1}$

17 a $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O$

$HCl + NaOH \rightarrow NaCl + H_2O$

$n(NaOH)_{flask} = 0.100 \times 0.03815 = 0.003815\,mol$

$\dfrac{n(HCl)}{n(NaOH)} = \dfrac{1}{1}$

$n(\text{HCl})_{\text{excess}} = \frac{1}{1} \times n(\text{NaOH}) = 0.003815\,\text{mol (in each titration} - 25\,\text{mL)}$

$n(\text{HCl})_{\text{total}} = \frac{250}{25} \times 0.003815 = 0.03815\,\text{mol (in the 250\,mL)}$

b $n(\text{HCl})_{\text{initial}} = cV = 2.00 \times 0.0500 = 0.100\,\text{mol}$

c $n(\text{HCl})_{\text{reacted}} = 0.100 - 0.03815 = 0.06185\,\text{mol}$

$\dfrac{n(\text{HCl})}{n(\text{CaCO}_3)} = \dfrac{2}{1}$

$n(\text{CaCO}_3) = \frac{1}{2} \times n(\text{HCl})_{\text{reacted}} = \frac{1}{2} \times 0.06185 = 0.030925\,\text{mol}$

$m(\text{CaCO}_3) = 0.030925 \times 100.09 = 3.0953\,\text{g}$

d $\%(\text{CaCO}_3) = \dfrac{3.0953}{3.86} \times 100 = 80.2\%$

18 a Sodium carbonate or potassium carbonate could be used as they are both good primary standards. They are also both bases, so they will neutralise the hydrochloric acid.

b To prepare a standard solution:

1 Weigh the pure solid on an electronic balance.

2 Transfer the solid into the volumetric flask using a clean, dry funnel.

3 Rinse any remaining solid particles into the flask using deionised water.

4 Half-fill the flask with deionised water and swirl vigorously to dissolve the solid.

5 Add deionised water up to the calibration line on the neck of the flask. The bottom of the meniscus of the solution should be on the mark when viewing at eye level.

6 Stopper and shake the solution to ensure an even concentration throughout.

c Rinse the burette with the acid solution, rinse the pipette with the base and rinse the conical flask with the deionised water.

d Reaction equation: $K_2CO_3(aq) + 2HCl(aq) \rightarrow 2KCl(aq) + CO_2(g) + 2H_2O(l)$

$n(\text{K}_2\text{CO}_3) = cV = 0.5000 \times 0.02500 = 0.01250\,\text{mol}$

$\dfrac{n(\text{HCl})}{n(\text{K}_2\text{CO}_3)} = \dfrac{2}{1}$; therefore, $n(\text{HCl}) = 0.01250 \times 2 = 0.02500\,\text{mol}$

$c(\text{HCl}) = \dfrac{n}{V} = \dfrac{0.02500}{0.01844} = 1.356\,\text{M}$

Dilution factor = 10

Concentration of undiluted cleaner = $1.356 \times 10 = 13.56\,\text{mol L}^{-1}$

e The concentration calculated should not be different if using a different base in the titration. The volume of base titrated and the concentration of the base may be different and therefore the mole ratio in the equation might be different, but the concentration of HCl in the concrete cleaner would be the same. If there were errors evident in either titration then there would be slight inaccuracies in the results and potentially a different concentration calculated.

19 a $\text{MgO} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}$

b $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

c This is a titration of a strong acid and a strong base, so most indicators could be used. Phenolphthalein has an easily observed endpoint – colourless to pink

d $n(\text{NaOH})_{\text{flask}} = 0.100 \times 0.01860 = 0.001860\,\text{mol}$

e $\dfrac{n(\text{HCl})}{n(\text{NaOH})} = \dfrac{1}{1}$

$n(\text{HCl})_{\text{excess}} = \frac{1}{1} \times n(\text{NaOH}) = 0.001860\,\text{mol (in each titration} - 20\,\text{mL)}$

$n(\text{HCl})_{\text{total}} = \frac{250}{20} \times 0.001860 = 0.02325\,\text{mol (in the 250\,mL)}$

f $n(\text{HCl})_{\text{initial}} = cV = 2.00 \times 0.0450 = 0.0900\,\text{mol}$

$n(\text{HCl})_{\text{reacted}} = 0.0900 - 0.02325 = 0.06675\,\text{mol}$

g $\dfrac{n(\text{HCl})}{n(\text{MgO})} = \dfrac{2}{1}$

$n(\text{MgO}) = \frac{1}{2} \times n(\text{HCl})_{\text{reacted}} = \frac{1}{2} \times 0.06675 = 0.033375\,\text{mol}$

$m(\text{MgO}) = 0.033375 \times 40.31 = 1.345\,\text{g}$

h $\%(\text{MgO}) = \dfrac{1.345}{1.75} \times 100 = 76.9\%$
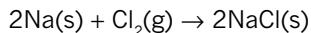
Chapter 8 **Redox reactions**

Section 8.1 **Oxidation and reduction**

Worked example: Try yourself 8.1.1

IDENTIFYING OXIDATION AND REDUCTION

Write the oxidation and reduction half-equations for the reaction with the overall equation: $$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$	
Thinking	**Working**
Identify the ions in the product.	NaCl is made up of Na^+ and Cl^- ions.
Write the half-equation for the oxidation of the reactant that forms positive ions and balance the equation with electrons.	$Na(s) \rightarrow Na^+(s) + e^-$
Write the half-equation for the reduction of the reactant and balance the equation with electrons.	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

Worked example: Try yourself 8.1.2

WRITING SIMPLE HALF-EQUATIONS

When a piece of copper metal is placed into a silver nitrate solution, silver metal is formed and the solution gradually turns blue, indicating the presence of copper(II) ions in solution. The oxidation and reduction reactions can be represented by two half-equations. Write these half-equations and identify the substances that are oxidised and reduced.	
Thinking	**Working**
Identify one reactant and the product it forms and write them on each side of the equation. Balance the equation for the element.	$Ag^+(aq) \rightarrow Ag(s)$
Add electrons to balance the equation for charge.	$Ag^+(aq) + e^- \rightarrow Ag(s)$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are gained, so this is reduction. The $Ag^+(aq)$ is being reduced.
Identify the second reactant and the product it forms, and write them on each side of the equation. Balance the equation for the element.	$Cu(s) \rightarrow Cu^{2+}(aq)$
Add electrons to balance the equation for charge.	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are lost, so this is oxidation. The $Cu(s)$ is being oxidised.

Worked example: Try yourself 8.1.3

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Potassium metal is oxidised by oxygen gas in air to form solid potassium oxide.
Write the half-equations for the reaction and hence write the balanced overall equation.

Thinking	Working
Identify one reactant and the product it forms, and write them on each side of the equation. Balance the equation for the element.	$O_2(g) \rightarrow 2O^{2-}(s)$
Add electrons to balance the equation for charge.	$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$
Identify the second reactant and the product it forms, and write them on each side of the equation. Balance the equation for the element.	$K(s) \rightarrow K^+(s)$
Add electrons to balance the equation for charge.	$K(s) \rightarrow K^+(s) + e^-$
Multiply one equation by a suitable factor to ensure that the number of electrons is balanced.	$(K(s) \rightarrow K^+(s) + e^-) \times 4$ $4K(s) \rightarrow 4K^+(s) + 4e^-$
Add the oxidation and the reduction half-equations together, cancelling out electrons so that none are in the final equation. Combine ions to create the formula of the product.	$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$ $4K(s) \rightarrow 4K^+(s) + 4e^-$ When the electrons have been cancelled, the overall equation is: $4K(s) + O_2(g) \rightarrow 2K_2O(s)$

8.1 KEY QUESTIONS

1 I_2, loses, oxidised, gains, reduced, I^-

2 **a** Oxidation
   b Oxidation
   c Reduction
   d Oxidation
   e Reduction
   f Reduction

3 **a** Fe(s) has been oxidised to $Fe^{2+}(aq)$.
   b $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
   c $H^+(aq)$
   d $H^+(aq)$ has been reduced to H_2
   e $2H^+(aq) + 2e^- \rightarrow H_2(g)$
   f Fe(s)

4 **a** $Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$ (oxidation)
   b $K(s) \rightarrow K^+(aq) + e^-$ (oxidation)
   c $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ (reduction)
   d $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$ (reduction)

5 **a** Zn(s)
   b Ca(s)
   c I^- ions

6 **a** Oxidant O_2, reductant Zn
   b Oxidant Cl_2, reductant Ca
   c Oxidant Cl_2, reductant I^- ions

7 $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
   As the nickel metal goes from solid metal to a positive ion it must be losing electrons, therefore being oxidised.

8 $Al(s) \rightarrow Al^{3+}(l) + 3e^-$ (oxidation)
   $S(l) + 2e^- \rightarrow S^{2-}(l)$ (reduction)

9 **a** $Ag^+(aq) + e^- \rightarrow Ag(s)$

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

   $M(s) + 3Ag^+(aq) \rightarrow M^{3+}(aq) + 3Ag(s)$

   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.

10 **a** Magnesium is oxidised, copper ions are reduced.

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

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

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

   e Oxidant Cu^{2+}; reductant Mg

   f Blue Cu^{2+} ions are reduced to salmon pink Cu(s).

11 **a** Cu^{2+}

   b Cu

12 **a** CaO

   b Ca(s)

   c $Ca(s) \rightarrow Ca^{2+}(s) + 2e^-$

   d $O_2(g)$

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

   f $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$

   g Calcium has been *oxidised* by *oxygen* to calcium ions. The *oxygen* has gained electrons from the *calcium*. The oxygen has been *reduced* by *calcium* to oxide ions. The *calcium* has lost electrons to the *oxygen*.

Section 8.2 **Oxidation numbers**

Worked example: Try yourself 8.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 8.2.1 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. Applying 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 elements.	Let the oxidation of N 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.	$\overset{+1\ +5\ -2}{NaNO_3}$

Worked example: Try yourself 8.2.2

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:

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

Thinking	Working
Determine the oxidation numbers of one of the elements on each side of the equation.	Choose Cu as the first element. As Cu can have different oxidation states, let the oxidation number $= x$ $x + -2 = 0$ $x = +2$ $\overset{+2}{C}uO(s) + H_2(g) \rightarrow \overset{0}{C}u(s) + H_2O(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of copper has decreased from +2 to 0, so the copper in CuO has been reduced.
Determine the oxidation numbers of a second element on the left-hand and the right-hand side of the equation.	Choose hydrogen as the second element. $CuO(s) + \overset{0}{H}_2(g) \rightarrow Cu(s) + \overset{+1}{H}_2O(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of H 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 O has not changed.

8.2 KEY QUESTIONS

1 a +2
   b +4
   c −4
   d 0
   e +4

2 K_2MnO_4: the oxidation state of K is +1, O is −2

   $2 \times +1 + x + 4 \times -2 = 0$; hence $x = +6$

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

4 a Oxidant Cl_2; reductant Mg
   b Oxidant O_2; reductant SO_2
   c Oxidant Fe_2O_3; reductant CO
   d Oxidant H_2O_2; reductant Fe^{2+}

5

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

Section 8.3 More complex redox equations

Worked example: Try yourself 8.3.1

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 molecules must be added to the RHS. $$MnO_4^- \rightarrow MnO_2 + 2H_2O$$
Balance the hydrogen atoms by adding H^+ ions. Acids provide a source of H^+ ions.	There are now 4 H atoms on the RHS and none on the LHS, so $4H^+$ must be added to the LHS. $$MnO_4^- + 4H^+ \rightarrow MnO_2 + 2H_2O$$
Balance the charge in the equation by adding electrons.	The charge on the LHS is $(-1) + (4 \times +1) = +3$ and on the RHS is 0 so 3 electrons must be added to the LHS to make the charges equal. $$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$
Add states to complete the half-equation.	$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$

Worked example: Try yourself 8.3.2

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 equation(s) by a suitable factor to ensure that the number of electrons on both sides of the arrow is equal.	Lowest common multiple = 12 $2 \times [SO_3^{2-}(aq) + 8H^+(aq) + 6e^- \rightarrow H_2S(g) + 3H_2O(l)]$ $3 \times [ClO^-(aq) + 2H_2O(l) \rightarrow ClO_3^-(aq) + 4H^+(aq) + 4e^-]$ $2SO_3^{2-}(aq) + 16H^+(aq) + 12e^- \rightarrow 2H_2S(g) + 6H_2O(l)$ $3ClO^-(aq) + 6H_2O(l) \rightarrow 3ClO_3^-(aq) + 12H^+(aq) + 12e^-$
Add the oxidation and the reduction half-equations together, cancelling electrons so that none are in the final equation. Also cancel H_2O and H^+ if these occur on both sides of the arrow.	$2SO_3^{2-}(aq) + \overset{4H^+}{\cancel{16H^+}}(aq) + \cancel{12e^-} \rightarrow 2H_2S(g) + \cancel{6H_2O(l)}$ $3ClO^-(aq) + \cancel{6H_2O(l)} \rightarrow 3ClO_3^-(aq) + \cancel{12H^+(aq)} + \cancel{12e^-}$ $2SO_3^{2-}(aq) + 4H^+(aq) + 3ClO^-(aq) \rightarrow 2H_2S(g) + 3ClO_3^-(aq)$

8.3 KEY QUESTIONS

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

2 **a** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
   b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
   c $3Zn(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

3 **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 $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
     $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
     $MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$

4 **a** **i** Ce^{4+} is reduced to Ce^{3+} and H_2S is 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^- is reduced to NO and Cu is oxidised to Cu^{2+}.
     ii $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$
       $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
     iii $2NO_3^-(aq) + 8H^+(aq) + 3Cu \rightarrow 2NO(g) + 4H_2O(l) + 3Cu^{2+}(aq)$
   c **i** H_2O_2 is reduced to H_2O and Br^- is 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 $2MnO_2(s) + 4H^+(aq) + S(s) \rightarrow 2Mn^{2+} + 2H_2O(l) + SO_2(g)$

Section 8.4 **The reactivity series of metals**

Worked example: Try yourself 8.4.1

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether copper will displace gold from a solution containing gold ions. If appropriate, write the overall redox equation for the reaction.

Thinking	Working
Locate the metal and the metal ions in the reactivity series.	Metals (reducing agents) are found on the right-hand side of the reactivity series and the metal ions (oxidising agents) are on the left-hand side of the reactivity series. $Au^{3+}(aq) + 3e^- \rightarrow Au(s)$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Determine whether the metal is below the metal ion in the table. If this is the case, there will be a reaction.	We can see from the reactivity series that Cu is on the right-hand side because it is a reducing agent and it is below Au^+, so there will be a reaction.
Write the reduction half-equation for the metal ion directly as it is written in the reactivity series. Include state symbols.	$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$
Write the oxidation half-equation for the metal, with the metal on the left-hand side of the arrow (as a reactant). Include state symbols.	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Combine the two half-equations, balancing electrons, to give the overall equation for the reaction.	$(Au^{3+}(aq) + 3e^- \rightarrow Au(s)) \times 2$ $\underline{(Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-) \times 3}$ $2Au^{3+}(aq) + 3Cu(s) \rightarrow 2Au(s) + 3Cu^{2+}(aq)$

8.4 KEY QUESTIONS

1   For reactions to occur spontaneously, the aqueous cation in the solution must be a stronger oxidant than the cation of the metal added.
   a no
   b no
   c yes
   d yes
   e yes
   f yes
   g no
2   **a** $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$
   b no reaction
   c $2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$
3   Use iron and lead to test the solutions.
   The copper(II) nitrate will react with both iron and lead.
   The tin nitrate will react only with the iron.
   The zinc nitrate will not react with either of the metals.

CHAPTER 8 REVIEW

1   **a**   Oxidation is the gain of oxygen; reduction is the loss of oxygen.
   b   Oxidation is the loss or donation of electrons; reduction is the gain or acceptance of electrons.

2   **a**   false
   b   false
   c   true
   d   false

3   loses, positive, loses, gains, negative, gains, 7, gains, bromide

4   Oxidation half-equation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$
   Reduction half-equation: $Ag^+(aq) + e^- \rightarrow Ag(s)$
   Overall: $Pb(s) + 2Ag^+(aq) \rightarrow Pb^{2+}(aq) + 2Ag(s)$

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

6   **a**   Charges are not balanced: $Ag(s) \rightarrow Ag^+(aq) + e^-$
   b   Electrons appear on both sides of the equation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
   c   State symbols are incorrect: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
   d   Atoms are not balanced: $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
   e   Electrons are being subtracted: $Na^+(aq) + e^- \rightarrow Na(s)$

7   **a** $Cu(s)$
   b $Br^-(l)$
   c $Zn(s)$
   d $Ni(s)$

8   **a** $Ag^+(aq) + e^- \rightarrow Ag(s)$
   b $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
   c $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

9   C. The equation is not balanced correctly as it is written. Because the silver ion has a +1 charge, Ag^+ ions and Cu atoms will react in a 2:1 ratio in the reaction. The equation is balanced when it is written as:
   $2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$

10   **a**   +4
    b   −2
    c   +6
    d   +6
    e   +4
    f   +2

11

Compound	Element	Oxidation number
$CaCO_3$	Ca	+2
HNO_3	O	−2
H_2O_2	O	−1
HCO_3^-	C	+4
HNO_3	N	+5
$KMnO_4^-$	Mn	+7
H_2S	S	−2
Cr_2O_3	Cr	+3
N_2O_4	N	+4

12 K_3N, N_2, N_2O, NO, N_2O_3, N_2O_4, $Ca(NO_3)_2$

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: $+4$

$Ca(NO_3)_2$: $+5$

13 Reactions 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 which 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

14 a $\underline{Cu}O$ +2

b $\underline{Fe}(OH)_3$ +3

c $H\underline{Cl}O_2$ +3

d $\underline{Mn}O_4^-$ +7

e $\underline{Cr}_2O_7^{2-}$ +6

15 a i 0

 ii +2

b i +5

 ii +4
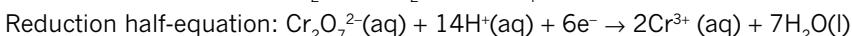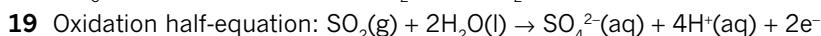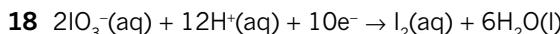
c oxidising agent HNO_3; reducing agent Cu

16
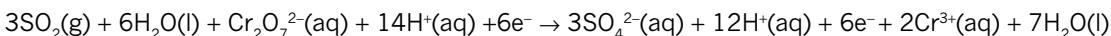
Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Fe(s) + I_2(aq) \rightarrow FeI_2(aq)$	$Fe(s)/Fe^{2+}(aq)$	$I_2(aq)/I^-(aq)$
$Mg(s) + FeCl_2(aq) \rightarrow MgCl_2(aq) + Fe(s)$	$Mg(s)/Mg^{2+}(aq)$	$Fe^{2+}(aq)/Fe(s)$
$10Br^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$	$Br^-(aq)/Br_2(aq)$	$MnO_4^-(aq)/Mn^{2+}(aq)$
$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$	$Cu(s)/Cu^{2+}(aq)$	$NO_3^-(aq)/NO_2(g)$

17
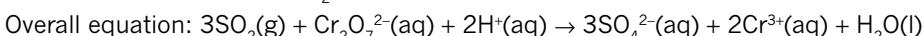
Step	Task	How it's done	Half-equation
1	Balance nitrogens.	Already balanced	$NO_3^- \rightarrow NO_2$
2	Balance oxygens by adding H_2O.	Add one H_2O molecule(s) to the right-hand side of the equation.	$NO_3^- \rightarrow NO_2 + H_2O$
3	Balance hydrogens by adding H^+.	Add $2H^+$ ion(s) to the left-hand side of the equation.	$NO_3^- + 2H^+ \rightarrow NO_2 + H_2O$
4	Balance charge by adding electrons.	Charge on left-hand side = $-1 + 2$ $= +1$ Charge on right-hand side = 0 Add one 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.	$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

18 $2IO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow I_2(aq) + 6H_2O(l)$

19 Oxidation half-equation: $SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

Reduction half-equation: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
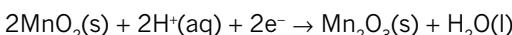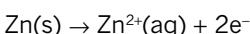
You will need to multiply the oxidation half-equation by 3 to cancel electrons.

$3SO_2(g) + 6H_2O(l) + Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 3SO_4^{2-}(aq) + 12H^+(aq) + 6e^- + 2Cr^{3+}(aq) + 7H_2O(l)$
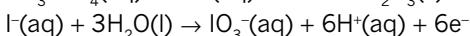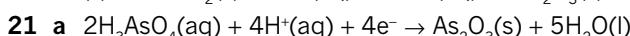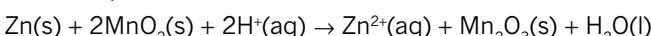
Then cancel electrons and H_2O and H^+.

Overall equation: $3SO_2(g) + Cr_2O_7^{2-}(aq) + 2H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$

20 Half-equations:

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

$2MnO_2(s) + 2H^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + H_2O(l)$

Overall equation:

$Zn(s) + 2MnO_2(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l)$

21 a $2H_3AsO_4(aq) + 4H^+(aq) + 4e^- \rightarrow As_2O_3(s) + 5H_2O(l)$

$I^-(aq) + 3H_2O(l) \rightarrow IO_3^-(aq) + 6H^+(aq) + 6e^-$
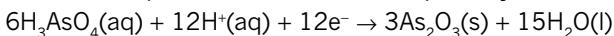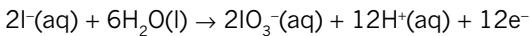
b Common multiple for electrons = 12

Reduction equation needs to be multiplied by 3.
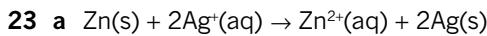
$6H_3AsO_4(aq) + 12H^+(aq) + 12e^- \rightarrow 3As_2O_3(s) + 15H_2O(l)$

Oxidation equation needs to be multiplied by 2.

$2I^-(aq) + 6H_2O(l) \rightarrow 2IO_3^-(aq) + 12H^+(aq) + 12e^-$

Cancel e^-, H_2O and H^+.

$6H_3AsO_4(aq) + 2I^-(aq) \rightarrow 3As_2O_3(s) + 2IO_3^-(aq) + 9H_2O(l)$

22 Ag, Cu, Sn, Ni, Mg, Li

23 a $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
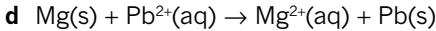
b no reaction

c no reaction

d $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$
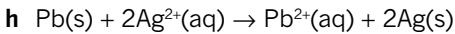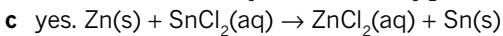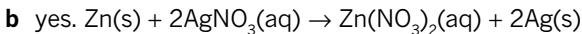
e no reaction

f no reaction

g no reaction

h $Pb(s) + 2Ag^{2+}(aq) \rightarrow Pb^{2+}(aq) + 2Ag(s)$

24 a no

b yes. $Zn(s) + 2AgNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + 2Ag(s)$

c yes. $Zn(s) + SnCl_2(aq) \rightarrow ZnCl_2(aq) + Sn(s)$

d yes. $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

25 Place 10 mL of each solution into a clean test-tube. Add a small piece of magnesium ribbon to each solution. The magnesium should be coated by displaced metal in the silver nitrate and lead nitrate solutions, but not in the sodium nitrate. The lead coating will be black. Over time, the silver coating will change from black to silver as more metal is deposited. To confirm the identity of the silver nitrate solution, take a fresh sample and add a small piece of copper. Copper will displace silver from the solution, giving silver deposit and a blue solution. Copper will not displace lead from the solution.

26 zinc
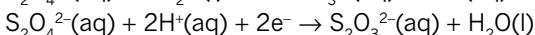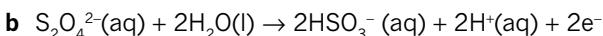
27 Coatings of metals other than iron would be expected on the nails placed in 1 M solutions of $CuSO_4$ and $Pb(NO_3)_2$. These solutions contain oxidants that are strong enough to react with iron metal. The iron, in turn, reduces the metal ions in the solution, forming a coating on the nail.

28 Individual students' responses required.

29 a i +3

ii +2

iii +4

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

$S_2O_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow S_2O_3^{2-}(aq) + H_2O(l)$
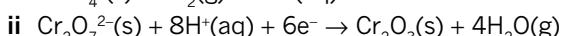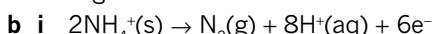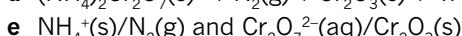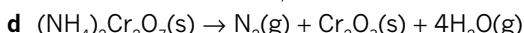
30 a Oxidation number of nitrogen in $(NH_4)_2Cr_2O_7$ is -3 and in N_2 it is 0.
Oxidation number of chromium in $(NH_4)_2Cr_2O_7$ is $+6$ and in Cr_2O_3 it is $+3$.
Nitrogen has been oxidised and chromium has been reduced.

b i $2NH_4^+(s) \rightarrow N_2(g) + 8H^+(aq) + 6e^-$
ii $Cr_2O_7^{2-}(s) + 8H^+(aq) + 6e^- \rightarrow Cr_2O_3(s) + 4H_2O(g)$
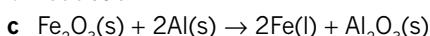
c Reaction i is oxidation, reaction ii is reduction

d $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$

e $NH_4^+(s)/N_2(g)$ and $Cr_2O_7^{2-}(aq)/Cr_2O_3(s)$
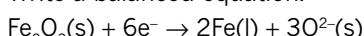
31 a $Fe_2O_3(s) + 6e^- \rightarrow 2Fe(l) + 3O^{2-}(s)$

b reduction

c $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s)$

d 1 Write a balanced equation.
$Fe_2O_3(s) + 6e^- \rightarrow 2Fe(l) + 3O^{2-}(s)$

2 Calculate the amount of the given reagent, Fe.

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

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

$\dfrac{n(Fe_2O_3)}{n(Fe)} = \dfrac{1}{2}$

$n(Fe_2O_3) = \dfrac{0.0663 \text{ mol}}{2} = 0.0332$ mol

4 Calculate the mass of of Fe_2O_3.
$m(Fe_2O_3) = 0.0332$ mol $\times 159.6$ g mol^{-1}
$= 5.29$ g (3 significant figures)

32 a $Ag^+(aq)$; $Mg^{2+}(aq)$

b $Mg(s)$; $Ag(s)$

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

d zinc and magnesium

33 Experiment 1 gives you evidence that T is a more reactive metal than R.

Experiment 2 suggests that S is a less reactive metal than T as it does not displace T from a solution of its salt, $T(NO_3)_2$.

Experiment 3 indicates that S is a less reactive metal than R as it does not displace R from a solution of its salt, RNO_3.

The information above tells you that S is less reactive than both T and R and that R is less reactive than T, so the correct order of increasing reactivity is $S < R < T$.
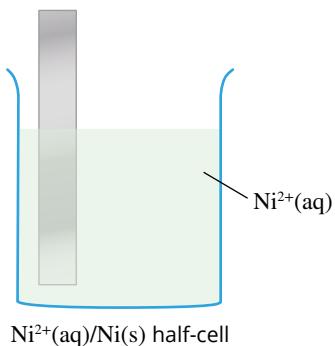
Chapter 9 **Galvanic cells**

## Section 9.1 **Galvanic cells**
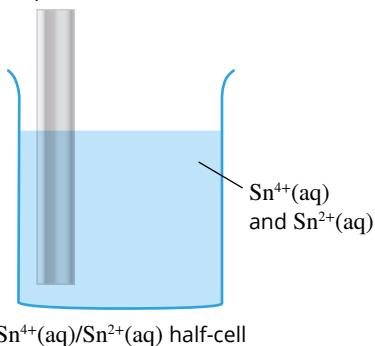
9.1 KEY QUESTIONS

1   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 do not flow into the half-cell where oxidation occurs (the anode).

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

2   **a**

nickel electrode

$Ni^{2+}(aq)$

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

b

platinum electrode

$Sn^{4+}(aq)$
and $Sn^{2+}(aq)$

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

c

platinum electrode

$H_2(g)$ ⟶   glass tube

$H^+(aq)$

$H^+(aq)/H_2(g)$ half-cell
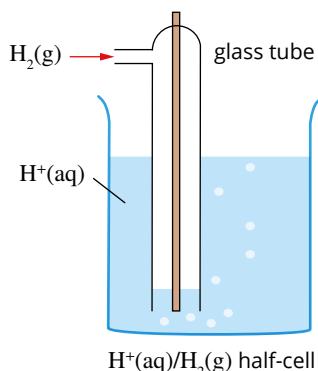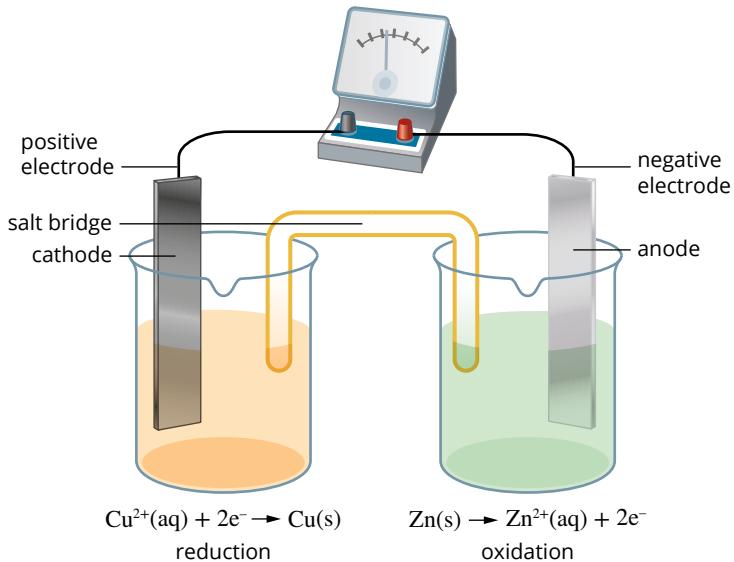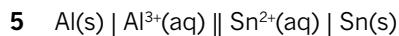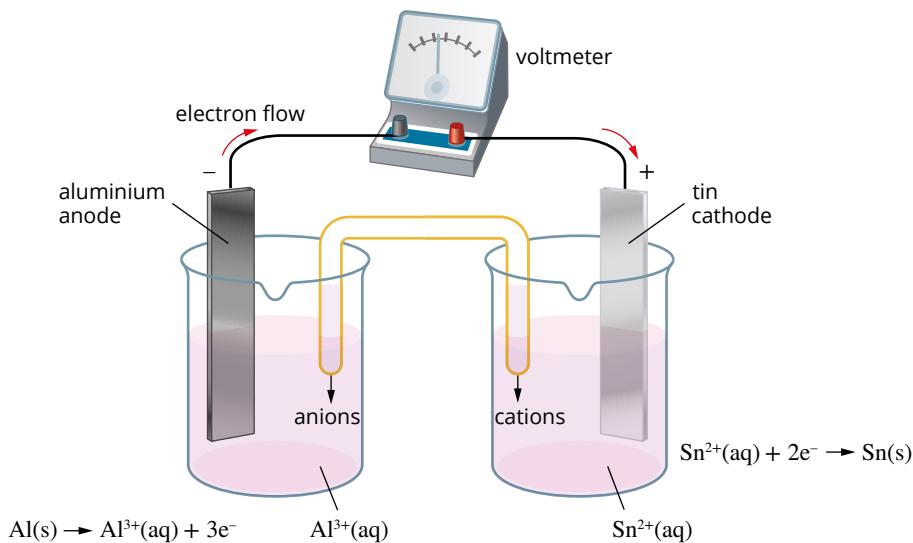
3   **a**   Reduction occurs at the cathode: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

b   Oxidation occurs at the anode: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

4

$$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$$

$$Al^{3+}(aq)$$

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

$$Sn^{2+}(aq)$$

5 Al(s) | Al³⁺(aq) ‖ Sn²⁺(aq) | Sn(s)

6 $$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

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

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$
oxidation

Section 9.2 **The electrochemical series**

Worked example: Try yourself 9.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL
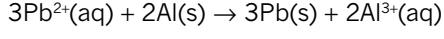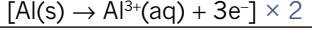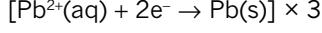
| A cell is made from Sn²⁺(aq)/Sn(s) and Ni²⁺(aq)/Ni(s) half-cells under standard conditions. Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.	
Identify the two relevant half-equations in the electrochemical series.	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ $E° = -0.14\,V$ $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E° = -0.24\,V$
Identify the strongest oxidising agent (the species on the left of the series with the most positive $E°$ value) and the strongest reducing agent (bottom right).	Because Sn²⁺ is higher on the left side of the table than Ni²⁺, it is the strongest oxidising agent. Ni, being lower on the right side of the table than Sn, is the strongest 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.)	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 will be the anode and the tin electrode will be the cathode.
Determine the direction of electron flow in the cell. The anode is negative; the cathode is positive.	Electrons flow from the negative electrode (anode) to the positive electrode (cathode).
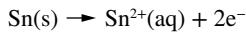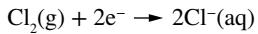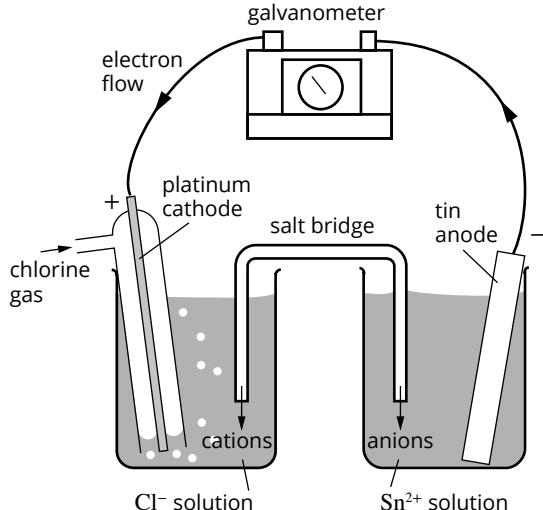
9.2 KEY QUESTIONS

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

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

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

$3Pb^{2+}(aq) + 2Al(s) \rightarrow 3Pb(s) + 2Al^{3+}(aq)$
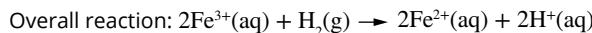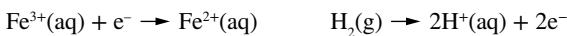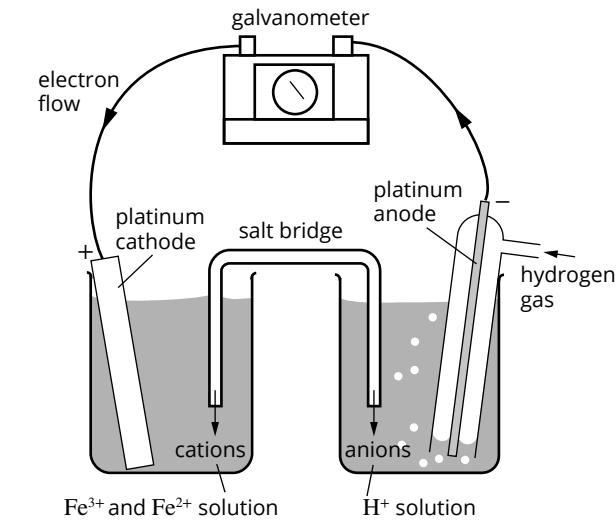
c The lead electrode will be the cathode and the aluminium electrode will be the anode.
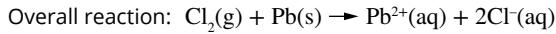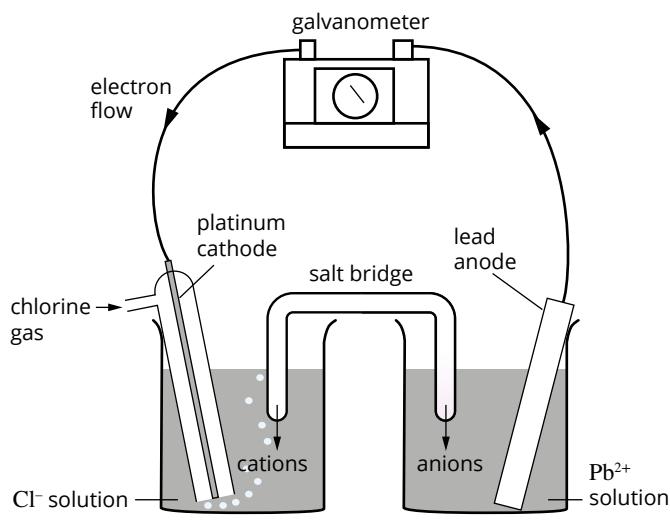
2

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

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

3 **a**

Fe³⁺ and Fe²⁺ solution   H⁺ solution

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

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

b

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

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

4 Question 1 cell:

cell potential difference = higher half-cell $E°$ − lower half-cell $E°$

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

$= -0.13 - (-1.68)$

$= 1.55\,V$

Question 2 cell:

cell potential difference = higher half-cell $E°$ − lower half-cell $E°$

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

$= +1.36 - (-0.14)$

$= 1.50\,V$

Question 3a cell:

cell potential difference = higher half-cell $E°$ − lower half-cell $E°$

$= E°(Fe^{3+}(aq)/Fe^{2+}(aq)) - E°(H^+(aq)/H_2(g))$

$= +0.77 - (0.00)$

$= 0.77\,V$

Question 3b cell:

cell potential difference = higher half-cell $E°$ − lower half-cell $E°$

$= E°(Cl_2(g)/Cl^-(aq)) - E°(Pb^{2+}(aq)/Pb(s))$

$= 1.36 - (-0.13)$

$= 1.49\,V$
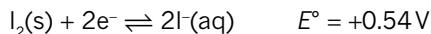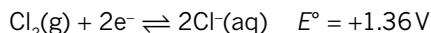
Section 9.3 **Predicting direct redox reactions**

Worked example: Try yourself 9.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations, which appear in the order shown in the electrochemical series:

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

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

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

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 $Cl^-(aq)$ 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.
	a $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $E° = +0.54\,V$
	      $Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$ $E° = -0.13\,V$
	      No reaction occurs because both I_2 and Pb^{2+} are oxidising agents.
	
	b $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E° = +1.36\,V$
	      $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $E° = +0.54\,V$
	      No reaction because the oxidising agent, I_2, is below the reducing agent, Cl^-, in the electrochemical series.
	
	c $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E° = +1.36\,V$
	      $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ $E° = -0.13\,V$
	      No reaction occurs because both Cl^- and Pb are reducing agents.

9.3 KEY QUESTIONS

1.   B. Cobalt is the only reducing agent below the oxidising agent, Pb^{2+}, in the electrochemical series.

2.   C. $Cl_2(g)$ is an oxidising agent above both reducing agents, H_2S and H_2O so not A. Mg and H_2S are both reducing agents so not B. Cu and H_2S are both reducing agents so not D.

3.   **a**   A reaction occurs because the oxidising agent, Cl_2, is above the reducing agent, Br^-, in the electrochemical series.
        $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$
     b   A reaction occurs because the oxidising agent, Cl_2, is above the reducing agent, I^-, in the electrochemical series.
        $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$
     c   No reaction because the oxidising agent, Br_2, is below the reducing agent, Cl^-, in the electrochemical series.
     d   A reaction occurs because the oxidising agent, Br_2, is above the reducing agent, I^-, in the electrochemical series.
        $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$

4.   **a** $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
     b   Chemical energy is transformed into heat energy.

5.   For a reaction to occur, the reducing agent, Fe, must be below the oxidising agent in the electrochemical series.

   $CuSO_4$: A reaction occurs because the reducing agent, Fe, is below the oxidising agent, Cu^{2+}. Cu^{2+} is reduced, forming a coating of copper on the nail.

   $MgCl_2$: No reaction occurs because the reducing agent, Fe, is above the oxidising agent, Mg^{2+}. No reaction occurs between Fe and Cl^- because they are both reducing agents.

   $Pb(NO_3)_2$: A reaction occurs because the reducing agent, Fe, is below the oxidising agent, Pb^{2+}. Pb^{2+} is reduced, forming a coating of lead on the nail.

   $ZnCl_2$: No reaction occurs because the reducing agent, Fe, is above the oxidising agent, Zn^{2+}. No reaction occurs between Fe and Cl^- because they are both reducing agents.

Section 9.4 **Everyday sources of power**

9.4 KEY QUESTIONS

1   Secondary cells can be recharged, whereas primary cells cannot.

2   A. On recharging batteries, non-spontaneous reactions take place to convert electrical energy into chemical energy. Cells in which chemical energy is produced from electrical energy are called electrolytic cells, making A the only correct answer.

3   B, C, G

4   A

5   **a** $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$
     b $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Section 9.5 **Corrosion**
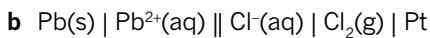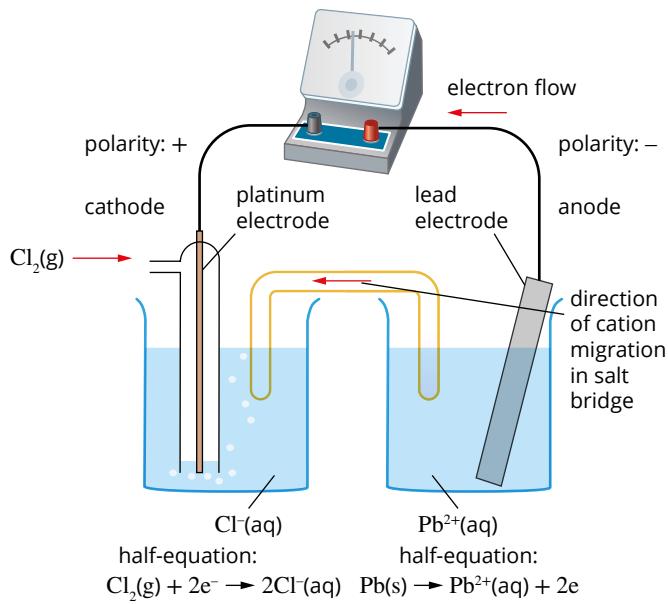
9.5 KEY QUESTIONS

1   $2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$
     $4Fe(OH)_2(s) + O_2(aq) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$
     In the first equation the oxidation number of iron increases from 0 to +2; in the second equation the oxidation number of iron increases from +2 to +3.

2   Near the coast, moisture in the air contains a higher amount of dissolved salts (e.g. NaCl(aq)). Salts are good electrolytes and accelerate the rusting process. They do this because they increase the conductivity of moisture on the surface of the iron.

3   **a** magnesium and zinc
     b Only metals more reactive (i.e. more easily oxidised) than iron will act as sacrificial anodes. These more reactive metals will be oxidised in preference to the iron. The iron will become the cathode (the site of reduction) and no oxidation of the iron will take place.

4   Reduction of oxygen occurs when there is plenty of moisture and the oxygen concentration is high; that is, at or just above the surface of the water. A cathodic region forms here. So, the anodic region is close to the cathode and where the oxygen concentration is less; that is, just below the surface. Oxidation, or corrosion, therefore occurs more rapidly below the surface.

5   Zinc is more reactive than iron or copper. It is also more reactive than steel so zinc will be the anode and steel will be the cathode. Oxidation, and so corrosion, of the nails will thus be prevented.
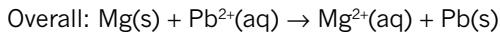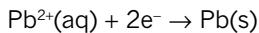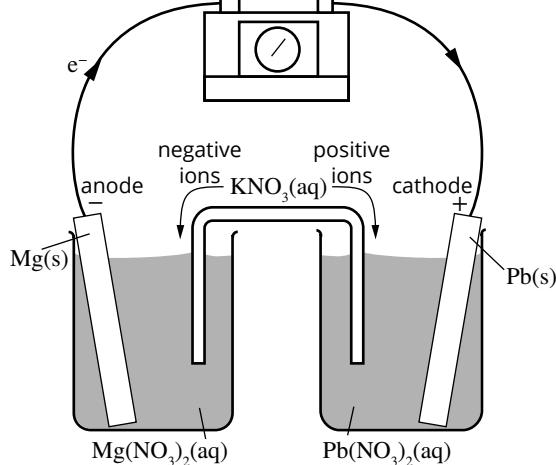
Chapter 9 **Review**

1   D. If no salt bridge were present, the solution in one half-cell would accumulate a negative charge and the solution in the other half-cell would accumulate a positive charge as the reaction proceeded. Such accumulations of charge would very quickly prevent further reaction, and hence prevent production of electricity.

2   A. If one of the conjugate redox pairs in a half-cell is not a metal, an inert (unreactive) electrode such as platinum or graphite is used. Compared with gold, iron is the least suitable for use as an electrode as it is more likely to react and become involved in a cell reaction.

3   **a** Oxidising agent: a substance that causes another substance to be oxidised and is reduced in the process. Reducing agent: a substance that causes another substance to be reduced and is oxidised in the process.
     b Anode: electrode at which oxidation occurs. Cathode: electrode at which reduction occurs.
     c Conjugate redox pair: an oxidant and its corresponding reduced form, e.g. Cu^{2+}/Cu. The reduced form has gained electrons. Conjugate acid–base pair: A conjugate acid contains one more hydrogen ion or proton than the base.
     d External circuit: section of a circuit where the electrons flow, e.g. through wires. Internal circuit: part of cell where the current is due to the movement of ions, e.g. in the salt bridge.

4 a

polarity: + electron flow polarity: −

cathode platinum electrode lead electrode anode

$Cl_2(g)$ →

direction of cation migration in salt bridge

$Cl^-(aq)$ $Pb^{2+}(aq)$

half-equation: half-equation:
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $Pb(s) \rightarrow Pb^{2+}(aq) + 2e$

b $Pb(s) \mid Pb^{2+}(aq) \parallel Cl^-(aq) \mid Cl_2(g) \mid Pt$

5 a

e^-

negative ions positive ions
anode $KNO_3(aq)$ cathode
− +

$Mg(s)$ $Pb(s)$

$Mg(NO_3)_2(aq)$ $Pb(NO_3)_2(aq)$

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 Lead electrode is the cathode; magnesium electrode is the anode

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

6 cell potential difference = higher half-cell $E°$ − lower half-cell $E°$
$= E° (Cu^{2+}(aq)/Cu(s)) − E° (Zn^{2+}(aq)/Zn(s))$
$= 0.34 − (−0.76)$
$= 1.10\,V$

7 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.

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

8 The correct order is:
- $Ni^{2+}(aq)/Ni(s)$ and $Br_2(l)/Br^-(aq)$
cell $E° = E° (Br_2(l)/Br^-(aq)) − E° (Ni^{2+}(aq)/Ni(s)) = 1.08 − (−0.24) = 1.32\,V$
- $Fe^{2+}(aq)/Fe(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$
cell $E° = E° (Fe^{3+}(aq)/Fe^{2+}(aq)) − E° (Fe^{2+}(aq)/Fe(s)) = 0.77 − (−0.44) = 1.21\,V$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$
cell $E° = E° (Fe^{3+}(aq)/Fe^{2+}(aq)) − E° (Ni^{2+}(aq)/Ni(s)) = 0.77 − (−0.24) = 1.01\,V$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{2+}(aq)/Fe(s)$
cell $E° = E° (Ni^{2+}(aq)/Ni(s)) − E° (Fe^{2+}(aq)/Fe(s)) = −0.24 − (−0.44) = 0.20\,V$
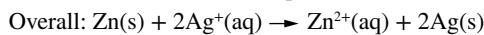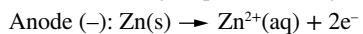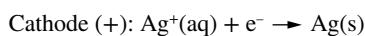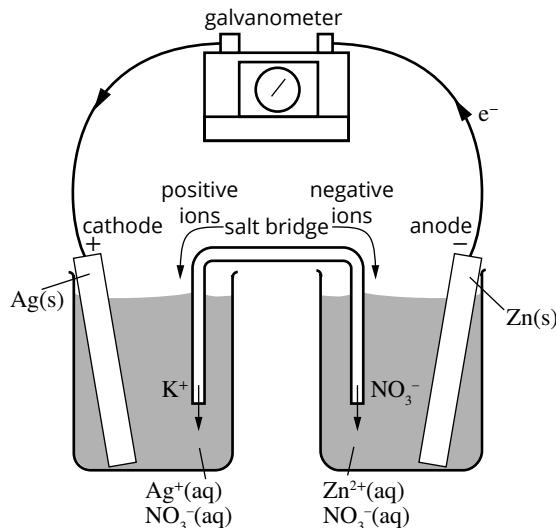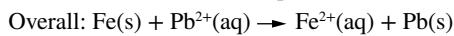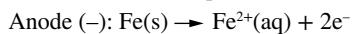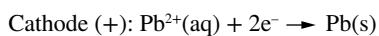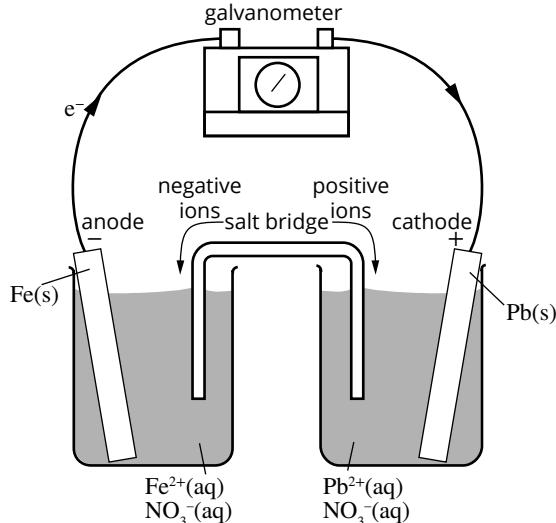
9 **a**

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

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

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

b

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

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

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

c

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

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

Overall: $Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s)$
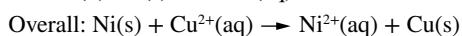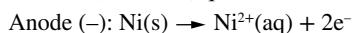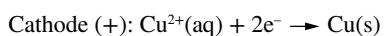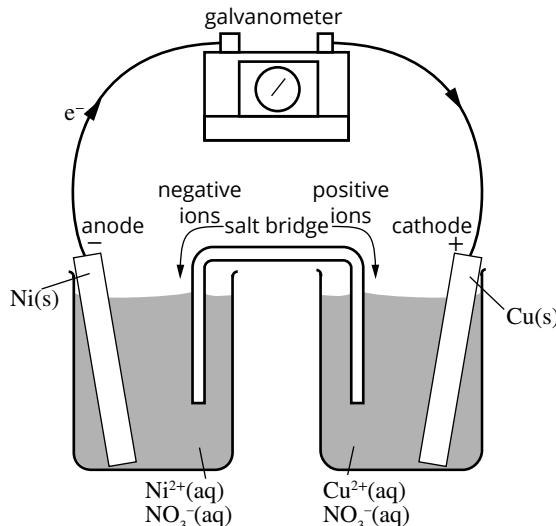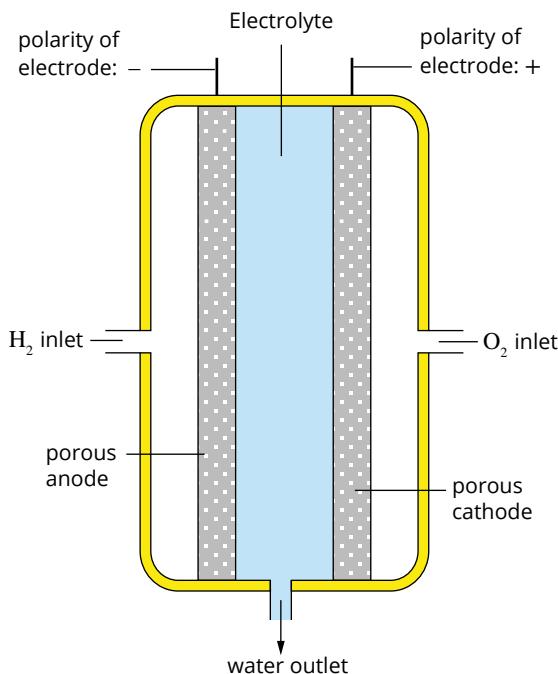
10 Reduction occurs at the cathode, which is the positive electrode. The half-cell containing the cathode contains the stronger oxidising agent, and therefore, the higher reduction half-cell potential. Only the cations in solution can be reduced so they are the oxidising agents in each half-cell.

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.

It can be concluded that the order of reduction half-cell potentials, from highest to lowest is $B^{2+} > A^{2+} > C^{2+} > D^{2+}$.

11 **a** **i** Reaction will 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
  c **i** Reaction will 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

12 **a** $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$
  b no reaction
  c $2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$
  d $2H^+(aq) + Fe(s) \rightarrow H_2(g) + Fe^{2+}(aq)$
  e no reaction

13 **a** $Ag^+(aq)$; $Mg^{2+}(aq)$
  b $Mg(s)$; $Ag(s)$
  c A coating of silver will form on the lead when it is placed in silver nitrate solution because Ag^+ ions are stronger oxidants than Pb^{2+} ions.
  d zinc and magnesium

14 **a** oxidising agent
  b strong reducing agent
  c true
  d false
  e true

15 **a** Predict $Fe^{2+}(aq)$ and $H^+(aq)$ are formed
  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. Alternatively, it 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.

16 Galvanic cell: Device that converts chemical energy into electrical energy

Primary cell: A non-rechargeable galvanic cell

Secondary cell: A rechargeable galvanic cell

Fuel cell: A cell in which reactants are supplied continuously

17 **a** Electrons flow away from the negative electrode (anode), through the external circuit, to the positive electrode (cathode). Therefore, oxidation occurs at the anode and reduction occurs at the cathode.
  b A battery consists of a number of cells connected together in series.
  c When a cell discharges, chemical energy is converted to electrical energy. When it is recharged, electrical energy is converted to chemical energy.

18

Electrolyte

polarity of electrode: −

polarity of electrode: +

H_2 inlet

O_2 inlet

porous anode

porous cathode

water outlet

19 A. CO is the fuel and O_2 is the oxidising agent. None of the other reactions is a redox reaction.

20 **a** all types of cells

b all types of cells

c all types of cells

d secondary cells only

e all types of cells

f primary and secondary cells only

g fuel cells only

21 While 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.

22 D. A coating of paint will prevent contact between the metal and oxygen and water, so corrosion will not occur as long as the coating of paint is complete.

23 $Fe^{2+}(aq) + OH^-(aq)$

$Fe(OH)_2(s)$

$Fe(OH)_3(s)$

$Fe_2O_3 \cdot xH_2O(s)$

24 Copper is not a very reactive metal and so is not easily oxidised.

25 Near the seaside, moisture in the air contains a higher amount of dissolved salts (e.g. NaCl(aq)). Salts are good electrolytes and accelerate the rusting process. They do this because they increase the conductivity of moisture on the surface of the steel, (which is composed mainly of iron).

26 half-cells, anode, cathode, negative, positive, cannot, can

27 By referring to the electrochemical series, you will see that the position of the Mn^{2+}/Mn pair in the series must be determined in relation to the Zn^{2+}/Zn pair and the H_2O/H_2, OH^- pair. The student could construct an electrochemical cell from an Mn^{2+}/Mn half-cell and a Zn^{2+}/Zn half-cell. If the manganese electrode was found to be the positive electrode, then Mn^{2+} would be a stronger oxidising agent than Zn^{2+} and the Mn^{2+}/Mn pair should be placed between the Zn^{2+}/Zn pair and the Fe^{2+}/Fe pair in the series.

If the manganese electrode were negative, then Mn^{2+} would be a weaker oxidising agent than Zn^{2+} and the Mn^{2+}/Mn pair should be placed below the Zn^{2+}/Zn pair. In this case, the student could determine whether to place the manganese pair above or below the H_2O/H_2, OH^- pair by constructing a cell from an Mn^{2+}/Mn half-cell and an H_2O/H_2, OH^- half-cell and finding the polarity of the manganese electrode.

28 a Bromine is a stronger oxidising agent than iodine, so it reacts with iodide ions. Because bromine is a weaker oxidising agent than chlorine, bromine does not react with chloride ions.

b Hydrogen peroxide acts as both a strong oxidising agent and as a weak reducing agent. (It appears in the electrochemical series on the left side of one half-reaction and the right side of another.) Hydrogen peroxide therefore reacts with itself. The reaction is very slow unless a catalyst such as manganese dioxide is added.

c Sn^{2+} ions can be oxidised to Sn^{4+} ions by a suitable oxidising agent. Tin metal can reduce Sn^{4+} ions so that they re-form Sn^{2+} ions.

d Zinc is a stronger reducing agent than iron and, if the two metals are in contact, the zinc is oxidised preferentially. For this reason, the presence of a zinc block on the iron hull of a ship protects the hull from corrosion.

29 The brown stain contains iodine (I_2). A reducing agent stronger than I^- ions would react with iodine. By referring to the electrochemical series, you can see that a solution containing Sn^{2+} ions might react and cause the stain to be removed.

30 The electrochemical series is based on reactions occurring under standard conditions of 25°C (298 K), 1 bar (100 kPa) pressure and $1\,mol\,L^{-1}$ concentration 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.

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

b The student should make two electrochemical cells consisting of the:
- Cu^{2+}/Cu half-cell and the 'alkaline zinc half-cell'
- Cu^{2+}/Cu half-cell and the Zn^{2+}/Zn half-cell as shown in the diagrams.

The cell voltages should 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).

32 a • Both cells are designed to convert chemical energy into electrical energy at relatively high efficiencies.
- Oxidation and reduction reactions take place in different places within the cells.
- Both have an anode, which is negative, at which an oxidation half-reaction occurs.
- Both have a cathode, which is positive, at which a reduction half-reaction occurs.
- Both have an electrolyte, which provides ions to balance charges formed at the electrodes; cations flow towards the cathode and anions flow towards the anode.

b • A fuel cell produces electrical energy continuously when reactants are provided; primary cells can produce power for only a limited time until their reactants are depleted.
- A fuel cell uses a combustible fuel and air or oxygen; primary cells can be made from different combinations of two conjugate redox pairs.
- The reactants in fuel cells are usually gaseous; a range of solids, liquids and gases can be used as the reactants in primary cells.
- Electrodes in fuel cells must be porous to allow contact between reactant gases and the electrolyte; electrodes in primary cells need not be porous.
- Catalysts are used in fuel cells to increase cell efficiency; catalysts are not required in primary cells.

33 Advantages:
- Much more efficient than power stations and fossil-fuel-driven vehicles
- Almost the only product apart from electricity is water, so fewer carbon emissions
- Generate power continuously as they are supplied with gaseous fuel, which is ideal for commercial power generation
- Operate more quietly than internal combustion engines
- Hydrogen can be generated using renewable energy or from biogas
- Heat produced as a by-product can be used for other purposes, including electricity generation.

Disadvantages:
- Costly to produce
- Rate of the cell reaction is slow, so expensive catalytic material is needed
- Most hydrogen is produced from fossil fuels, in a process that creates greenhouse gases and consumes energy
- Lack of a hydrogen distribution network and the costs associated with the construction of pipelines, filling stations etc.
- Storage issues caused by hydrogen's low energy content per unit volume
- Safety issues due to the explosive nature of hydrogen

Chapter 10 Electrolysis
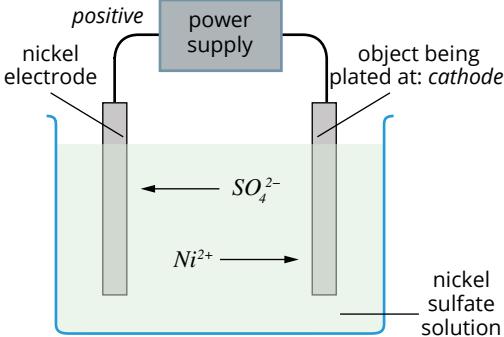
Section 10.1 Electrolytic cells

10.1 KEY QUESTIONS

1 A

2 B. The only ions present are $K^+(l)$ and $I^-(l)$.
   The anode reaction is: $2I^-(l) \rightarrow I_2(g) + 2e^-$
   The cathode reaction is: $K^+(l) + e^- \rightarrow K(l)$

3 non-spontaneous, electrical energy, chemical energy, positive, negative, oxidation, reduction

4 Anode half-equation: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
   Cathode half-equation: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$
   Overall reaction: $Zn^{2+}(l) + 2Cl^-(l) \rightarrow Cl_2(g) + Zn(l)$

5 **a** Nickel will be formed at the negatively charged nickel rod.
   b At the cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
       At the anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
   c $2Ni^{2+}(aq) + 2H_2O(l) \rightarrow 2Ni(s) + O_2(g) + 4H^+(aq)$
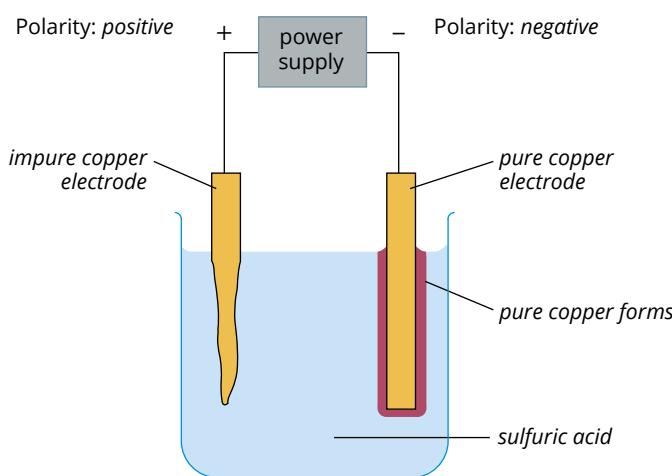
Section 10.2 Industrial applications of electrolysis

10.2 KEY QUESTIONS

1 D. Electrolysis involves non-spontaneous reactions. In these cells, the anode is positive, electrons flow through the connecting wires, ions flow in the electrolyte and energy is consumed by the cell.

2 **a**

electrode polarity:

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

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

d SO_4^{2-} ions will be attracted to the positive anode and Ni^{2+} ions will be attracted to the negative cathode. The SO_4^{2-} ions do not react at the electrode.

3 **a**
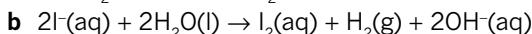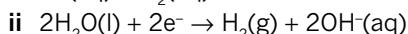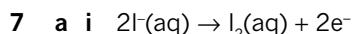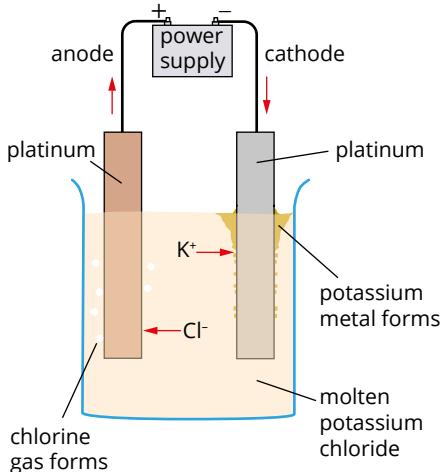
b $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

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

4 Cu^{2+} ions are produced at the anode at the same rate as they are consumed at the cathode. The concentration of the ions therefore remains constant.

CHAPTER 10 **REVIEW**

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 The correct terms are (clockwise from top left): chemical energy, non-spontaneous reactions, electrolyte, anode, cathode.

3 D. In the electrolyte, cations move towards the cathode and anions move towards the anode in order to balance charges formed by the half-reactions occurring at the electrodes.

4 **a** Galvanic cells

b Electrolytic cells

c Both

d Galvanic cells

e Both

5 Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Cathode: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$

Overall: $Zn^{2+}(l) + 2Cl^-(l) \rightarrow Zn(l) + Cl_2(g)$

6

7 a i $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

   ii $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

   b $2I^-(aq) + 2H_2O(l) \rightarrow I_2(aq) + H_2(g) + 2OH^-(aq)$
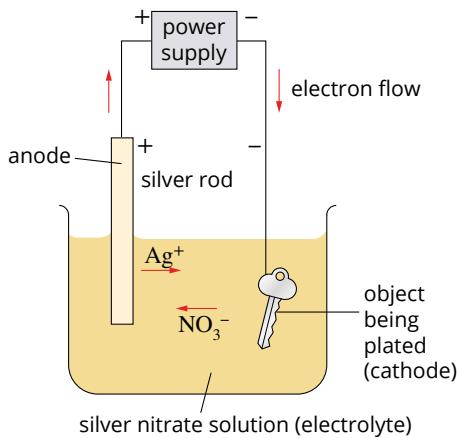
8 cathode, reduction, positive, oxidation

9 B. Tin a less reactive metal (a weaker reducing agent) than iron. Therefore, the thin layer of tin is applied to the steel to prevent corrosion.

**10** Iron is likely to rust in the wet environment of a bathroom. Nickel and chromium layers are deposited on bathroom taps by an electroplating process in order to prevent contact between the iron and water and oxygen. The surface of the taps also gains a lustrous, attractive appearance. (Nickel is used in combination with chromium to improve corrosion resistance.)

11 C. In an electroplating cell, the object to be plated is the cathode of the cell. The silver ions in the electrolye are reduced to silver metal on the surface of the cathode. Because electrons are pumped by the battery to the cathode, this electrode is described as the negative electrode.

12 a

   b The reactions at the electrodes would be reversed. The silver plating would dissolve from the key and be redeposited on the silver electrode.

13 A. In an electrorefining cell for copper, impure copper is placed at the anode and a thin sheet of pure copper is placed at the cathode. The anode is positive and the cathode is negative. Copper ions in the electrolyte solution are reduced to copper metal at the cathode, so this electrode increases in mass.

14 anode, oxidation, negative, reduction, cathode, anode, cathode.
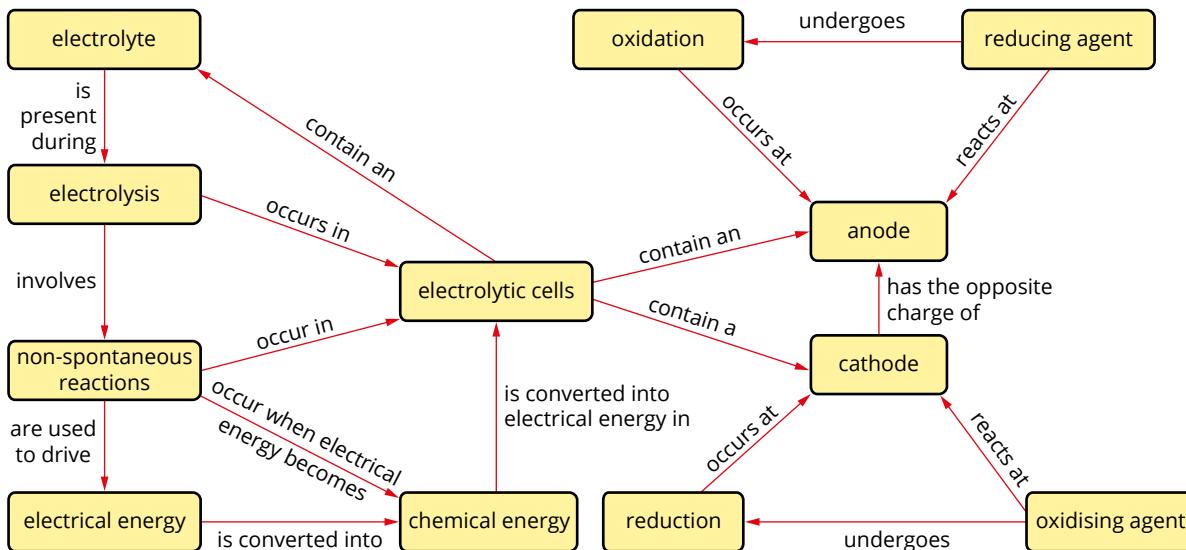
15 a A spontaneous reaction occurs naturally, either in electrochemical cells or when chemicals are mixed directly. The reaction does not need to be driven by an external source of energy. Non-spontaneous reactions are the reverse of spontaneous reactions; they are reactions that would not normally occur without the application of electrical energy.

   b The anode is an electrode where oxidation occurs; the cathode is an electrode where reduction occurs.

   c An electrochemical cell is a device that converts chemical energy into electrical energy, or vice versa. Both galvanic and electrolytic cells are electrochemical cells. An electrolytic cell only converts electrical energy into chemical energy.

   d Electrorefining is a process of purification of a metal by electrolysis. Electroplating is a process that uses electrolysis to deposit a layer of metal on the surface of another material.

16

17 By definition, oxidation always occurs at the anode. The process of oxidation involves loss of electrons. In a galvanic cell, since negatively-charged electrons are produced at the anode, this electrode is described as negative.

In an electrolytic cell, however, the positive terminal of the power supply is connected to the positive electrode of the cell. The power supply draws electrons away from the electrode, causing an oxidation reaction to occur. The positive electrode is therefore the anode.

18 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 electrolysis 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.

Unit 3 Review: Worked solutions

SECTION 1: MULTIPLE CHOICE
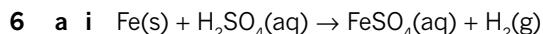
1   A. Relevant oxidation numbers for nitrogen are: NH_4^+ –3, N_2 0, NO + 2, NO_3^- +5.

2   D. For appreciable reaction, the oxidising agent must have a higher $E°$ value than the reducing agent. D is the only reaction shown where the oxidising agent has a lower $E°$ value (Pb^{2+} at –0.13 V) than the reducing agent (I^- at +0.54 V).

3   D. Cu^{2+} is the stronger oxidising agent, Ni is the stronger reducing agent.

At the positive cathode $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. Cu^{2+} is consumed and so the blue colour fades.

At the negative anode $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$. Ni is consumed and so nickel electrode mass decreases.

4   C. Recharging a secondary cell involves reversing the spontaneous reactions that occur during discharge, and so a reversible reaction is needed.

5   B. Activation energy is the difference between the initial enthalpy and the maximum enthalpy on the energy profile. For the reverse reaction this value is 390 – 260 = 130. Activation energy is always a positive value. ΔH is the difference between the final enthalpy and the initial enthalpy. For the reverse reaction, this value is negative because the products have lower enthalpy than the reactants.

6   B. Water in the pipette will dilute the acid and so require a smaller volume of potassium hydroxide for neutralisation to occur. Flasks are routinely rinsed with water, as this does not affect the results. The errors in A and D would both result in a higher titre.

7   C. A catalyst does not affect either the initial or final states of a chemical reaction. It provides an alternative pathway with lower activation energy, so more collisions will be successful, allowing the reaction rate to increase.

8   B. Lower temperatures give higher yields for an exothermic reaction (ΔH is negative). Higher pressures will move the equilibrium to the right as there are fewer gaseous product molecules than gaseous reactant molecules and so the forward reaction is pressure reducing.

9   C. The equilibrium constant gives information about the extent of the reaction. The extremely high value of K in this reaction indicates that the equilibrium lies far to the right, and that at equilibrium the mixture will be almost exclusively products. The value of K gives no indication of the value of the activation energy and rate of the reaction.

10   D. A defines the equivalence point of the titration. At this point, the added volumes may not be equal (for example the solutions may have different concentrations and will not mix in a 1:1 ratio by volume). The pH at the equivalence point depends on the nature of the chemicals present in the titration flask, and so is not always 7. Colour change defines the endpoint.

11   A. We require the two half-cells with the smallest difference in the values of $E°$. Referring to the standard reduction potentials ($E°$) gives the differences as A (–0.24 – (–1.18)) = 0.94 V, B (–0.44 – (–2.36)) = 1.92 V, C (–1.18 – (–2.36)) = 1.18 V, D (–0.24 – (–2.36)) = 2.12 V.

12   D. The flask contents are basic at the start, so the indicator colour will be yellow. As the acid is added the pH decreases until the colour change to red at the endpoint. At the equivalence point the titration flask will contain the products of the reaction, water, chloride ion and the conjugate acid of ammonia (NH_4^+). This acidic species gives the solution a pH of less than 7 at the endpoint.

SECTION 2: SHORT ANSWER
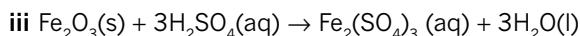
1 **a** **i** The concentration of sodium thiosulfate is higher, so there will be more frequent collisions between reactant particles. While the probability of any particular collision being successful is unchanged, the higher frequency of collisions overall will increase the frequency of successful collisions and hence the rate of reaction.

  ii The higher temperature means the particles in the mixture will be moving faster and hence colliding more frequently. Also, and more significantly, having faster-moving particles means there will be a higher proportion of collisions that are successful, because there is a greater chance of a collision having energy greater than the activation energy. These two factors combine to give a higher frequency of successful collisions and hence a higher rate of reaction.

  b **i** The rates of the forward and reverse reactions are equal up until time T.

  ii The addition of reactant W increases the frequency of collisions between reactants and 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 increases the concentration of the products, so the reverse reaction speeds up. When the two rates become equal again, equilibrium has been re-established and no further change in the rates occurs.

    iii Because the forward reaction is faster (the reverse reaction has slowed to a greater extent), there will be a net forward reaction and the equilibrium shifts to the right.

    iv Exothermic. Lowering the temperature will always induce a shift in the position of equilibrium in the direction of the exothermic reaction, which in this case must be the forward reaction since that is the direction of the shift.

    v Both rates increase equally. This is the characteristic effect of a catalyst.

2 **a** A is NO_2. B is N_2O_4.

  b $K = \dfrac{[NO_2]^2}{[N_2O_4]}$

  c Final concentration will be unchanged, but reached in less time.

  d **i** Increase. Shift right (to side with more gas particles) to increase pressure, hence amount of NO_2 increases.

    ii Decrease. Initial volume increase decreases concentration of NO_2 (only partially offset by increased amount due to shift to the right).

    iii No change. The added inert gas (at constant volume) does not disrupt the equilibrium because it does not change the concentrations (or partial pressures) of the reacting gases.

3 **a** **i** $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

    ii $Li^+(l) + e^- \rightarrow Li(l)$

    iii 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.

    iv 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^+.

  b Graphite is a good electrical conductor, relatively inexpensive, relatively inert and it has a high melting temperature.

  c Metallic cathodes are always inert because 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 of the electrode itself rather than the desired electrode reaction.

4 **a** Both types of cell contain a pair of electrodes (anode and cathode) and an electrolyte.

  b In a galvanic cell, reactants undergo spontaneous reaction to generate electricity. The energy transformation is: chemical energy $\rightarrow$ electrical energy.

  In an electrolytic cell, electricity is used to drive non-spontaneous reactions to produce useful chemical products (often very reactive ones). The energy transformation is: electrical energy $\rightarrow$ chemical energy.

  c Electrons always flow from the site of oxidation (the anode) to the site of reduction (the cathode). In a galvanic cell, the electrons flow spontaneously from the oxidation reaction at the anode, which is therefore designated negative. In an electrolytic cell, the electrons are driven through the cell from the negative terminal of an external power source to its positive terminal. Thus, the electrode designated negative in the electrolytic cell receives electrons from the power source and is the site of reduction, making it the cathode.

  d A galvanic cell employs a spontaneous redox reaction (favourable oxidising–reducing agents combination) to produce an electron flow. If the reactants come into direct contact, electrons flow directly between them and no current is produced. In an electrolytic cell, there are no favourable combinations and instead non-spontaneous reactions occur by forcing a current through the cell, forming reactive products that would react spontaneously if allowed to come into contact.

5 **a** **i** $H_2S(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + H_3O^+(aq)$

    ii $K = \dfrac{[H_3O^+][HS^-]}{[H_2S]}$

  b $n(H_2S) = \dfrac{m}{M} = \dfrac{1.7}{34.1}$ mol

    $[H_2S] = \dfrac{n}{V} = \dfrac{1.7}{34.1 \times 0.5000} = 1.0 \, mol \, L^{-1}$

  c **i** A solution that resists changes in pH over a small range of values.

    ii This buffer system contains the weak acid hydrogen sulfide and its conjugate weak base the hydrogen sulfide ion. The equilibrium can be written as:

    $H_2S(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + H_3O^+(aq)$

    If a small amount of the strong acid HCl is added, the extra H_3O^+ will move the position of equilibrium to the left so as to partly compensate for the increase in concentration of product according to Le Châtelier's principle. The concentration of H_3O^+ will fall and so the pH will rise to near (but still below) its original value.

  d $2Ag^+(aq) + H_2S(aq) \rightarrow 2Ag(s) + S(s) + 2H^+(aq)$

6 a i $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$
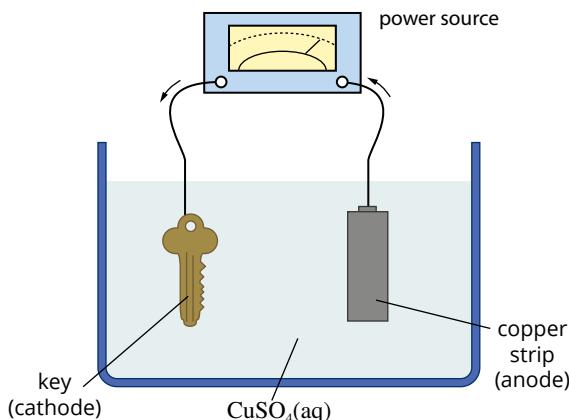
ii The Fe atoms have lost electrons to form Fe^{2+} ions, while the H^+ ions have gained electrons to form H_2 molecules. Redox reactions involve this type of electron transfer. Or the oxidation number of Fe increases from 0 to +2 and the oxidation number of H reduces from +1 to 0.

iii $Fe_2O_3(s) + 3H_2SO_4(aq) \rightarrow Fe_2(SO_4)_3(aq) + 3H_2O(l)$

iv O^{2-} ions have gained H^+ ions to form H_2O, while H_2SO_4 molecules have lost H^+ ions to form SO_4^{2-} ions. Acid–base reactions involves this type of proton (H^+) transfer.

b i
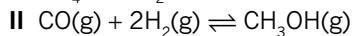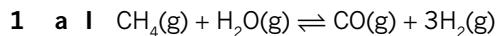
ii The key needs to be connected to the negative electrode.

iii The cathode

iv The concentration of Cu^{2+} ions in the electrolyte does not change because the copper ions are continually supplied by the oxidation of the copper anode as copper ions are consumed at the cathode.

v Reaction at the anode would be: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$. As H^+ ions are produced, the pH would decrease.

SECTION 3: EXTENDED ANSWER

1 a I $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

II $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
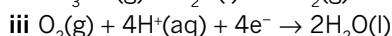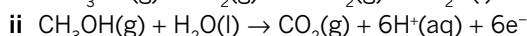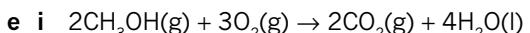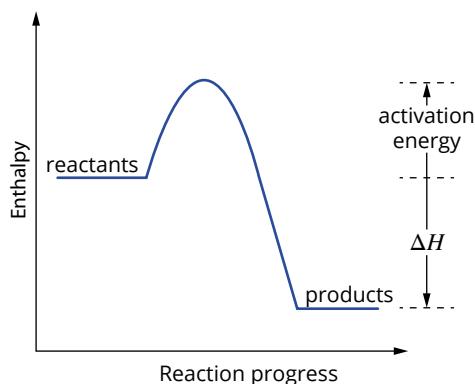
b i Catalysts

ii The yield would be poorer. Because the reaction is exothermic, increasing the temperature would favour the reactants/shift the position of equilibrium to the left/lower the equilibrium constant.

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.

c Exposure to CO will drive the first reaction to the right. This lowers the concentration of free haemoglobin (Hb_4), which drives the second reaction to the left, removing Hb_4O_2.

d

e i $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

ii $CH_3OH(g) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

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

iv In a fuel cell chemical energy is converted to electrical energy, with some loss of heat energy. In direct combustion, chemical energy is converted to thermal energy.

v For example: They are similar in that both have electrodes and an electrolyte. They are different in that fuel cell electrodes have a catalytic function, while those in galvanic cells do not.

f **i** $PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

  ii $1.69 - (-0.36) = 2.05$ V

  iii $E°$ values are determined at standard conditions ($1.0\,mol\,L^{-1}$ solutions). Concentrations in the lead-acid cell are not $1.0\,mol\,L^{-1}$, and so electrode potential values may differ.

  iv Discharging is operating as a galvanic cell. Oxidation occurs at the negative anode.

  v Positive to positive. Negative to negative.

2 **a** **i** An acid that only partially ionises in water.

  ii $K = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$

b **i** To show that the reaction is complete.

  ii $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

  iii $n(NaOH) = cV = 0.100 \times 18.5 \times 10^{-3}\,mol = 1.85 \times 10^{-3}\,mol$

   $n(CH_3COOH) = n(NaOH)$ mol in 20.00 mL $= 1.85 \times 10^{-3}$ mol

   $n(CH_3COOH)_{total} = n(CH_3COOH) \times \dfrac{250.0}{20.00}$ mol $= 0.0231$ mol

   $[CH_3COOH] = \dfrac{n}{V} = \dfrac{0.0231}{10.0 \times 10^{-3}} = 2.31\,mol\,L^{-1}$

  iv NaOH completely dissociates in water.

   $[OH^-] = 0.10$

   $[H_3O^+] \times [OH^-] = 10^{-14}$

   $\therefore 0.10 \times [H_3O^+] = 10^{-14}$

   $\therefore [H_3O^+] = 10^{-13}\,mol\,L^{-1}$

   $\therefore pH = -\log_{10}[H_3O^+] = -\log_{10}10^{-13} = 13$

c **i** 25.0 mL

  ii $0.10\,mol\,L^{-1}$ HCl has a pH of 1.0

  iii 7.0

  iv Greater than 7.0. At the equivalence point the titration flask will contain the products of the reaction, including the conjugate base of ethanoic acid (CH_3COO^-). This basic species gives the solution a pH of greater than 7 at the equivalence point.

d **i** $H_2O_2(aq) + H_2O(l) \rightleftharpoons HO_2^-(aq) + H_3O^+(aq)$

  ii The rate of the decomposition reaction is slow, especially without the catalytic action of light (storage in dark bottles). Cooling the solution further slows the rate at which the H_2O_2 reacts with itself.

e **i** The self-ionisation reaction of water produces ions which allow the liquid to conduct. However, the concentration of ions is extremely low, accounting for the very poor conductivity.

   $2H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$

  ii $K_w = [H_3O^+] \times [OH^-]$

   $[H_3O^+] = [OH^-]$

   $[H_3O^+]^2 = 1.85 \times 10^{-15}$

   $[H_3O^+] = 4.3 \times 10^{-8}$

   $pH = 7.4$

  iii $K_w = [H_3O^+] \times [OH^-]$

   $[H_3O^+] = [OH^-]$

   $[OH^-]^2 = 2.09 \times 10^{-14}$

   $[OH^-] = 1.45 \times 10^{-7}\,mol\,L^{-1}$

  iv Oxidising agent

Chapter 11 Key products from the chemical industry

Section 11.1 Yield and the chemical industry

Worked example: Try yourself 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

A 50.0 mL volume of 0.250 mol L^{-1} silver nitrate aqueous solution is mixed with excess sodium chloride solution. The precipitate is filtered and dried to give 1.37 g of silver chloride. Calculate the percentage yield of this reaction.

Thinking	Working
Write a balanced equation for the reaction.	$Ag^+(aq) + Cl^- \rightarrow AgCl(s)$
Use the appropriate formula, in this case $n = c \times V$, to determine the amount, in moles, of reactant.	$n(Ag^+) = n(AgCl) = 0.250 \times 0.050 = 1.25 \times 10^{-2}$ 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 reacted.	Mole ratio $= \dfrac{n(Ag^+)}{n(AgCl)} = \dfrac{1}{1}$ $n(AgCl) = \dfrac{1}{1} \times n(Ag^+)$ $\qquad\qquad = 1.25 \times 10^{-2}$ 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.	$m(AgCl) = n \times M$ $\qquad\qquad = 1.25 \times 10^{-2} \times 143.35$ $\qquad\qquad = 1.79$ g
Calculate the percentage yield for this reaction from the formula: percentage yield $= \dfrac{\text{actual yield}}{\text{theoretical yield}} \times \dfrac{100}{1}$	Percentage yield $= \dfrac{1.37}{1.79} \times \dfrac{100}{1}$ $\qquad\qquad\qquad = 76.5\%$

Worked example: Try yourself 11.1.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of D from A if it proceeds by a three-step synthesis:

A → B followed by B → C followed by C → 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: $\dfrac{90}{100} \times \dfrac{80}{100} \times \dfrac{60}{100} \times \dfrac{100}{1}$ $= 43.2\%$

11.1 KEY QUESTIONS

1 $M(C_2H_4) = 28.052$

   $n(C_2H_4) = \dfrac{150}{28.052} = 5.347$ mol

   $n(C_2H_5OH) = n(C_2H_4) = 5.347$ mol
   Theoretical mass $(C_2H_5OH) = 5.347 \times 46.07 = 246.34$ g

2 $M(C_2H_5OH) = 46.07$

$n(C_2H_5OH) = \frac{20.0}{46.07} = 0.43412 \, mol$

$n(CH_3COOH) = n(C_2H_5OH) = 0.43412 \, mol$
Theoretical mass $(CH_3COOH) = 0.43412 \times 60.052 = 26.07 \, g$

Yield $= \frac{21.5}{26.07} \times 100 = 82.5\%$

3   **a** Overall yield $= \frac{70}{100} \times \frac{50}{100} \times \frac{90}{100} = 31.5\%$

   b The overall yield would be reduced by a factor of 5 (because the yield of step B → C is reduced by a factor of 5).
   This can be calculated by:

   $\frac{70}{100} \times \frac{10}{100} \times \frac{90}{100} = 6.3\%$

4 $n(Ca_3(PO_4)_2) = \frac{m}{M} = \frac{1500}{310.18} = 4.836 \, mol$

$n(H_3PO_4) = 2 \times n(Ca_3(PO_4)_2) = 9.672 \, mol$
For 100% yield, $m(H_3PO_4) = n \times M = 9.672 \times 97.994 = 9.478 \times 10^2 \, g$
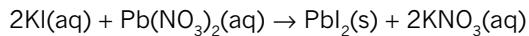
For 67% yield, $m(H_3PO_4) = 9.478 \times 10^2 \times \frac{67}{100} = 6.350 \times 10^2 \, g$

Section 11.2 Calculations involving limiting reagents

Worked example: Try yourself 11.2.1

MASS–MASS STOICHIOMETRY CALCULATION WITH ONE REACTANT IN EXCESS

A solution containing 0.600 g of lead(II) nitrate is added to a solution containing 2.60 g of potassium iodide. An equation for the reaction is:

$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

a Which reactant is the limiting reagent?

b What is the mass of precipitate formed?

Thinking	Working
a Calculate the number of moles of each of the reactants in the equation using $n = \frac{m}{M}$ or $n = c \times V$ or $n = \frac{PV}{RT}$ as appropriate.	Use the equation $n = \frac{m}{M}$. For $Pb(NO_3)_2$: $n(Pb(NO_3)_2) = \frac{0.6}{331.22} = 1.812 \times 10^{-3} \, mol$ For KI: $n(KI) = \frac{2.6}{166.0} = 1.566 \times 10^{-2} \, mol$
Use the coefficients of the equation to find the limiting reagent.	The equation shows that 2 mol of KI reacts with 1 mol of $Pb(NO_3)_2$. So to react all of the KI, you will require: $\frac{2}{1} \times n(Pb(NO_3)_2)$ of KI $\frac{2}{1} \times 1.812 \times 10^{-3} = 3.624 \times 10^{-3} \, mol$ As there is $1.566 \times 10^{-2} \, mol$ available, the KI is in excess. So, $Pb(NO_3)_2$ is the limiting reagent (it will be completely consumed).

b Find the mole ratio of the unknown substance to the limiting reagent from the equation coefficients: $\text{mole ratio} = \dfrac{\text{coefficient of unknown}}{\text{coefficient of limiting reagent}}$	From the equation coefficients: $\dfrac{\text{coefficient of PbI}_2}{\text{coefficient of Pb(NO}_3)_2} = \dfrac{1}{1}$
Calculate the number of moles of the unknown substance using the number of moles of limiting reagent: $n(\text{unknown}) = n(\text{limiting reagent}) \times \text{mole ratio}$	$n(\text{PbI}_2) = n(\text{Pb(NO}_3)_2) \times \dfrac{1}{1}$ $= 1.812 \times 10^{-3} \times \dfrac{1}{1}$ $= 1.812 \times 10^{-3}\,\text{mol}$
Calculate the mass of the unknown substance using: $m(\text{unknown}) = n(\text{unknown}) \times \text{molar mass}$	Molar mass of $\text{PbI}_2 = 461.0\,\text{g mol}^{-1}$ $m(\text{PbI}_2) = 1.812 \times 10^{-3} \times 461.0$ $\quad\quad\quad\ = 0.837\,\text{g}$
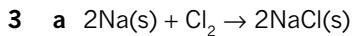
11.2 KEY QUESTIONS

1 II Calculate the number of moles of aluminium and of oxygen.

IV Refer to the balanced equation.

I Use mole ratios to determine which reactant is limiting.

V Calculate the number of moles of aluminium oxide that forms.

III Calculate the mass of aluminium oxide that forms.

2

Nitrogen molecules available	Hydrogen molecules available	Ammonia molecules produced	Nitrogen molecules in excess	Hydrogen molecules in excess
2	10	4	0	4
879	477	318	720	0
9 mol	6 mol	4 mol	7 mol	0 mol

Explanation

- Both nitrogen molecules will react with $2 \times 3 = 6$ hydrogen molecules to produce $2 \times 2 = 4$ ammonia molecules, so $10 - 6 = 4$ hydrogen molecules will be in excess.

- All 477 hydrogen molecules will react with $477 \times \dfrac{1}{3} = 159$ nitrogen molecules to produce $477 \times \dfrac{2}{3} = 318$ ammonia molecules. $879 - 159 = 720$ nitrogen molecules will be in excess.

- All 6 mol hydrogen molecules will react with $6 \times \dfrac{1}{3} = 2\,\text{mol}$ nitrogen molecules to produce $6 \times \dfrac{2}{3} = 4\,\text{mol}$ ammonia molecules. $9 - 2 = 7$ nitrogen molecules will be in excess.

3 **a** $2\text{Na(s)} + \text{Cl}_2 \rightarrow 2\text{NaCl(s)}$

b $n(\text{Na}) = \dfrac{m}{M} = \dfrac{25.0}{23.0} = 1.09\,\text{mol}$

$n(\text{Cl}_2) = \dfrac{m}{M} = \dfrac{50.0}{71.0} = 0.704\,\text{mol}$

$\dfrac{n(\text{Na})}{n(\text{Cl}_2)} = \dfrac{2}{1}$

Sodium is the limiting reagent; use the moles of sodium to calculate $n(\text{NaCl})$:

$\dfrac{n(\text{NaCl})}{n(\text{Na})} = \dfrac{1}{1}$

$n(\text{NaCl}) = n(\text{Na}) = 1.09\,\text{mol}$

$m(\text{NaCl}) = n \times M = 1.09 \times 58.5 = 63.8\,\text{g}$

4 **a** In the equation for the reaction:

$$\frac{\text{coefficient of KI}}{\text{coefficient of Pb(NO}_3)_2} = \frac{2}{1} = 2$$

2 mol of KI react with 1 mol of $Pb(NO_3)_2$

In this case, not all the $Pb(NO_3)_2$ can react and it will be in excess.

From the equation:

$$n(Pb(NO_3)_2) \text{ reacted} = \frac{1}{2} \times n(KI) = \frac{1}{2} \times 1.0 = 0.50 \text{ mol}$$

So, $Pb(NO_3)_2$ is in excess by $(1.0 - 0.50) = 0.50$ mol.

b In the equation for the reaction:

$$\frac{\text{coefficient of KI}}{\text{coefficient of Pb(NO}_3)_2} = \frac{2}{1} = 2$$

2 mol of KI react with 1 mol of $Pb(NO_3)_2$.

In this case, not all the $Pb(NO_3)_2$ can react and it will be in excess.

From the equation:

$$n(Pb(NO_3)_2) \text{ reacted} = \frac{1}{2} \times n(KI)$$

$$= \frac{1}{2} \times 0.5 = 0.25 \text{ mol}$$

So, $Pb(NO_3)_2$ is in excess by $(2.0 - 0.25) = 1.75$ mol

c $n(Pb(NO_3)_2) = \frac{1.00}{331} = 0.00302 \text{ mol}$

$n(KI) = \frac{1.50}{166} = 0.00904 \text{ mol}$

In the equation for the reaction:

$$\frac{\text{coefficient of KI}}{\text{coefficient of Pb(NO}_3)_2} = \frac{2}{1} = 2$$

2 mol of KI react with 1 mol of $Pb(NO_3)_2$.

In this case, not all of the KI can react and some of it will be in excess. This means that $Pb(NO_3)_2$ is the limiting reactant.

The equation shows that 1 mol of PbI_2 precipitate will form for every 1 mol of $Pb(NO_3)_2$ that reacts.

$n(PbI_2) = n(Pb(NO_3)_2) = 0.00302 \text{ mol}$

$m(PbI_2) = 0.00302 \times 461 = 1.39 \text{ g}$

d $n(Pb(NO_3)_2) = c \times V = 1.00 \times 0.0500 = 0.0500 \text{ mol}$

$n(KI) = c \times V = 0.500 \times 0.0750 = 0.0375 \text{ mol}$

$$\frac{\text{coefficient of KI}}{\text{coefficient of Pb(NO}_3)_2} = \frac{2}{1} = 2$$

2 mol of KI react with 1 mol of $Pb(NO_3)_2$.

In this case, not all of the $Pb(NO_3)_2$ can react and some of it will be in excess. This means KI is the limiting reactant.

The equation shows that 1 mol of PbI_2 precipitate will form for every 2 mol of KI that reacts.

$$n(PbI_2) = \frac{1}{2} \times n(KI) = \frac{1}{2} \times 0.0375 = 0.00188 \text{ mol}$$

$$m(PbI_2) = 0.00188 \times 461 = 8.64 \text{ g}$$

Section 11.3 Some key products

11.3 KEY QUESTIONS

1 A and D

A is correct because air is about 78% N_2 and the N_2 is recovered from the air by fractional distillation.

D is correct because it is estimated that about 80% of N in the protein in a person's body is from NH_3 made by the Haber process.

B is incorrect because most NH_3 is used to make fertilisers.

C is incorrect because CO_2 is one of the products from steam re-forming of methane. The C in the CO_2 has not been part of the carbon cycle for millions of years, so its release adds more CO_2 to the atmosphere, contributing to global warming.

E is incorrect because the overall yield in the Haber process is about 98%.

2   a

	Increase	Decrease	No change
Reaction rate	Addition of a catalyst Increasing pressure	Reducing temperature	
Equilibrium yield	Reducing temperature Increasing pressure		Addition of a catalyst

    b Increasing the partial pressure of nitrogen will increase the frequency of collisions between nitrogen and hydrogen molecules and so increase the rate of the forward reaction. The yield of ammonia at the new equilibrium will also increase as the rate of forward reaction will be higher at the new equilibrium than it was at the original equilibrium.

3   A = $N_2(g)$

    B = $H_2(g)$

    C = $N_2(g)$, $H_2(g)$ and $NH_3(g)$

    D = $NH_3(l)$

    E = $N_2(g)$ and $H_2(g)$

4   D. Oleum is formed in the second last step in the production of sulfuric acid. It is formed by the absorption of SO_3 in concentrated sulfuric acid in the absorption tower. The sulfur is reacted with air in the burner; sulfur dioxide is converted to sulfur trioxide in the converter; there is no dilution tower in the contact process.

5

Burner	Converter	Absorption tower
$O_2(g)$, $S(l)$	$O_2(g)$, $SO_2(g)$	$SO_3(g)$, $H_2SO_4(l)$

6   Sulfur dioxide dissolves in rain, making rain acidic due to formation of sulfurous acid. Also, sulfur dioxide corrodes metal and is harmful to plants and aquatic animals.

Chapter 11 **REVIEW**

1   **a** Working: molar ratio of salicylic acid to aspirin is 1 : 1

      $M(C_7H_6O_3) = 138\,g\,mol^{-1}$

      $n(C_7H_6O_3) = \dfrac{2.5}{138}$

               $= 0.0181\,mol$

      $n(aspirin) = 0.0181\,mol$

      $M(aspirin) = M(C_9H_8O_4)$

                $= 180\,g\,mol^{-1}$

      $m(aspirin) = 0.0181 \times 180$

                $= 3.26\,g$

    b % yield $= \dfrac{2.35}{3.26} \times 100 = 72.1\%$

2   **a** Overall yield $= 0.95 \times 0.80 \times 0.90 \times 100 = 68.4\%$

    b $n(NH_3) = \dfrac{m}{M} = \dfrac{1.5 \times 10^6}{17.034} = 8.81 \times 10^4\,mol$

      $n(NO_2) = n(NO) = n(NH_3) = 8.81 \times 10^4\,mol$

      $n(HNO_3) = \dfrac{2}{3} \times n(NO_2) = \dfrac{2}{3} \times 8.81 \times 10^4 = 5.87 \times 10^4\,mol$

      $m(HNO_3) = n \times M = 5.87 \times 10^4 \times 63.008 = 3.70 \times 10^6\,g$

    c Actual $m(HNO_3) = 0.684 \times 3.70 \times 10^6 = 2.53 \times 10^6\,g$

3 $n(NH_3) = \frac{m}{M} = \frac{5.5 \times 10^6}{17.034} = 3.23 \times 10^4 \, mol$

$n(H_2) = \frac{3}{2} \times n(NH_3) = \frac{3}{2} \times 3.23 \times 10^5 = 4.84 \times 10^5 \, mol$

If 100% yield, $m(H_2) = 2.016 \times 4.84 \times 10^5 = 9.76 \times 10^5 \, g$

For 98% yield, $m(H_2) = 9.76 \times 10^5 \times \frac{100}{98} = 9.96 \times 10^5 \, g$

4 The reaction of sulfur dioxide and oxygen is reversible, and the yield of this reaction will be affected by the reaction conditions. The other two reactions in the process are not reversible.

5

Carbon atoms available	Oxygen molecules available	Carbon dioxide molecules produced	Carbon atoms in excess	Oxygen molecules in excess
8	20	8	0	12
1000	3000	1000	0	2000
9 mol	6 mol	6 mol	3 mol	0 mol

6 **a** Oxygen is in excess.

b 1.5 mol of sodium oxide is produced.

$\frac{n(O_2)}{n(Na)} = \frac{1}{4}$

Since the $n(O_2)$ required is 0.75 mol, oxygen is in excess and sodium is the limiting reagent.

Next, calculate the number of moles of sodium oxide from the number of moles of sodium.

$\frac{n(Na_2O)}{n(Na)} = \frac{2}{4} = \frac{1}{2}$

$n(Na_2O) = 3 \times \frac{1}{2} = 1.5 \, mol$

7 **a** $m(S) = 22.6 \, g$

$n(H_2S) = \frac{16}{34} = 0.471 \, mol$

$n(SO_2) = \frac{20}{64} = 0.313 \, mol$

From the balanced equation the number of moles of H_2S needs to be double that of SO_2. It is not; therefore, H_2S is the limiting reactant.

$n(S) = \frac{3}{2} \times 0.471 = 0.707 \, mol$

$\therefore m(S) = n \times M = 0.707 \times 32 = 22.6 \, g$

b $m(SO_2) = 4.93 \, g$

This is calculated by following the steps below.

$n(SO_2 \text{ reacting}) = \frac{1}{2} \times 0.471 = 0.236 \, mol$

$n(SO_2 \text{ remaining}) = 0.313 - 0.236 = 0.077 \, mol$

$\therefore m(SO_2) = n \times M = 0.077 \times 64 = 4.93 \, g$

8 $n(N_2) = \frac{m}{M} = \frac{2.00 \times 10^6}{28.02} = 7.13 \times 10^4 \, mol$

$n(H_2) = \frac{m}{M} = \frac{1.50 \times 10^6}{2.016} = 7.44 \times 10^5 \, mol$

1 mol N_2 needs 3 mol H_2 for complete reaction

thus, $7.13 \times 10^4 \, mol \, N_2$ needs $2.14 \times 10^5 \, mol \, H_2$ for complete reaction

Therefore, there is excess H_2 and N_2 is the limiting reagent.

$n(NH_3) = 2 \times n(N_2) = 1.43 \times 10^5 \, mol$

$m(NH_3) = 1.43 \times 10^5 \times 17.034 \times 0.96 = 2.43 \times 10^6 \, g$

9 a Rock phosphate is insoluble in water and plants can only absorb nutrients through their roots when the nutrients are dissolved in water.

b $n(Ca_3(PO_4)_2) = \dfrac{800\,000}{310.18} = 2.579 \times 10^3\,mol$

$m(H_2SO_4) = 1\,220\,000 \times \dfrac{62}{100} = 7.564 \times 10^5\,g$

$n(H_2SO_4) = \dfrac{7.564 \times 10^5}{98.096} = 7.711 \times 10^3\,mol$

1 mol $Ca_3(PO_4)_2$ needs 2 mol H_2SO_4 for complete reaction.

Thus, 2.579×10^3 mol $Ca_3(PO_4)_2$ 5.158×10^3 mol H_2SO_4 for complete reaction.

Therefore, there is excess H_2SO_4 and $Ca_3(PO_4)_2$ is the limiting reagent.

$n(Ca(H_2PO_4)_2) = n(Ca_3(PO_4)_2) = 2.579 \times 10^3$ mol
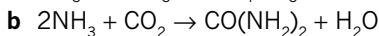
$m(Ca(H_2PO_4)_2) = 2.579 \times 10^3 \times 234.052 = 6.037 \times 10^5\,g$

$n(CaSO_4 \cdot 2H_2O) = 2 \times n(Ca_3(PO_4)_2) = 5.158 \times 10^3$ mol

$m(CaSO_4 \cdot 2H_2O) = 5.158 \times 10^3 \times 172.192 = 8.882 \times 10^5\,g$

Thus, mass of superphosphate $= 6.037 \times 10^5 + 8.882 \times 10^5 = 1.492 \times 10^6\,g = 1492\,kg$

10 Ammonia has a higher boiling point than both nitrogen and hydrogen. This is because there are only dispersion forces of attraction between neighbouring nitrogen molecules and neighbouring hydrogen molecules, while there are dispersion and hydrogen bonding forces between neighbouring ammonia molecules. This means more energy is needed to overcome the force of attraction between neighbouring ammonia molecules.

11 a $NH_3 + HNO_3 \rightarrow NH_4NO_3$

b $2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$

c For each gram of ammonium nitrate, $m(N) = \dfrac{1}{80.052} \times 28.02 = 0.350\,g$
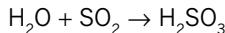
For each gram of urea, $m(N) = \dfrac{1}{60.062} \times 28.02 = 0.466\,g$

Thus, on a gram basis, urea provides more nitrogen than ammonium nitrate.

12 The steam reforming process used to recover the hydrogen from methane releases the greenhouse gas CO_2 to the atmosphere. As methane is the main component of natural gas, a fossil fuel, the carbon released in the CO_2 has not been a part of the carbon cycle for millions of years, which leads to an increase in CO_2 in the atmosphere and so contributes to global warming.

13 a A = molten sulfur; B = sulfur dioxide; C = sulfur trioxide; D = unreacted sulfur dioxide; E = oleum diluted to form sulfuric acid

b If moisture is present in the air, it may react with sulfur dioxide to form sulfurous acid as shown in the reaction:

$H_2O + SO_2 \rightarrow H_2SO_3$

14 converter, V_2O_5, moderate, beds, cooled, SO_2, absorption tower, converter, SO_2

15 C. SO_2 reacts with water in the atmosphere to produce sulfurous acid (H_2SO_3), which can corrode metal and carbonate structures.

16 D. The activation energy of any reaction is a constant under all conditions.

A is incorrect because the equilibrium constant (K) is temperature-dependent, so a change in temperature changes the value of K.

B, C are incorrect because the rates of both the forward and reverse reactions are decreased at lower temperatures.

17 a Yield of H_2 will be maximised under conditions of high temperature and low pressure. Le Châtelier's principle predicts that increasing the temperature of a reaction favours the endothermic direction, so in this case the forward reaction will be favoured, thus increasing yield of H_2. Le Châtelier's principle predicts that decreasing the pressure of a reaction favours the side with most gas molecules, so in this case the forward reaction will be favoured, thus increasing yield of H_2.

b The high temperature will increase the rate of reaction because a higher proportion of collisions will have energy above the activation energy. The low pressure will reduce the rate of reaction because this will reduce the frequency of collisions between reactant molecules.

18 a 75–100 atm

b Both the forward and reverse reaction rates will be smaller at the new equilibrium because at the lower temperature the proportion of molecules colliding with energy above the activation energy will be smaller (as well, the frequency of collisions between molecules will be less). Le Châtelier's principle predicts that lowering the temperature of a reaction favours the exothermic direction, so in this case the forward reaction will be favoured, thus increasing yield of NH_3.

c Both the forward and reverse reaction rates will be less at the new equilibrium because at the lower pressure the frequency of collisions between molecules will be less. Le Châtelier's principle predicts that reducing the pressure in a gaseous reaction will favour the side with more gas molecules, so in this case the reverse reaction will be favoured, thus decreasing yield of NH_3. The combination of increased yield from the lower temperature and decreased yield from the lower pressure means the yield remains at about 20%.

19 a $n(SO_2) = n(NiS) = \dfrac{3.5 \times 10^6}{90.76} = 3.86 \times 10^4 \, \text{mol}$

$V(SO_2) = \dfrac{nRT}{P} = \dfrac{3.86 \times 10^4 \times 8.314 \times 303.15}{101.3} = 9.59 \times 10^5 \, \text{L}$

b Mole relationship: $1 \, \text{mol} \, SO_2 \rightarrow 1 \, \text{mol} \, SO_3 \rightarrow 1 \, \text{mol} \, H_2SO_4$

Therefore, for 100% yield, $n(H_2SO_4) = 3.86 \times 10^4 \, \text{mol}$

$m(H_2SO_4) = 3.86 \times 10^4 \times 98.086 = 3.78 \times 10^6 \, \text{g}$
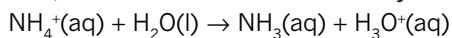
Overall yield = $0.98 \times 0.98 \times 100 = 96.04\%$

Thus, actual yield of pure H_2SO_4: $m(H_2SO_4) = 0.9604 \times 3.78 \times 10^6 = 3.63 \times 10^6 \, \text{g}$

Mass of 70% concentration solution produced = $\dfrac{100}{70} \times 3.63 \times 10^6 = 5.19 \times 10^6 \, \text{g}$

20 a $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

b Release of ammonium ions from the ammonium sulfate allows them to undergo hydrolysis to produce hydronium ions, which increases the soil acidity.

$NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq)$

Chapter 12 Resources and the environment
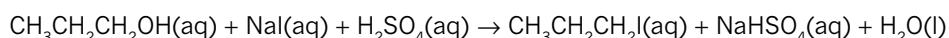
Section 12.1 Green chemistry

Worked example: Try yourself 12.1.1

CALCULATING ATOM ECONOMY

Calculate the atom economy for the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol. The equation for the reaction is: $$CH_3CH_2CH_2OH(aq) + NaI(aq) + H_2SO_4(aq) \rightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$$	
Thinking	**Working**
Calculate the total molar mass of the reactants.	$M(CH_3CH_2CH_2OH) + M(NaI) + M(H_2SO_4)$ $= [(3 \times 12.01) + (8 \times 1.008) + 16.00] + (22.99 + 126.9)$ $+ [(2 \times 1.008) + 32.07 + (4 \times 16.00)]$ $= 308.1\,g\,mol^{-1}$
Calculate the molar mass of the required product.	$M(\text{iodopropane})$ $= (3 \times 12.01) + (7 \times 1.008) + 126.9$ $= 170.0\,g\,mol^{-1}$
Calculate the atom economy for the reaction using the formula: $$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$	$$\text{Atom economy} = \frac{170.0}{308.1} \times 100$$ $$= 55.2\%$$

12.1 KEY QUESTIONS

1   Green chemistry is a philosophy of designing resource-efficient, environmentally friendly and low-hazard chemical products and processes.

2   The focus of green chemistry is to eliminate waste and pollution through technological and engineering means before they are generated, whereas environmental chemistry studies chemical processes that occur in the natural environment and how they are affected by human activities such as mining and pollution.

3   Prevent waste, design safe chemicals and products, design less hazardous chemical syntheses, use renewable raw materials, use catalysts, avoid using excess reactants, avoid chemical derivatives, maximise atom economy, use safer solvents and reaction conditions, increase energy efficiency, design for degradation, analyse in real time to prevent pollution and minimise the potential for accidents.

4   Using renewable materials ensures that there is a constant, environmentally friendly source of raw material as opposed to using non-renewable materials that will eventually run out.

5   The new ibuprofen synthesis has a much higher atom economy, which means less costly raw material ends up as waste products. Also, because there are fewer steps in the newer synthesis, it is likely that it is much faster-acting than the old one.

6   Water is a highly polar molecule, whereas hydrophobic substances such as oil and grease are non-polar. A non-polar solvent is required to form dispersion forces with the non-polar oil and grease.

7   Glycine is environmentally benign, cheaper, recyclable and non-toxic and can be used for *in situ* leaching.

8   Introduce an additional source of fresh, oxygenated water to the Peel–Harvey Estuary. Reduce the use of phosphate-containing fertilisers in the Peel–Harvey region.

CHAPTER 12 **REVIEW**

1 D. Green chemistry aims at reducing the risk chemicals pose to both people and the environment. It might accomplish this by designing a new chemical and ideally would not adversely affect profits, but these are not the aim of green chemistry. The study of chemical processes that occur in nature is environmental chemistry.

2 C. Avoiding using artificial chemicals is not a principle of green chemistry, rather it is ensuring the chemicals that are used are safe, renewable, used efficiently and don't harm the environment. Referring to naturally sourced chemicals does not imply they are safe chemicals.

3 False. The application of green chemistry should not incur additional cost to industry.

4 A. The application of green chemistry should not incur additional cost to industry. If waste products can be turned into a profitable commodity, this is the best outcome for both industry and the environment.

5 False, but the principles of green chemistry can be applied to all types of farming.

6 Use fewer reagents, generate less waste, use renewable materials and be more energy efficient.

7 Storing, treating and disposing of waste costs significant amounts of money. Reducing the amount of waste produced would reduce running costs, thereby increasing profit margins. Also, using renewable materials means that production would not have to cease once a finite starting resource has been exhausted.

8 Catalysts allow reactions to use less energy and to proceed at a rate that does not necessitate high concentrations, thereby using fewer resources.

9 Using nearby resources reduces the requirement to transport large quantities of materials over large distances, which consumes a large amount of energy.

10 This would have caused air pollution as a result of incinerating waste, resulting in photochemical smog (due to the release of volatile organic compounds and oxides of nitrogen) and acid rain (due to the release of oxides of sulfur and nitrogen).

11 By using smaller quantities of reagents and disposing of chemicals correctly according to the teacher's instructions.

12 Carbon dioxide: asphyxiant in high concentrations and liquid may cause cold burns. Perchloroethylene: eye and skin irritation, toxic if swallowed, irregular heartbeat and possible carcinogen.
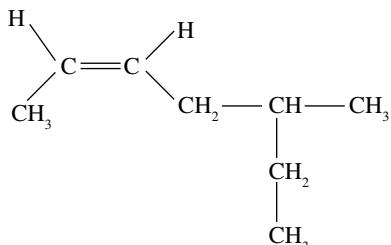
Chapter 13 Structure of organic molecules

Section 13.1 Diversity of carbon compounds

Worked example: Try yourself 13.1.1

NAMING A *cis–trans* ISOMER OF AN ALKENE
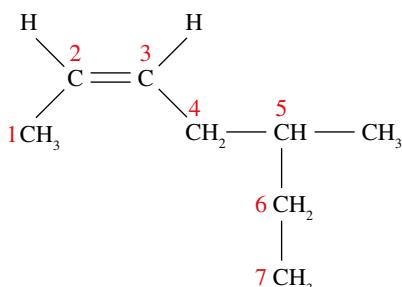
Write the systematic name of the following alkene.
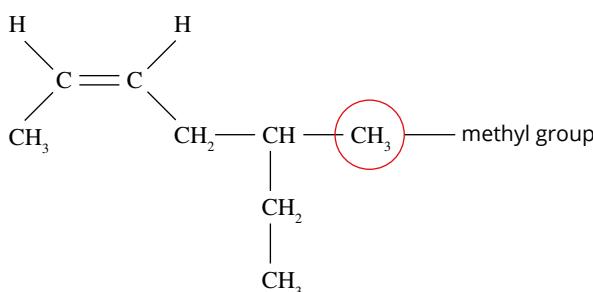
| Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms that contains the carbon–carbon double bond.	 There are seven carbon atoms in the longest continuous chain, so the parent name is heptene.
Identify any alkyl side chains by counting the number of carbon atoms in any branches.	 There is one carbon atom in the alkyl group, so it is a methyl group.
Number the chain from the end closest to the double bond and identify the lowest numbered carbon atom in the double bond.	 The lowest numbered carbon atom in the double bond is 2, so the parent name becomes hept-2-ene.
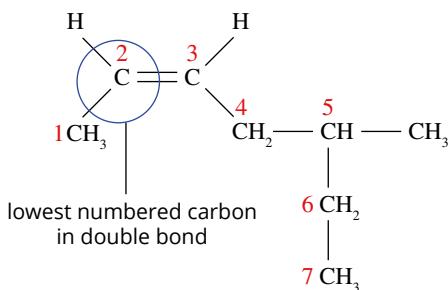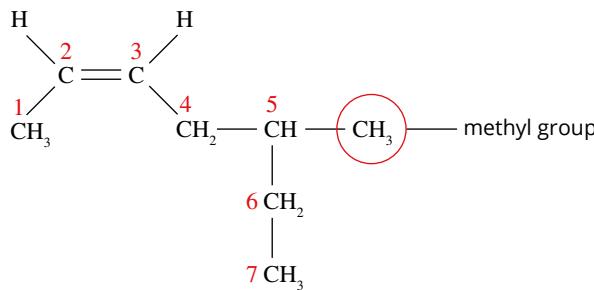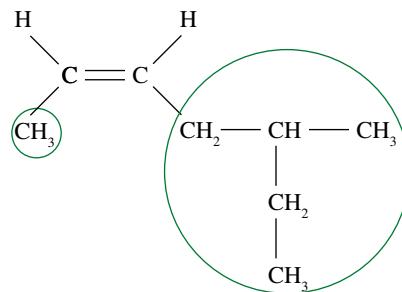
Number any alkyl side chains using the numbers of the carbon atoms to which they are attached.	 The methyl group is attached to carbon number 5.
Identify whether the molecule is a *cis* or *trans* isomer.	 Both of the carbons in the double bond are attached to a hydrogen atom and another carbon in the chain. The carbon atoms are on the same side of the double bond so this is a *cis* isomer.
Name the isomer.	The name of the isomer is *cis*-5-methylhept-2-ene.
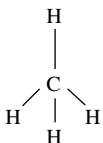
13.1 KEY QUESTIONS

1   A, D

2   **a** CH_4

   b   Methane is a hydrocarbon because it is a compound of carbon and hydrogen.

   c   Carbon has the electronic configuration of 2,4. Each carbon atom needs four electrons to complete its outer shell. Hydrogen has an electronic configuration of 1. Each hydrogen atom needs one electron to complete its outer shell. Because both atoms need electrons, they will share electrons; that is, form covalent bonds. It will take four hydrogen atoms to provide the four electrons required by each carbon atom.

   d   This tetrahedral arrangement gives minimum electrostatic repulsion between the four pairs of bonding electrons. The hydrogen atoms are arranged around the central carbon atom in a tetrahedral configuration.
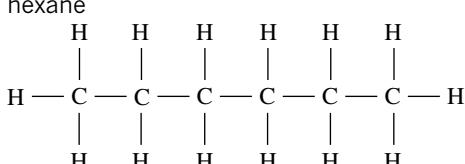

3   **a**   Propane. This hydrocarbon contains three carbon atoms, so the stem name is prop-. Its formula fits the general formula of an alkane, C_nH_{2n+2} ($n = 3$ so $2 \times 3 + 2 = 8$). Hence the name of the hydrocarbon is propane.

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

   c
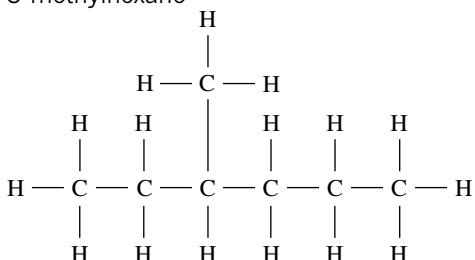
   d $CH_3CH_2CH_3$

4   **a**   Butane. The longest chain of carbon atoms is 4 and there are no branches.

   b   Heptane. The longest chain of carbon atoms is 7 and there are no branches. Note that the prefix hept- rather than sept- is used to denote 7.

   c   2-Methylpentane. The longest chain of carbon atoms is 5, giving the stem name of pentane, and there is one methyl ($-CH_3$) branch on carbon number 2 when numbered from the end closest to the branch.
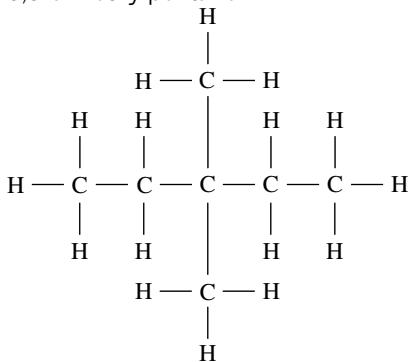
d 2-Methylbutane. The longest chain of carbon atoms is 4, giving the stem name of butane, and there is one methyl (–CH$_3$) branch on carbon number 2 when numbered from the end closest to the branch.

e 2,4-Dimethylpentane. The longest chain of carbon atoms is 5, giving the stem name of pentane, and there are two methyl (–CH$_3$) branches: one on carbon number 2 and the other on carbon number 4 when numbered in either direction. Dimethyl is used in addition to the two numbers to indicate the presence of two separate methyl groups.

5 **a** butane

  b methylpropane

  c 2,4-dimethylpentane

  d 3-methylhexane

6 **a** hexane

```
     H   H   H   H   H   H
     |   |   |   |   |   |
H —  C — C — C — C — C — C — H
     |   |   |   |   |   |
     H   H   H   H   H   H
```

  b 3-methylhexane

```
                 H
                 |
            H — C — H
     H   H   |   H   H   H
     |   |   |   |   |   |
H —  C — C — C — C — C — C — H
     |   |   |   |   |   |
     H   H   H   H   H   H
```

  c 3,3-dimethylpentane

```
                 H
                 |
            H — C — H
     H   H   |   H   H
     |   |   |   |   |
H —  C — C — C — C — C — H
     |   |   |   |   |
     H   H   |   H   H
            H — C — H
                 |
                 H
```
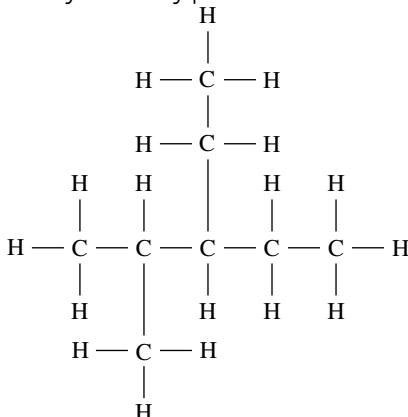
  d 3-ethyl-2-methylpentane

```
                 H
                 |
            H — C — H
                 |
            H — C — H
     H   H   |   H   H
     |   |   |   |   |
H —  C — C — C — C — C — H
     |   |   |   |   |
     H   |   H   H   H
        H — C — H
             |
             H
```

7 **a** methylbut-2-ene

  b *cis*-4-ethylhex-2-ene

8
```
     H    CH₃   CH₃   H   H
     |    |     |     |   |
H —  C —  C  =  C  —  C — C — H
     |                |   |
     H                H   H
```
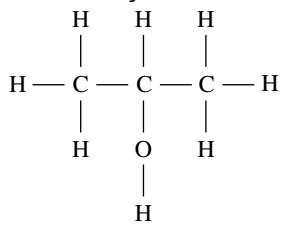
Section 13.2 **Functional groups**

Worked example: Try yourself 13.2.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.

```
    H   H   H
    |   |   |
H — C — C — C — H
    |   |   |
    H   O   H
        |
        H
```
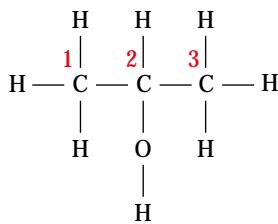
| Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are three carbons in the longest chain. The name is based on propane.
Identify the functional group that is present.	There is a hydroxyl group present.
Number the carbon atoms, starting from the end closest to the functional group.	``` H H H 1| 2| 3| H — C — C — C — H			H O H	H ```
Identify the position(s) and the type(s) of branch.	There are no branches in this molecule.
Combine all components. Place the number for the position of the branch in front of the prefix, and the number for the position of the hydroxyl group in front of the –*ol* ending.	The name of the molecule is propan-2-ol.
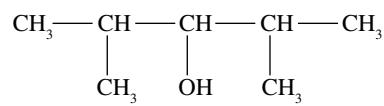
Worked example: Try yourself 13.2.2

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.

```
CH₃— CH — CH — CH — CH₃
      |    |    |
      CH₃  OH   CH₃
```

Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are five carbons in the longest chain. The name is based on pentane.
Identify the functional group that is present.	There is a hydroxyl group present.
Number the carbon atoms, starting from the end closest to the functional group.	The functional group will be on C3.
Identify the position(s) and the type(s) of branches.	There is a methyl (–CH_3) group on C2 and on C4 so the prefix 'dimethyl' is used.
Combine all components. Place the number for the position of the branch in front of the prefix, and the number for the position of the hydroxyl group in front of the –*ol* ending.	The name of the molecule is 2,4-dimethylpentan-3-ol.
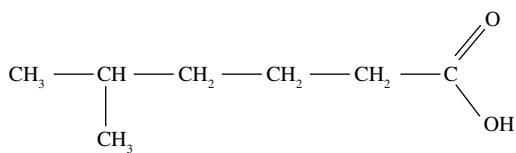
Worked example: Try yourself 13.2.3

IUPAC NAMING SYSTEM FOR CARBOXYLIC ACIDS

Write the systematic name for the following molecule:

$$CH_3 — CH — CH_2 — CH_2 — CH_2 — C \overset{O}{\underset{OH}{<}}$$
$$\;\;\;\;\;\;\;\;\;\;| $$
$$\;\;\;\;\;\;\;\;\;CH_3$$
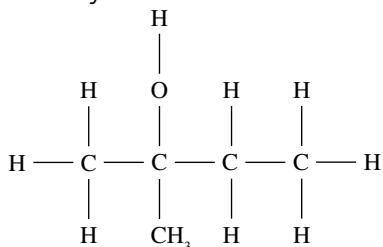
Thinking	Working
Identify the functional group that is present.	There is a carboxyl group present.
Identify the longest carbon chain that includes the carboxyl carbon. This atom will be C1. The stem name of the molecule is based on this longest chain.	There are six carbons in the longest chain, so the stem name is based on hexane.
Number the carbon atoms, starting from the end incorporating the functional group.	The functional group will be on C1.
Identify the position(s) and the type(s) of branches.	There is a methyl group on C5.
Combine all components. Place the number for the position of the branch in front of the prefix and using the –oic acid ending.	The name of the molecule is 5-methylhexanoic acid.

## Worked example: Try yourself 13.2.4

IUPAC NAMING SYSTEM FOR ESTERS

Write the systematic name for the following molecule:
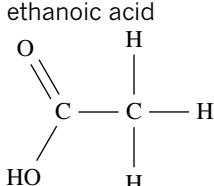
Thinking	Working
Locate the ester functional group. Starting from the carbonyl carbon, determine the number of carbon atoms in the chain attached to it and name according to the stem name, adding the suffix '-oate'.	There are four carbons in the chain, including the carbonyl carbon, so the last part of the ester's name is butanoate.
Count how many carbons are bonded to the singly bonded oxygen atom. The alkyl group bonded to the singly bonded oxygen atom is then added in front of the name.	There is one carbon bonded to the single bonded oxygen atom, so the alkyl group is methyl.
Combine the two components, placing the alkyl part of the name first.	The name of the molecule is methyl butanoate.

13.2 KEY QUESTIONS

1   2-methylbutan-2-ol

2 **a** pentan-1-ol
   b octan-4-amine

3 **a** ketones
   b aldehydes
   c amides
   d esters

4 **a** methyl methanoate
   b methanoic acid
   c propyl butanoate
   d methyl ethanoate
   e ethyl hexanoate

5 ethanoic acid


Section 13.3 Properties of organic compounds

13.3 KEY QUESTIONS

1 alkane, weak dispersion forces, increase, insoluble, weaker, hydrogen bonding
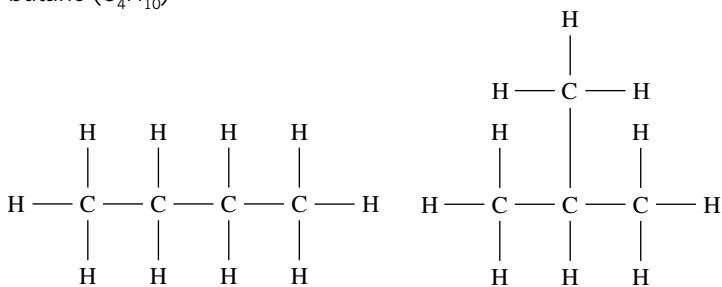
2 $CH_3CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
   Boiling point will increase with molecular size. The presence of branching within the molecule will produce a lower boiling point compared to a molecule of similar size with a straight chain structure.

3 $CHCH$, CH_3CHCH_2, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COOH$

Section 13.4 Isomers overview

13.4 KEY QUESTIONS

1 **a** butane (C_4H_{10})
   b

2 The carbon atoms in hydrocarbons have four bonds to other atoms. According to the valence shell electron 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 zig-zag shaped.

3 **a** Alkenes i, iii, iv and v have *cis–trans* isomers because each carbon in the double bond has two different groups attached.
   b Alkenes i and iii are *cis* isomers because the two alkyl chains are on the same side of the double bond.
   c Alkene ii does not have *cis–trans* isomerism because there must be two different groups attached to each of the carbon atoms in the double bond.

![Pearson logo]
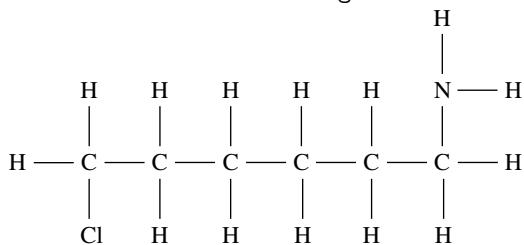
Section 13.5 IUPAC nomenclature overview

Worked example: Try yourself 13.5.1

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 and so the prefix chloro- will be used.
Number the carbon chain, giving the highest 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.
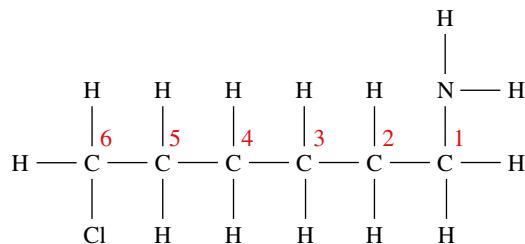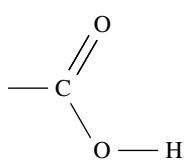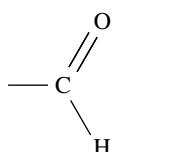
13.5 KEY QUESTIONS

1   a

   b

   c

d

e
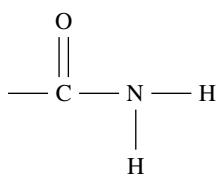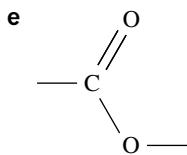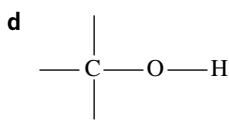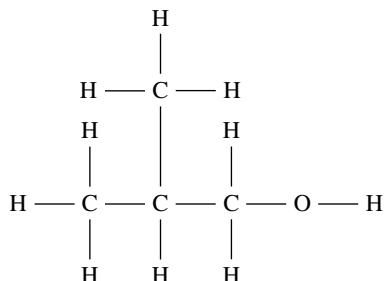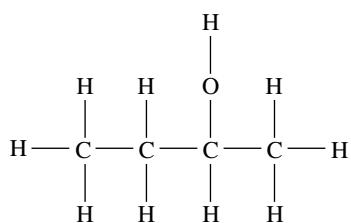
2 a 3-hydroxybutanoic acid
  b 3-methylpentan-2-amine
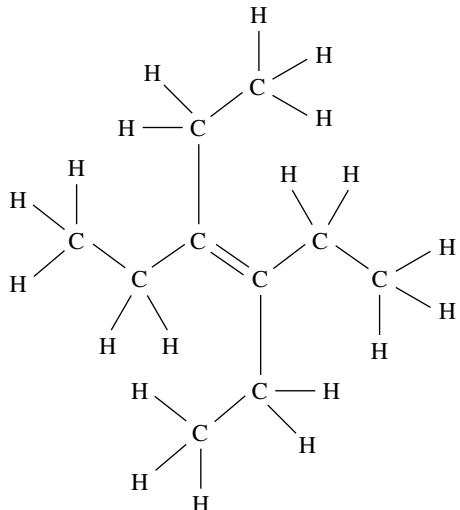
3 a

  b

  c

4 a i $NH_2CH_2CH_2CH_3$
    ii $CH_3CH(OH)CH(CH_2CH_3)CH_3$
  b The name of an amine is given by the suffix amine, so the name of the structure in part **a(i)**. should be propanamine. The name of an alcohol is given the suffix -ol, so the first correction is naming this butan-2-ol to represent the position of the hydroxyl group on the second carbon. The second correction is naming the branched alkyl, which in this case is ethyl. This part of the name is not incorrect, so the correct name is 3-ethylbutan-2-ol.

Section 13.6 **Determining formulae of organic compounds**

Worked example: Try yourself 13.6.1

CALCULATING PERCENTAGE COMPOSITION OF ORGANIC COMPOUNDS

8.38 g of an organic compound contains 5.44 g carbon, 1.13 g hydrogen and 1.81 g oxygen. Determine the percentage composition of the compound. Give all answers to three significant figures.

Thinking	**Working**
Divide the mass of the first element by the total mass of the compound and multiply by 100.	% carbon $= \dfrac{\text{mass of carbon present}}{\text{total mass of the compound}} \times 100$ $= \dfrac{5.44}{8.38} \times 100$ $= 64.9\%$
Divide the mass of the second element by the total mass of the compound and multiply by 100.	% hydrogen $= \dfrac{\text{mass of hydrogen present}}{\text{total mass of the compound}} \times 100$ $= \dfrac{1.13}{8.38} \times 100$ $= 13.5\%$
Repeat the previous step for any further elements in the compound.	% oxygen $= \dfrac{\text{mass of oxygen present}}{\text{total mass of the compound}} \times 100$ $= \dfrac{1.81}{8.38} \times 100$ $= 21.6\%$
Add up all the elemental percentages to check that they equal 100%. (If they don't, then check your calculations and rounding off.)	If your calculations above are correct, then Total % elements = % carbon + % hydrogen + % oxygen $= 64.9 + 13.5 + 21.6$ $= 100\%$

Worked example: Try yourself 13.6.2

CALCULATING EMPIRICAL FORMULA FROM PERCENTAGE COMPOSITION

Chemical analysis of an organic compound present in the gaseous emissions from a factory shows that its percentage composition is 40.0% carbon, 6.7% hydrogen and the remainder is oxygen. Find its empirical formula.

Thinking	**Working**
Assume that there is 100 g of the compound, so percentages convert directly to masses. Write down the mass, in g, of all elements present in the compound.	C: 40.0 g H: 6.7 g O: $100 - 40.0 - 6.7 = 53.3$ g
Calculate the amount, in mol, of each element in the compound using: $n = \dfrac{m}{M}$	$n(\text{C}) = \dfrac{40.0}{12.0}$ $= 3.33$ $n(\text{H}) = \dfrac{6.7}{1.0}$ $= 6.7$ $n(\text{O}) = \dfrac{53.3}{16.0}$ $= 3.33$

Simplify the ratio by dividing all of the numbers of moles by the smallest number of moles calculated above. This gives you a ratio by number of atoms.	$C = \frac{3.33}{3.33}$ $= 1$ $H = \frac{6.7}{3.33}$ $= 2$ $O = \frac{3.33}{3.33}$ $= 1$
Find the simplest whole number ratio.	C : H : O 1 : 2 : 1
Write the empirical formula.	CH_2O

Worked example: Try yourself 13.6.3

CALCULATING THE EMPIRICAL FORMULA OF A COMPOUND

A compound was found to contain 72 g of carbon and 18 g hydrogen. Determine the empirical formula of the compound.	
Thinking	**Working**
Calculate the number of moles of carbon and hydrogen using: $n = \frac{m}{M}$	$n(C) = \frac{72}{12.01}$ $= 6 \, \text{mol}$ $n(H) = \frac{18}{1.008}$ $= 18 \, \text{mol}$
Find the simplest whole number ratio.	C : H 6 : 18 1 : 3
Write the empirical formula.	CH_3

Worked example: Try yourself 13.6.4

CALCULATING THE MOLECULAR FORMULA OF A COMPOUND

A compound has the empirical formula CH. The molar mass of this compound is 78 g mol⁻¹. What is the molecular formula of the compound?	
Thinking	**Working**
Calculate the molar mass, in g mol⁻¹, of one unit of the empirical formula.	$M(CH) = 12.01 + 1.008$ $= 13.0$
Determine the number of empirical formula units in the molecular formula.	Number of empirical formula units $= \frac{\text{molar mass}}{\text{molar mass of empirical formula unit}}$ $= \frac{78}{13.0}$ $= 6$
Multiply the empirical formula by this factor to determine the molecular formula of the compound.	The molecular formula is $6 \times CH$ i.e. C_6H_6

13.6 KEY QUESTIONS

1 D. $\frac{4.66}{6.84} \times 100 = 68.1\%$

2 % of element = $\frac{\text{mass of element present}}{\text{total mass of the compound}} \times 100$

  % of carbon = $\frac{6.13}{8.00} \times 100 = 76.6\%$

  % of hydrogen = $\frac{0.51}{8.00} \times 100 = 6.4\%$

  mass of oxygen = mass of compound – mass of carbon – mass of hydrogen

  $= 8.00 - 6.13 - 0.51 = 1.36\,\text{g}$

  % of oxygen = $\frac{1.36}{8.00} \times 100 = 17\%$

3 **a** Carbon = 60.0 g; oxygen = 26.7 g; hydrogen = 100.0 – 60.0 – 26.7 = 13.3 g

  b $n(C) = \frac{60.0}{12.0} = 5.00\,\text{mol}$

  $n(O) = \frac{26.7}{16.0} = 1.67\,\text{mol}$
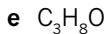
  $n(H) = \frac{13.3}{1} = 13.3\,\text{mol}$

  c $C = \frac{5.00}{1.67} = 2.99$

  $O = \frac{1.67}{1.67} = 1$

  $H = \frac{13.3}{1.67} = 7.96$

  d C : O : H = 3 : 1 : 8

  e C_3H_8O

4 $M(\text{mannitol}) = \frac{m}{M} = \frac{152.7}{0.8390} = 182.0\,\text{g\,mol}^{-1}$

  $M(\text{EF}) = (3 \times 12.0) + (7 \times 1.0) + (3 \times 16.0) = 91.0\,\text{g\,mol}^{-1}$

  number of empirical formula units = $\frac{\text{molar mass}}{\text{molar mass of empirical formula unit}}$

  $= \frac{182.0}{91} = 2$

  molecular formula = $2 \times C_3H_7O_3 = C_6H_{14}O_6$

5 $n(C) = \frac{72.0}{12.0} = 6.00\,\text{mol}$, $n(H) = \frac{18.0}{1.00} = 18.0\,\text{mol}$, $n(O) = \frac{48.0}{16.0} = 3.00\,\text{mol}$

  C : H : O

  6.00 : 18.0 : 3.00

  2 : 6 : 1
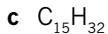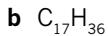
  empirical formula = C_2H_6O

CHAPTER 13 REVIEW

1 Carbon can form a large number of compounds for several reasons. Carbon atoms can use two electrons each to bond to form very long chains. This leaves the other two valence electrons able to bond other non-metal atoms onto the chain. In addition, there can be double and triple bonds between carbon atoms, as well as ring structures. All these possible variations mean that an enormous number of different compounds containing carbon can be formed.

2 A

3 **a** alkanes

  b $C_{17}H_{36}$

  c $C_{15}H_{32}$

d percentage by mass of an element

$$= \frac{\text{mass of element in 1 mol of compound}}{\text{mass of 1 mol of compound}} \times 100$$

$M(C_{16}H_{34}) = 226\,\text{g mol}^{-1}$
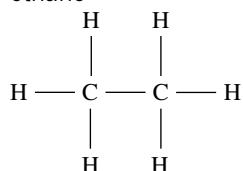
$\therefore \%(C) = \frac{16 \times 12.0}{226} \times 100$

$= 85.0\%$
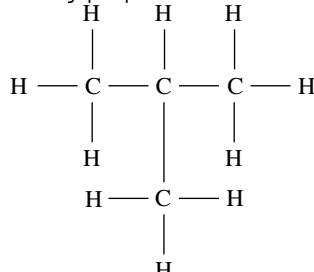
So, $M(C)$ in 275 g of compound $= \frac{85.0 \times 275\,\text{g}}{100}$

$= 234\,\text{g}$
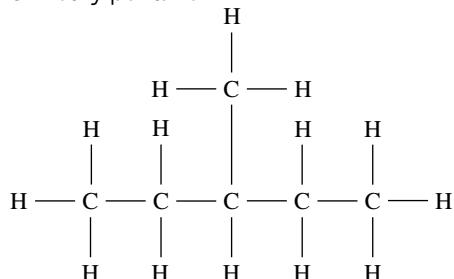
4 a ethane
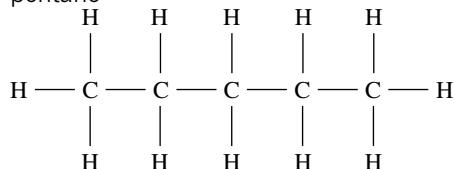
b methylpropane
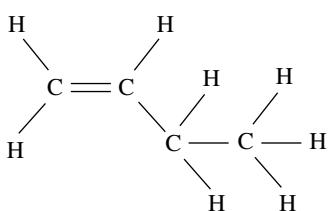

**c** 3-methylpentane
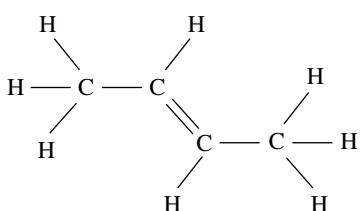

d pentane
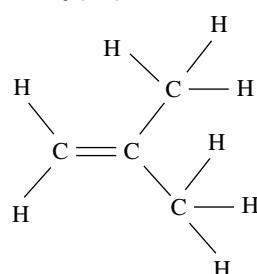
5 but-1-ene   but-2-ene   methylpropene

6 hydroxyl; polar; hydrogen; intermolecular; small

7 a True. A functional group is an atom or group of atoms that changes the chemical and physical properties of a molecule.

b true

c False. Alcohols contain the hydroxyl functional group.

8 D. Only Option D contains the carboxyl functional group (–COOH).

9 A
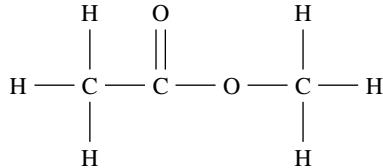
10 a pentanoic acid

**b** 3-methylbutanoic acid
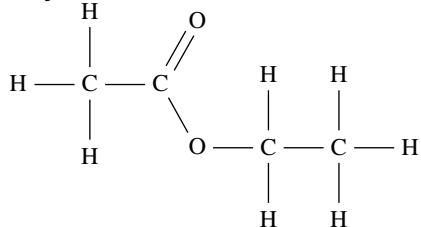
**c** 4-methylhexanoic acid

**d** 3-ethylpentanoic acid
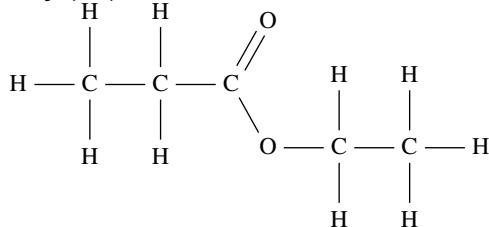
11 a methyl ethanoate
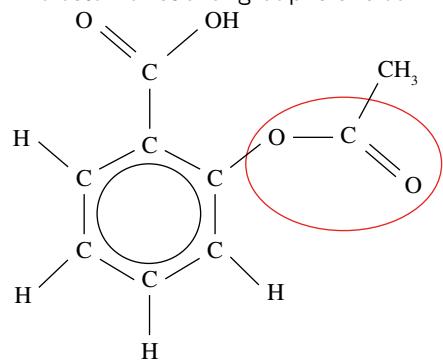

b ethyl ethanoate
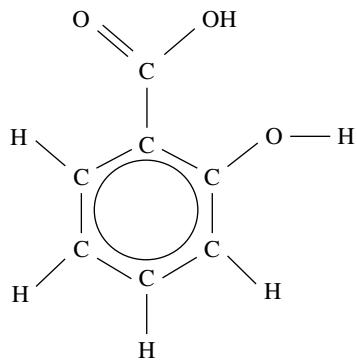

c ethyl propanoate
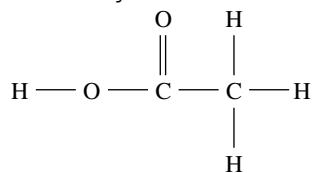

12 a The ester functional group is circled.
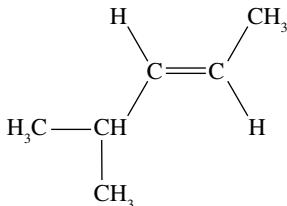
b the alcohol
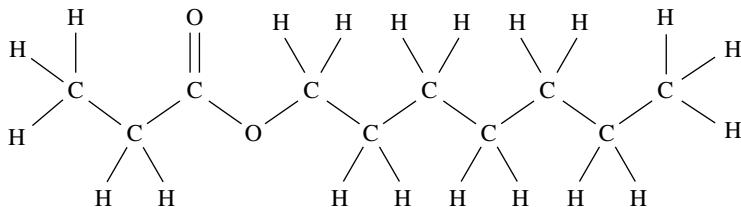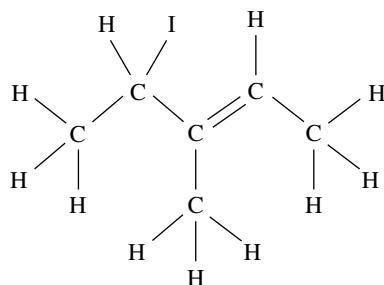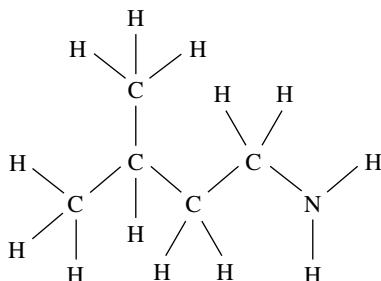
the carboxylic acid

13 Aldehydes contain a carbonyl group at the end of a carbon chain, ketones contain a carbonyl group within the chain, 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.

14 Alcohols contain a hydroxyl group so hydrogen bonds can form between alcohol molecules. Hydrogen bonds are stronger than the dispersion forces between alkane molecules. This results in alcohols having a higher boiling point than their corresponding alkane.

15 Hydrogen bonds and dispersion forces are the intermolecular forces in both methanol and butan-1-ol, but butan-1-ol has a higher boiling point because it is a larger molecule, so the dispersion forces between its molecules are stronger.

16 As the length of the carbon chain increases, the proportion of the carboxylic acid molecule that is non-polar increases, decreasing its solubility in water.

17



18 *cis*-5-methylhept-2-ene

19 a butyl ethanoate

  b *trans*-2-methylhex-3-ene

  c *cis*-1-bromobut-2-ene

20 a

  b

  c

21 $m(C) = 92.3\% \times$ mass of hydrocarbon $= 1.15\,g$

mass of hydrocarbon $= \dfrac{1.15}{92.3\%} = \dfrac{1.15}{0.923} = 1.25\,g$

$m(H) =$ mass of hydrocarbon $- m(C) = 1.25 - 1.15\,g = 0.10\,g$

22

Empirical formula	Relative molecular mass	Molecular formula
CH	78.0	C_6H_6
CH_3	30.0	C_2H_6
CH_2O	90.0	$C_3H_6O_3$
C_3H_6O	116.0	$C_6H_{12}O_2$
CH_2	98.0	C_7H_{14}

23 a The molecular formula is always a whole-number multiple of the empirical formula. The empirical formula provides the simplest whole-number ratio of atoms in a compound. The amount of each atom is found by using $n = \dfrac{m}{M}$, where m is the mass in grams and M is the molar mass in $g\,mol^{-1}$.

	C	H
Mass	85.7 g	14.3 g
Molar mass	$12\,g\,mol^{-1}$	$1\,g\,mol^{-1}$
Amount using $n = \dfrac{m}{M}$	$n = \dfrac{85.7}{12.0} = 7.14\,mol$	$n = \dfrac{14.3}{1.0} = 14.3\,mol$
Divide all by the smallest amount	$\dfrac{7.14}{7.14} = 1$	$\dfrac{14.3}{7.14} = 2$

$\therefore$ empirical formula is CH_2

b Molar mass of a CH_2 unit (empirical formula) = $12 + 2 = 14\,g\,mol^{-1}$

Molar mass of the compound (molecular formula) = between 40 and $50\,g\,mol^{-1}$

$\therefore$ Number of CH_2 units in one molecule = 3

$\therefore$ Molecular formula is C_3H_6

c alkene

24 a

	C	H	O
Mass	40.0 g	6.7 g	53.3 g
Molar mass	$n = \dfrac{40.0}{12.0} = 3.33\,mol$	$n = \dfrac{6.7}{1.0} = 6.7\,mol$	$n = \dfrac{53.3}{16.0} = 3.33\,mol$
Simplest mole ratio	$\dfrac{3.33}{3.33} = 1$	$\dfrac{6.7}{3.33} = 2$	$\dfrac{3.33}{3.33} = 1$

$\therefore EF = CH_2O$

b $M(\text{compound}) = \dfrac{m}{n} = \dfrac{15.0}{0.250} = 60.0\,g\,mol^{-1}$

$M(EF) = 12.0 + (2 \times 1.0) + 16.0 = 30.0\,g\,mol^{-1}$

$\text{number of empirical formula units} = \dfrac{\text{molar mass}}{\text{molar mass of empirical formula unit}}$

$\dfrac{60.0}{30.0} = 2$

molecular formula = $2 \times CH_2O = C_2H_4O_2$

25 $m(C) = 4.40 \times \left(\dfrac{12.01}{44.01}\right) = 1.201\,g$, $n(C) = \dfrac{1.201}{12.00} = 0.100\,mol$

$m(H) = 2.70 \times \dfrac{2.00}{18.00} = 0.300\,g$, $n(C) = \dfrac{0.300}{1.00} = 0.300\,mol$

C : H

$C = \dfrac{0.100}{0.100} = 1$, $H = \dfrac{0.300}{0.100} = 3$

empirical formula is CH_3

26 a single covalent bond

b hydroxyl group

c methyl group

d carboxyl group

27 student poster

28 a An alkene contains one double carbon–carbon bond, which requires two carbon atoms. The first alkene is therefore ethene.

b The carbon atom has four electrons in the outer shell, which are available for sharing with other atoms to produce four covalent bonds.

29 a Polyunsaturated: contains many double bonds; mono-unsaturated: contains one carbon–carbon double bond; saturated: contains only single bonds between carbon atoms.

b Individual student response required.

30 a The double bond cannot be in the '4' position as 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 longest chain in this arrangement is 5 carbons long, so the stem should be pent- and the branch should be methyl. The correct name is 2-chloro-3-methylpentane.

c The double bond has higher priority than the methyl groups so the name should be 4,4-dimethylpent-2-ene.

d The longest chain in this arrangement is 7 carbons long, so the stem should be hept- and there are no branches. The correct name is 4-bromoheptane.

31 a i primary alcohol

   ii heptan-1-ol

b i chloroalkane

   ii 4-chloroheptane

c i secondary alcohol

   ii hexan-2-ol

d i carboxylic acid

   ii pentanoic acid

e i amine

   ii butan-2-amine

f i alkane

   ii 2-methyloctane

g i alkene

   ii 2-methylpropene

Chapter 14 Reactions of organic molecules

Section 14.1 Chemical properties of alkenes

14.1 KEY QUESTIONS
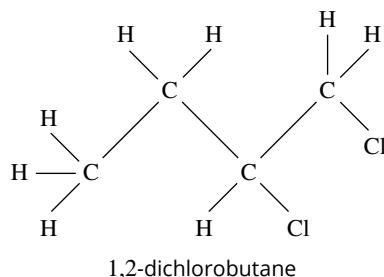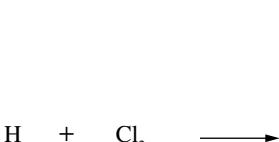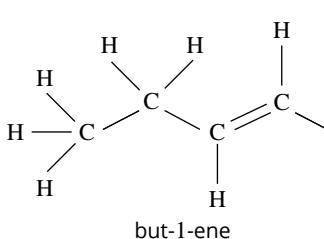
1 **a** chloroethane
   b 1,2-dichloroethane
   c ethanol
   d ethane

2 **a**

but-1-ene + Cl$_2$ → 1,2-dichlorobutane

   b

but-2-ene + HBr → 2-bromobutane
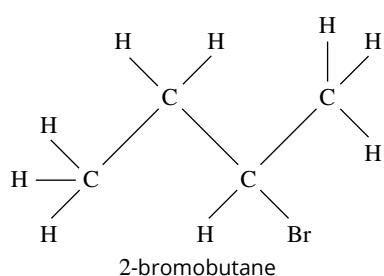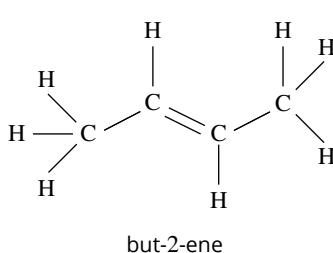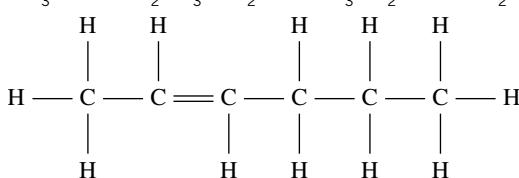
3 **a** ethanol
   b 3-chlorohexane or 4-chlorohexane

4 **a** $CH_2CHCH_3 + H_2 \rightarrow CH_3CH_2CH_3$
   b $CH_3CHCHCH_3 + I_2 \rightarrow CH_3CHICHICH_3$
   c $CH_3CHCHCH_2CH_3 + H_2O \rightarrow CH_3CH_2CHOHCH_2CH_3$
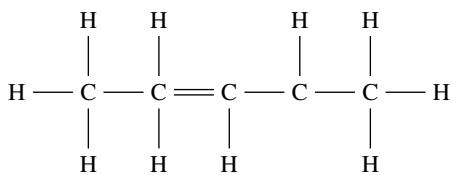
5 **a**

   b

Section 14.2 **Chemical properties of alcohols**
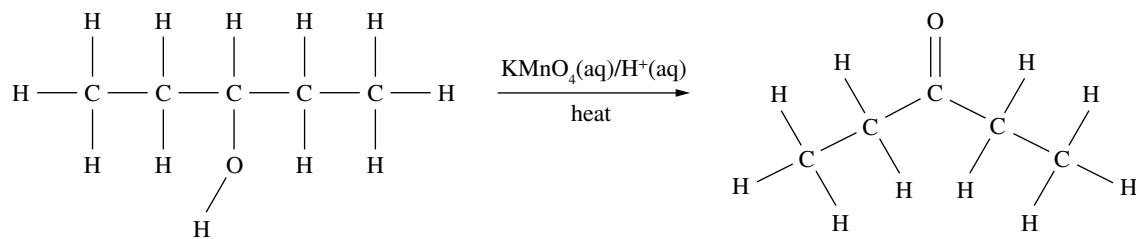
Worked example: Try yourself 14.2.1

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Butan-1-ol is oxidised with acidified sodium dichromate under mild conditions to form butanal.

Write the half-equations for the reaction and hence write the balanced overall equation.

| Thinking	Working
Write the half-equation for the oxidation of the alcohol.	$C_4H_9OH(aq) \rightarrow C_4H_8O(aq) + 2H^+(aq) + 2e^-$
Write the half-equation for the reduction of the oxidising agent. (This can normally be found in your Chemistry Data Booklet.)	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Multiply one equation or both equations by a suitable factor to ensure that the number of electrons is balanced.	$3C_4H_9OH(aq) \rightarrow 3C_4H_8O(aq) + 6H^+(aq) + 6e^-$ $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Add the oxidation and the reduction half-equations together, cancelling out electrons so that none are in the final equation. Cancel out any species, such as H_2O or H^+, that appear on both sides of the equation.	$3C_4H_9OH(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3C_4H_8O(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$
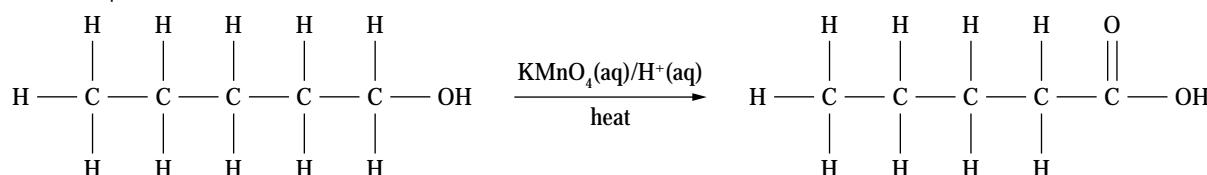
14.2 KEY QUESTIONS

1 a $2C_5H_{12}O(g) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(g)$
   b pentan-3-ol, secondary; 2-methylbutan-2-ol, tertiary; pentan-1-ol, primary
   c Pentan-3-ol will oxidise to pentan-3-one. The solution will change from deep purple to colourless as the reaction proceeds.

2-Methylbutan-2-ol is a tertiary alcohol so will not react under the conditions described. No colour change will be observed; the solution will remain deep purple.
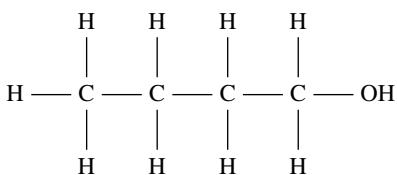
Pentan-1-ol will oxidise to the carboxylic acid. The solution will change from deep purple to colourless as the reaction proceeds.
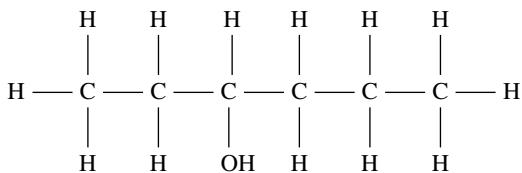
Reasoning: The aldehyde will be produced first but because there is no mention of how harsh the reaction conditions are, assume complete oxidation to the carboxylic acid.
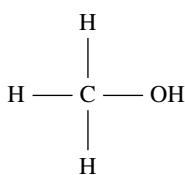
2 a butan-1-ol
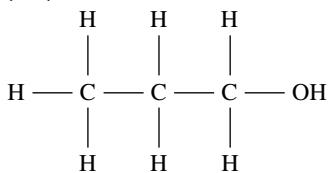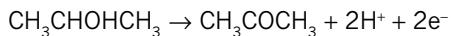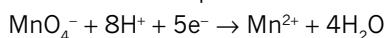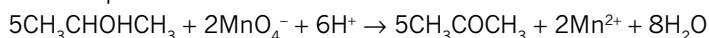
$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

b hexan-3-ol

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

c methanol

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

d propan-1-ol

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

3 a Oxidation half-equation:

$CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + 2H^+ + 2e^-$

Reduction half-equation:

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

Redox equation:

$5CH_3CHOHCH_3 + 2MnO_4^- + 6H^+ \rightarrow 5CH_3COCH_3 + 2Mn^{2+} + 8H_2O$

b Oxidation half-equation:

$CH_3CH_2CH_2CH_2OH + H_2O \rightarrow CH_3CH_2CH_2COOH + 4H^+ + 4e^-$

Reduction half-equation:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Redox equation:

$3CH_3CH_2CH_2CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CH_2CH_2COOH + 4Cr^{3+} + 11H_2O$
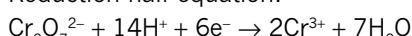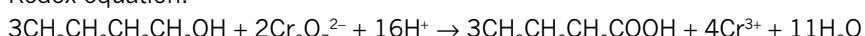
Section 14.3 **Chemical properties of carboxylic acids**

14.3 KEY QUESTIONS

1 a $CH_3CH_2CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COO^-(aq) + H_3O^+(aq)$

Note: Double arrows must be used to indicate that the reaction is an equilibrium.

b $H_2O > CH_3CH_2CH_2COOH > CH_3CH_2CH_2COO^- = H_3O^+$

Butanoic acid, like other carboxylic acids, is a weak acid and will ionise only to a small extent. That is, the acid ionisation constant is much less than one and thus when butanoic acid is mixed with water only a small percentage of butanoic acid molecules will ionise to form hydronium ions and butanoate ions.

2 $CH_3CH_2COO^-$; propanoate ion

3 a $CH_3COOH(aq) + HCO_3^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l) + CO_2(g)$

b $2Na(s) + 2CH_3CH_2COOH(aq) \rightarrow 2CH_3CH_2COO^-(aq) + 2Na^+(aq) + H_2(g)$

4 A. Reaction B is an acid plus metal hydroxide (base) reaction producing a salt and water; reaction C is an acid plus metal reaction producing a salt and hydrogen gas; reaction D is an acid plus carbonate reaction producing a salt, water and carbon dioxide gas. In each of these reactions the salt produced is magnesium methanoate. No reaction occurs when the substances in A are mixed.

5 $HCOOH + CH_3CH_2CH_2OH \rightleftharpoons HCOOCH_2CH_2CH_3 + H_2O$

Name of organic product: propyl methanoate

6 **a** pentan-1-ol and ethanoic acid
   b ethanol and octanoic acid
   c hexan-1-ol and propanoic acid
   d propan-1-ol and butanoic acid

Section 14.4 Creating molecules: an introduction to organic synthesis

Worked example: Try yourself 14.4.1

DESIGNING A CHEMICAL SYNTHESIS PATHWAY FOR AN ESTER

Design a reaction pathway for the synthesis of methyl ethanoate, starting with ethene and methanol.

Thinking	Working
Write the structure of the ester to help determine which carboxylic acid and alcohol are required.	 The name methyl ethanoate indicates this is an ester. It is formed by a condensation reaction between an alcohol and a carboxylic acid. The first part of the name, 'methyl', indicates the alcohol that reacted (methanol) and the second part of the name, 'ethanoate', indicates the carboxylic acid (ethanoic acid).
Write an equation for the reaction that forms the ester from the alcohol and carboxylic acid identified above.	$CH_3COOH + CH_3OH \xrightarrow{H_2SO_4} CH_3COOCH_3$
Identify the reactions that will produce each of the two reactants in the step above.	Ethanoic acid is made by the oxidation of ethanol: Ethanol is made by the hydration of ethene:
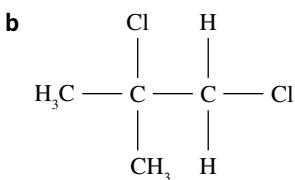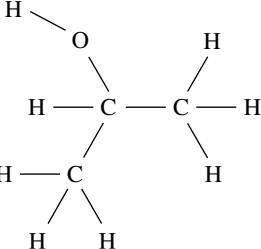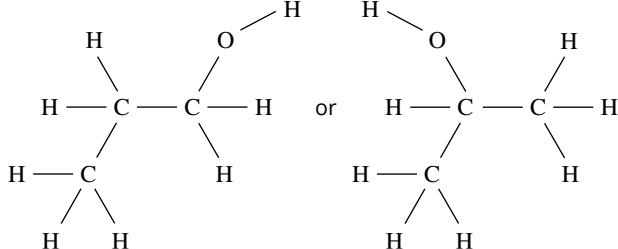
14.4 KEY QUESTIONS

1 **a** Butan-1-ol $\xrightarrow{Cr_2O_7{}^{2-},\ H^+}$ butanoic acid

b Pent-1-ene $\xrightarrow{H_2O,\ H_3PO_4}$ pentan-2-ol $\xrightarrow{Cr_2O_7{}^{2-},\ H^+}$ pentan-2-one

2 **a** Ethene $\xrightarrow{H_2O,\ H_3PO_4}$ ethanol

b 1 methanol $\xrightarrow{K_2Cr_2O_7,\ H^+}$ methanoic acid

2 Propan-1-ol + methanoic acid $\xrightarrow{H^+}$ 1-propyl methanoate

3 This synthesis is carried out in three parts: (1) synthesis of ethanol, (2) synthesis of ethanoic acid and (3) synthesis of ethyl ethanoate.

1 ethene $\xrightarrow{H_2O,\ H_3PO_4}$ ethanol

2 ethanol $\xrightarrow{K_2Cr_2O_7,\ H^+}$ ethanoic acid

3 ethanoic acid + ethanol $\xrightarrow{H^+}$ ethyl ethanoate + water

4 Continual addition of ethene and steam keeps the reactant concentrations high and the system never reaches an equilibrium. This means the forward reaction rate is always greater than the reverse so favouring production of ethanol.

CHAPTER 14 REVIEW

1

Reactants	Type of reaction	Product(s)
Alkene and hydrogen	Addition (hydrogenation)	Alkane
Alkene and hydrogen bromide	Addition	Bromoalkane
Alkene and water (with a catalyst and heat)	Addition (hydration)	Alcohol
Alkene and bromine	Addition	Dibromoalkane
Alkene in the presence of a catalyst	Addition polymerisation	Saturated hydrocarbon polymer

2 **a**

b

3 **a** hydrogen bromide

b hydrogen chloride

c chlorine gas

d hydrogen gas and nickel catalyst (or other suitable metal—usually a transition metal such as platinum or palladium)

4 **a** C_3H_8; propane; alkane
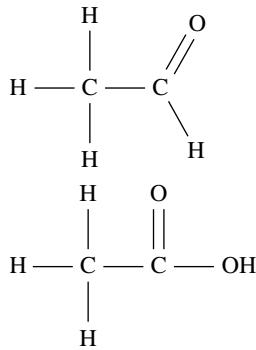
b C_2H_6O; ethanol; alcohol

5 **a** aldehyde, carboxylic acid
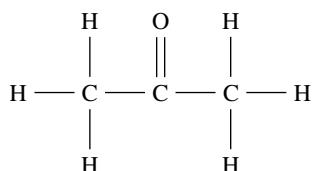
b ketone

c No reaction will occur.
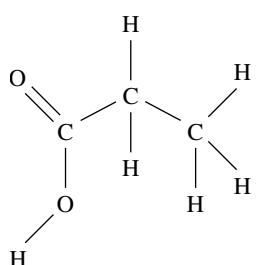
6 **a**
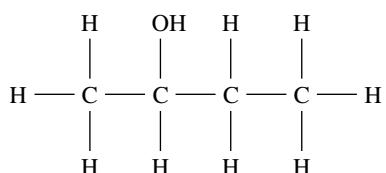
b
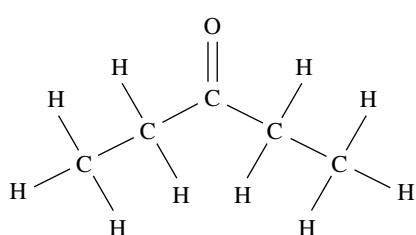
7 **a**
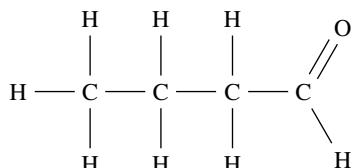
b

c
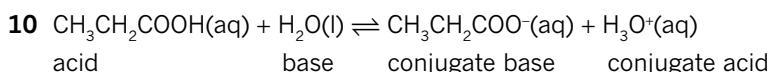
d

8 Oxidation half-equation: $CH_3CH_2CH_2OH + H_2O \rightarrow CH_3CH_2COOH + 4H^+ + 4e^-$

Reduction half-equation: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
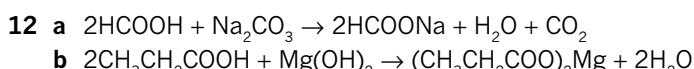
Redox equation: $5CH_3CH_2CH_2OH + 4MnO_4^- + 12H^+ \rightarrow 5CH_3CH_2COOH + 4Mn^{2+} + 11H_2O$

9 In this test, the determination of whether an unknown alcohol is primary, secondary or tertiary depends on observing if any colour change in the permanganate solution from purple to colourless occurs. If the permanganate is added rapidly and in excess, any colour change will be masked by the excess permanganate; the solution will be purple despite any possible reaction occurring.

10 $CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$

    acid   base   conjugate base   conjugate acid
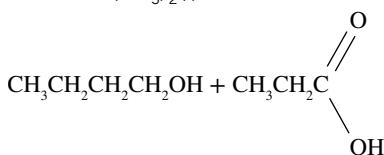
Propanoic acid, like all carboxylic acids, is a weak acid so concentrations of the propanoate and hydronium ions will be much less than those of the propanoic acid and water molecules.

11 a zinc ethanoate, carbon dioxide and water

  b zinc ethanoate and water

  c zinc ethanoate and hydrogen gas

  d zinc ethanoate and water

12 a $2HCOOH + Na_2CO_3 \rightarrow 2HCOONa + H_2O + CO_2$

  b $2CH_3CH_2COOH + Mg(OH)_2 \rightarrow (CH_3CH_2COO)_2Mg + 2H_2O$
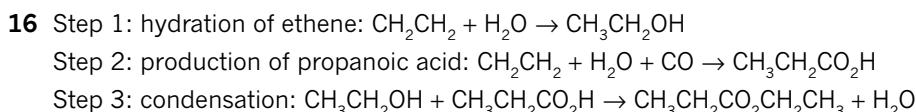
13 a $CH_3CH_2COOCH_3(l)$

  b $CH_3COO(CH_2)_4CH_3(l)$

  c $HCOOCH(CH_3)_2(l)$

  d

$$CH_3CH_2CH_2CH_2OH + CH_3CH_2C\begin{smallmatrix}O\\\\OH\end{smallmatrix}$$
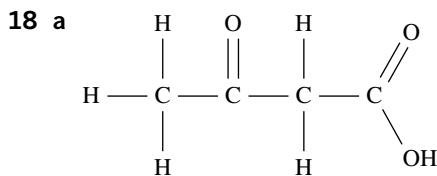
14 a CH_2CH_2

  b H_3PO_4

  c H^+

  d CH_3COOH

  e H_2SO_4

  f $CH_3COOCH_2CH_3$

15 Step 1: hydration (addition). Step 2: oxidation. Step 3: condensation

16 Step 1: hydration of ethene: $CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH$

Step 2: production of propanoic acid: $CH_2CH_2 + H_2O + CO \rightarrow CH_3CH_2CO_2H$

Step 3: condensation: $CH_3CH_2OH + CH_3CH_2CO_2H \rightarrow CH_3CH_2CO_2CH_2CH_3 + H_2O$

17 In the redox reaction of alcohols with permanganate and dichromate, hydrogen ions are needed as a reactant. The sulfuric acid added to the permanganate and dichromate solutions is the source of hydrogen ions. In the condensation reaction of an alcohol with a carboxylic acid, the sulfuric acid acts as a catalyst increasing the rate of reaction.

18 a
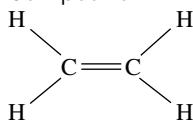
The functional group produced is a ketone.
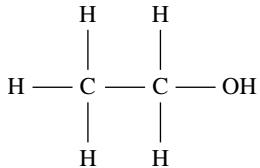
  b During the oxidation of alcohols by dichromate, there is an increase in the number of C–O bonds and a simultaneous decrease (at the same carbon atom) in the number of C–H bonds. Like the tertiary C atom in tertiary alcohols, the carboxylic acid C atom has no C–H bonds so cannot be oxidised by dichromate.

19 a Theoretically, yield will be improved by a low temperature. The reaction is exothermic, so a low temperature will favour the exothermic reaction, which is the forward reaction. (Note: in practice to achieve a reasonable rate of reaction, a compromise temperature of about 300°C is used.)

A high pressure will favour a high yield because there is one molecule of gas on the product side of the reaction versus two molecules of gas on the reactant side. Thus, a high pressure will favour the forward reaction. (A high pressure will also favour the rate of reaction, but in practice a pressure of 60–70 atm is used, which in industrial terms is not especially high. If too high a pressure is used, ethene will polymerise. Also, it is expensive to build the pipes and reaction vessels needed to withstand very high pressures.)

  b Cooling condenses only the ethanol because it has a higher boiling point than ethene. Ethanol has hydrogen bonding and dispersion forces as its intermolecular forces, while non-polar ethene has only dispersion forces as its intermolecular force.

20 a Compound A:

H   H
 \ /
  C = C
 / \
H   H

Compound B:

```
     H   H
     |   |
H —— C — C —— OH
     |   |
     H   H
```

Compound C:

```
     H   H   H   H
     |   |   |   |
H —— C — C — C — C —— OH
     |   |   |   |
     H   H   H   H
```

Compound D:

```
     H   H   H   O
     |   |   |   ||
H —— C — C — C — C —— OH
     |   |   |
     H   H   H
```
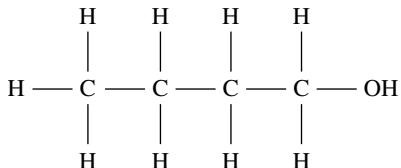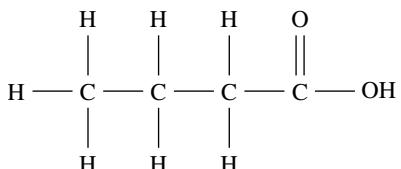
b Compound B will have higher water solubility than compound C. Both compounds display hydrogen bonding, so will hydrogen bond with water molecules, but compound C has stronger dispersion forces than does compound B. For one substance to dissolve in another, the solute–solute attractions need to be overcome by solute–solvent attractions. Because compound C has stronger dispersion forces, the attractive forces between neighbouring C molecules will be greater than those between neighbouring B molecules, and so C will have lower water solubility.

Chapter 15 From monomers to polymers

Section 15.1 Polymers: a diverse class of materials

15.1 KEY QUESTIONS
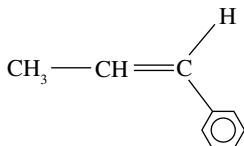
1 **a** Polymers are covalent molecular substances composed of many small molecules joined together to form a long chain.
   b Monomers are small molecules that react together to form long polymer chains.
   c Repeating units are identical small segments that are repeated along a polymer chain.

2 Thermosetting and thermoplastic polymers differ in their behaviour upon heating. Thermosetting polymers have extensive covalent cross-linking between polymer chains and burn or decompose upon heating. Thermoplastic polymers do not have cross-linking and melt when heated, allowing them to be reshaped.

3 Polymer A, with less branching, would have stronger intermolecular forces between polymer chains because the reduced branching allows polymer chains to pack together more closely. Branching increases the distance between polymer chains and hence reduces the strength of the dispersion forces.

4 Natural rubber exhibits properties typical of elastomers. Therefore, it would be expected to have occasional cross-linking, but not to be extensively cross-linked. The polymer chains need to be able to move past each other when stretched, but also to have sufficient cross-linking to pull the chains back to their original position when the stretching force is removed.

Section 15.2 Addition polymerisation

Worked example: Try yourself 15.2.1

ADDITION POLYMERS: FORMING POLYMERS
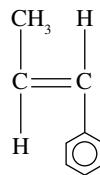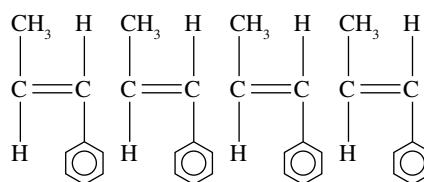
Thinking	Working
Write the chemical formula for the monomer so that the double bond is horizontal and the bonds to all other groups are perpendicular to the carbon centres.	
Repeat this several times so that the C=C double bonds of neighbouring monomers are adjacent to one another.	
Remove the double bonds and connect all carbon centres with single bonds. This gives you the structure of the polymer.	
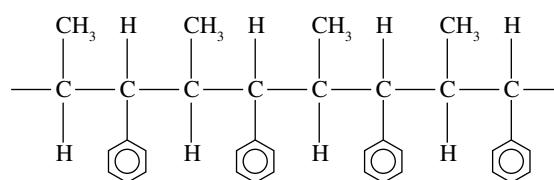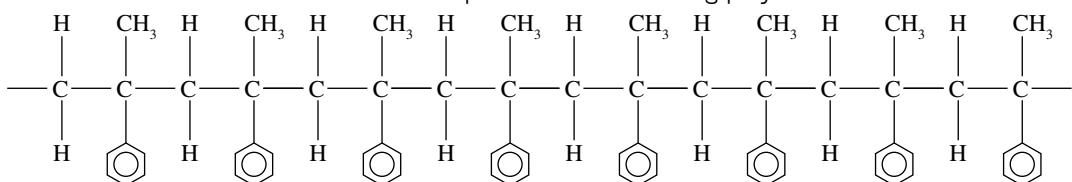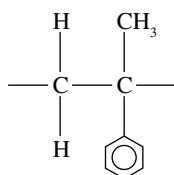
Worked example: Try yourself 15.2.2

ADDITION POLYMERS: DETERMINING THE MONOMER UNIT
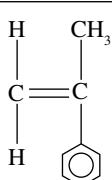
Draw the structure of the monomer that produces the following polymer.
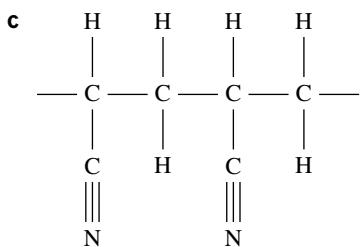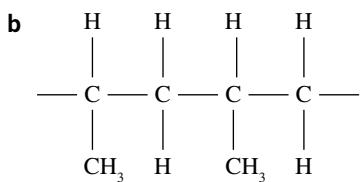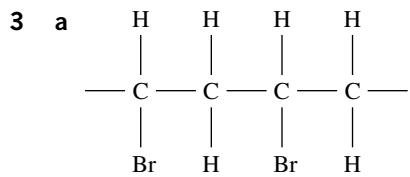
Thinking	Working
Identify the repeating unit of the polymer. It will contain just two adjacent carbon atoms from the polymer backbone.	
Remove every second single bond along the length of the chain and form the double bond between the two carbon atoms of the monomer. This gives you the structure of the monomer.	

15.2 KEY QUESTIONS

1 D. Addition polymerisation involves breaking a carbon–carbon double or triple bond and forming new carbon–carbon bonds between monomers. Reactions between functional groups on the end of each monomer are involved in the condensation polymerisation process.

2 The repeating units from the monomer are $–CH_2CF_2–$ so there are four in this segment.

3 a

b

c

4 a $CHCl=CHCl$
b $CH_3CH=CHCl$
c $CHF=CH_2$
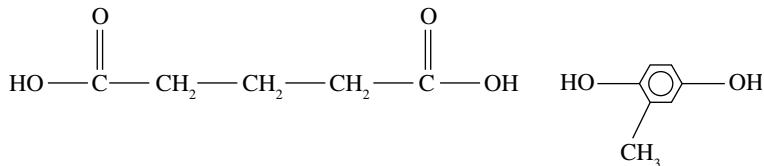
5 **a** High-density polyethene (HDPE) is made of relatively unbranched chains of polyethene, which can pack more closely together than the chains of low-density polyethene (LDPE) can. LDPE contains branched chains of polyethene that cannot pack together as closely. Therefore, HDPE is stronger and slightly less flexible than LDPE. Both HDPE and LDPE are chemically unreactive, waterproof non-conductors and only slightly permeable to gases.

    b **i** LDPE
      ii HDPE
      iii LDPE

Section 15.3 Condensation polymerisation

Worked example: Try yourself 15.3.1

CONDENSATION POLYMERISATION: FORMING POLYMERS
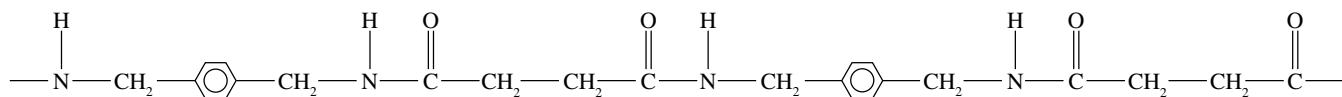
Draw the condensation polymer produced from the following monomers. Include at least two repeating units.

Thinking	Working
Examine the functional groups on the monomer(s) and determine whether a polyamide or polyester will be formed. Remember an alcohol and carboxylic acid condense to form an ester, and an amine and carboxylic acid condense to form an amide.	The monomers are a diol and a dicarboxylic acid. Therefore they will react to form a polyester.
To form the ester group in the polymer, remove the hydroxyl groups from the dicarboxylic acid and the hydrogen atoms from the hydroxyl groups of the diol.	
Construct the repeating unit by joining the two halves.	
Write the repeating unit inside square brackets with a subscript n to indicate it is a polymer.	

Worked example: Try yourself 15.3.2

CONDENSATION POLYMERISATION: DETERMINING THE MONOMER UNITS

Draw the structure of the monomer(s) used to produce the following polymer.
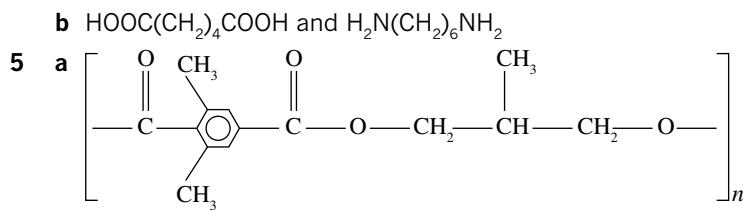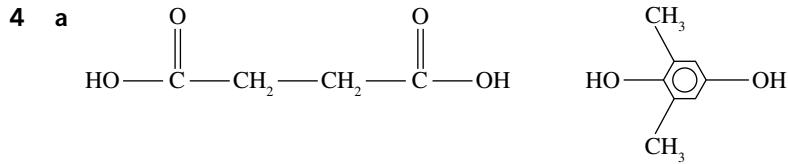
Thinking	Working
Determine whether the polymer is a polyamide or a polyester and circle the amide or ester linkages.	The polymer is a polyamide, due to the presence of the amide (CO-NH) groups.
Identify the repeating unit. Note that this may be composed of one or two separate monomers.	
Within the repeating unit, split the amide group at the C–N bond.	
Draw the two monomers individually, adding the H and OH groups to re-form the alcohol, carboxylic acid or amine functional groups on the monomer(s).	
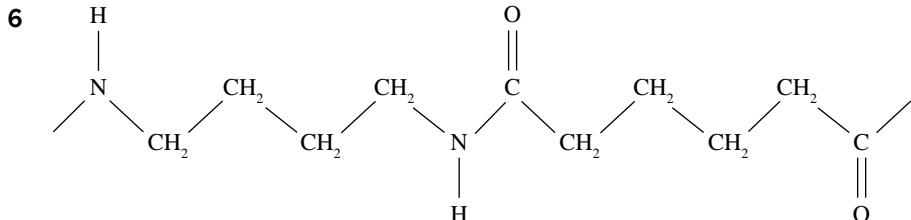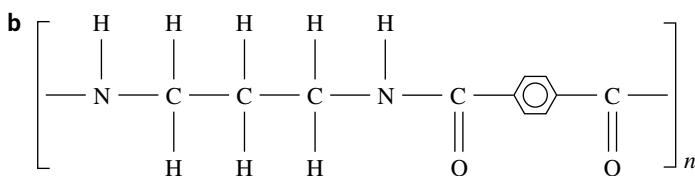
15.3 KEY QUESTIONS

1 C

2 water

3 **a** polyamide
   b polyamide
   c polyester
   d polyester

4 **a**

b $HOOC(CH_2)_4COOH$ and $H_2N(CH_2)_6NH_2$

5 **a**

b

6
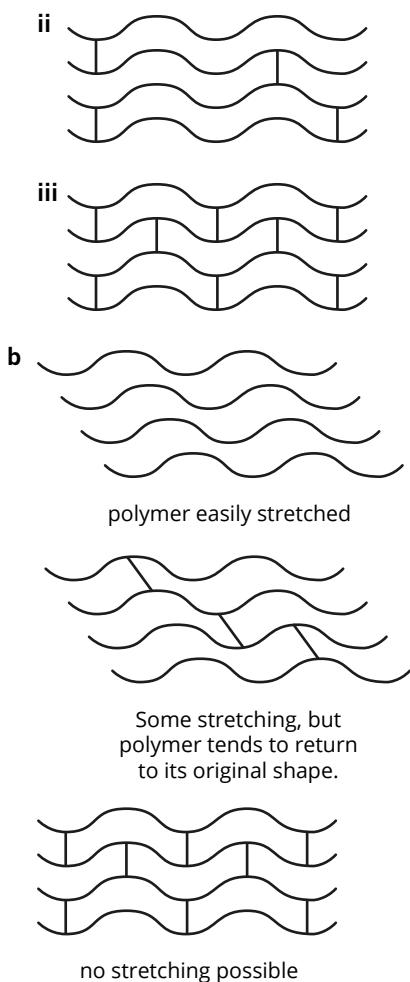
Section 15.4 **Designing polymers for a purpose**

15.4 KEY QUESTIONS

1   **a** weak dispersion forces
    b dipole–dipole attractions
    c weak dispersion forces
    d weak dispersion forces
    e dipole–dipole attractions
2   The monomers are ethene and tetrafluoroethene.
3   –H (in polyethene)
    –F (in Teflon)
    –Cl (in polyvinyl chloride)
    $-C_6H_5$ (in polystyrene)
    $-NC_{12}H_8$ (in polyvinyl carbazole)
4   **a** increase the crystallinity
    b increase the crystallinity
    c decrease the crystallinity
5   **a** increase flexibility
    b improved heat insulating properties or mechanical properties
    c increased crystallinity, resulting in a harder, more brittle polymer

CHAPTER 15 REVIEW

1   **a** A monomer is a small molecule that can react to form long chains of repeating units, called polymers. Monomers often contain a carbon–carbon double bond.
    b Thermoplastic materials soften when heated because the bonds between molecules break and the molecules become free to move.
    c Thermosetting materials do not melt when heated, but at high temperatures covalent bonds are broken and the material decomposes or burns. They cannot be moulded into a different shape.
    d A cross-link is one or more covalent bonds that connect neighbouring polymer chains.
    e A plasticiser is a chemical added to plastics to make them more flexible.
2   **a** false
    b false
    c false
    d true
3   **a i**

ii

iii

b

polymer easily stretched

Some stretching, but
polymer tends to return
to its original shape.

no stretching possible
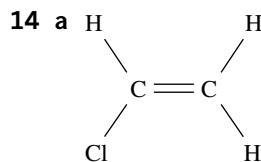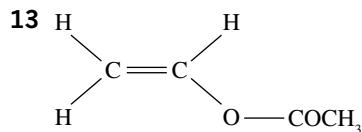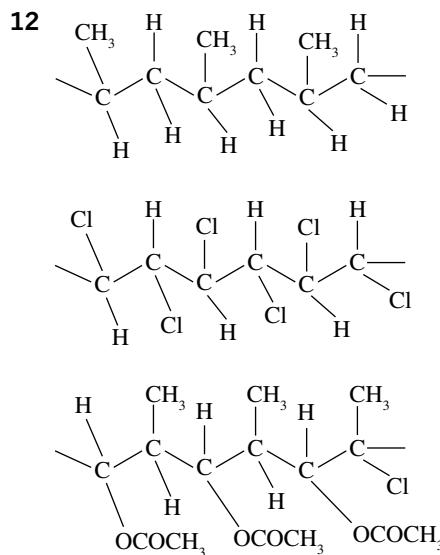
4 An elastomer has occasional cross-linking that prevents the chains from slipping past each other too far and pulls the chains back to their original positions when the force is removed. See Figure 15.1.15.

5 Thermosetting polymers have much stronger inter-chain bonds than thermoplastic polymers.

6 The inter-chain bonds in thermosetting polymers are about the same strength as the covalent bonds within chains. When heated to a high temperature, both the inter-chain and covalent bonds break.

7 Distinguishing between thermoplastic and thermosetting polymers is important. The former get soft when heated, whereas the latter remain rigid and will burn if heating continues.

  a thermosetting

  b thermoplastic

  c thermosetting

  d thermoplastic

  e thermoplastic

8 **a** the polymer used in saucepan handles

  b Saucepan handles are much harder and more resistant to the effect of heat than elastic bands. The polymer on the outside of the golf ball is also very hard, but, unlike the polymer in saucepan handles, is quite elastic.

9 A, C, and D can act as monomers in addition polymerisation; B, propane cannot because it does not contain a double bond.

10 **a** The ethene molecule has a carbon–carbon double bond.

  b

$$\begin{array}{ccc} H & & H \\ \diagdown & & \diagup \\ & C = C & \\ \diagup & & \diagdown \\ H & & H \end{array}$$

Ethene has this structural formula because it ensures each atom has a stable outer-electron shell, and this arrangement of atoms gives the minimum repulsion between electron pairs.

  c Ethane cannot undergo addition polymerisation because it is a saturated compound.
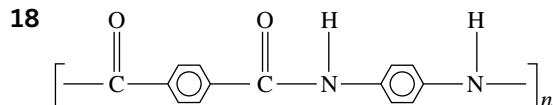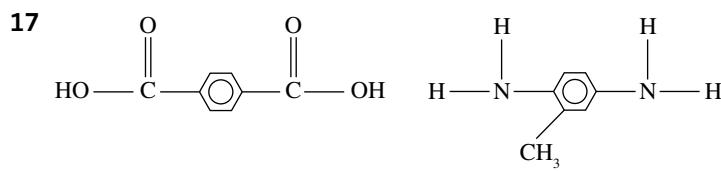
11 a Several thousand ethene monomers react to make one molecule of polyethene.

   b Ethene ($CH_2{=}CH_2$) is unsaturated because it contains a double bond. Polyethene is saturated because it contains only single bonds between carbon atoms.

   c The empirical formula is the simplest whole-number ratio of elements in a compound. The empirical formula of ethene ($CH_2{=}CH_2$) is CH_2.

12

13

14 a

   b 6
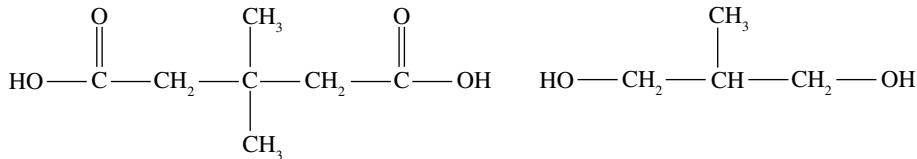
   c dipole–dipole bonds

15 a PVC is flexible, non-conducting and strong, has a high melting point and low flammability.

   b PVC has no free charged particles to conduct electricity. It has strong inter-chain bonding due to dipoles, which increase its strength and raise its melting point. PVC contains strong bonds that does not burn easily and it produces chemicals that extinguish flames when burned. PVC is plasticised to make it flexible.

16 Polytetrafluorethene (Teflon) has a higher melting point than polyethene due to the stronger dispersion forces between polymer chains. Both polymers are non-polar, but the Teflon monomers have a higher molar mass compared to ethene. This means a greater number of electrons are present in the polymer and hence the dispersion forces are greater.

17

18

19 c and d

20

HO—C(=O)—CH₂—C(CH₃)(CH₃)—CH₂—C(=O)—OH   HO—CH₂—CH(CH₃)—CH₂—OH

21 A single monomer that can be used to produce a polyester must contain both a carboxylic acid and an alcohol in the same molecule. Similarly, to produce a polyamide using a single monomer, the monomer must contain both an amine and a carboxylic acid functional group. So your structure should include one of these combinations of two functional groups.

22 As the polymer chains are held further apart by the plasticisers, it makes it easier for the polymer chains to slide over each other. As a result, these materials have a lower softening temperature, and are more malleable and soft.

23 Polymers without extensive branching and with regular chain structures are most likely to form crystalline regions.

24 Left: C_8H_8; middle: C_3H_3N; right: C_4H_6

25 a thermoplastic with high melting temperature
b lower density/more transparent polymer

26 thermoplastic

27 The monomers used to create addition polymers must be unsaturated. For condensation polymerisation, the monomers may be saturated or unsaturated, but they must each contain two functional groups that react together. For addition polymerisation, no side-products are produced during the polymerisation reaction. For condensation polymerisation, small molecules (usually water) are released during the reaction.

28 The relative molecular mass would have increased. The melting point of the polymer would have increased. The overall strength of inter-chain forces would have increased. The electrical conductivity of the polymer would have remained the same.
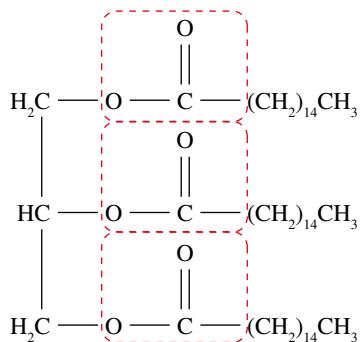
Chapter 16 From fats and oils to soaps and biodiesel

Section 16.1 Fats and oils
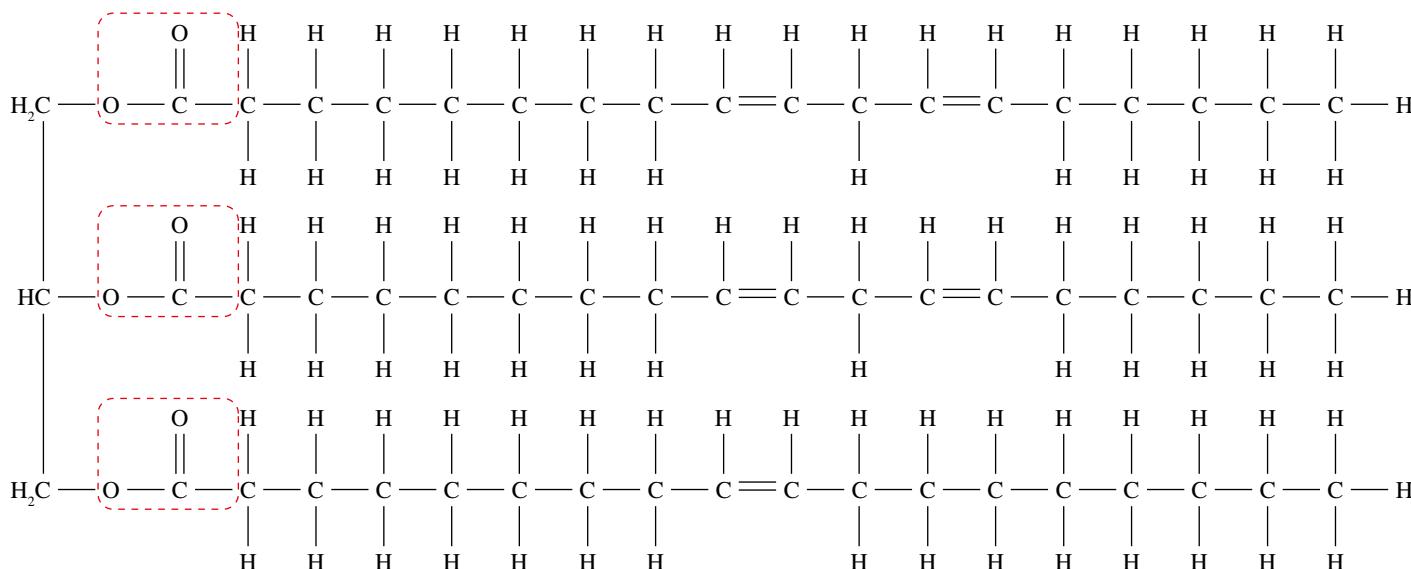
16.1 KEY QUESTIONS

1 a Most likely to be from an animal source because it is a saturated fat (stearin).
   b Most likely to be from a plant source because it is an unsaturated fat (predominant triglyceride in sunflower oil).
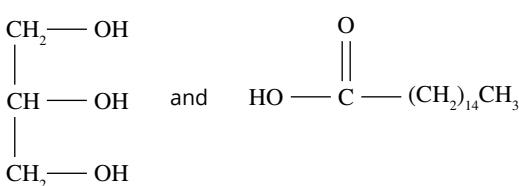
2 a

   b

3
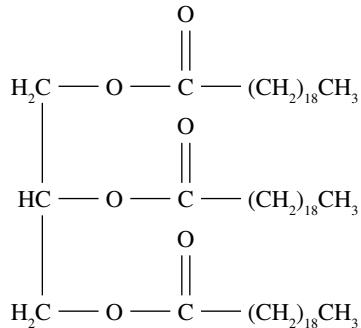
Section 16.2 **Production of soaps**

Worked example: Try yourself 16.2.1

DETERMINING THE PRODUCTS OF SAPONIFICATION FROM A TRIGLYCERIDE
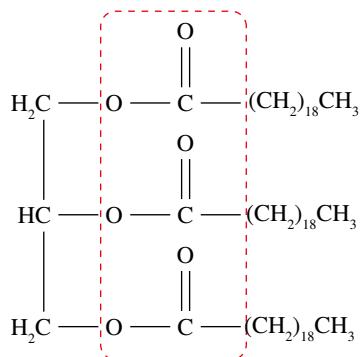
The following triglyceride was reacted with potassium hydroxide to form a soap. Give the products of this reaction.

$$H_2C - O - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$$

$$HC - O - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$$

$$H_2C - O - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$$
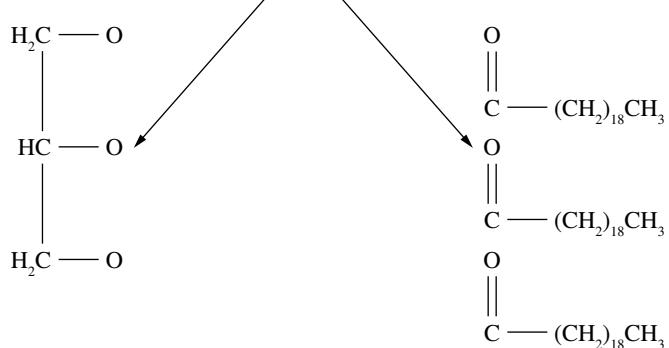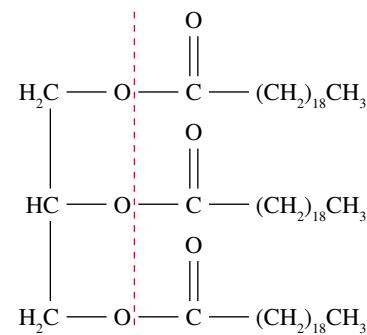
Thinking	**Working**
Identify the ester groups in the triglyceride.	$H_2C - \boxed{O - \overset{\overset{\displaystyle O}{\|}}{C} - } (CH_2)_{18}CH_3$ $HC - \boxed{O - \overset{\overset{\displaystyle O}{\|}}{C} - } (CH_2)_{18}CH_3$ $H_2C - \boxed{O - \overset{\overset{\displaystyle O}{\|}}{C} - } (CH_2)_{18}CH_3$
Split the molecule between each oxygen atom and the carbon in the fatty acid.	$H_2C - O \vdots - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$ $HC - O \vdots - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$ $H_2C - O \vdots - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$ $H_2C - O$ $\quad\mid$ $HC - O$ $\quad\mid$ $H_2C - O$ $\overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$ $\overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$ $\overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{18}CH_3$
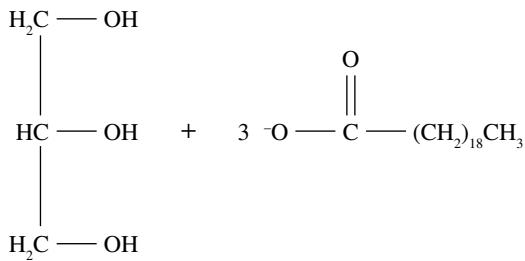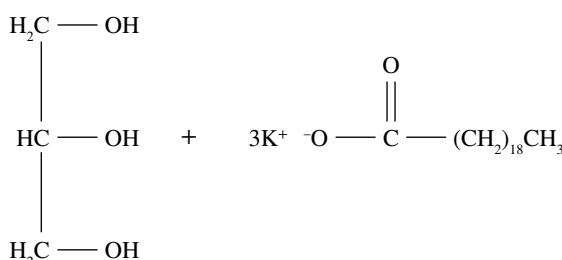
Oxygen and hydrogen from potassium hydroxide must be introduced to produce glycerol and the carboxylate ion. A hydrogen atom is added to form glycerol. O is added to form the carboxylate ion.	H_2C —— OH HC —— OH + 3 $^-$O —— $\overset{\overset{\textstyle O}{\|}}{C}$ —— $(CH_2)_{18}CH_3$ H_2C —— OH
Add the metal ion from the hydroxide used to produce the molecule of soap made. Potassium hydroxide was used. Note: In order to show the ionic nature of the bond between potassium and the ion of the fatty acid, charges are given in the structure.	H_2C —— OH HC —— OH + $3K^+$ $^-$O —— $\overset{\overset{\textstyle O}{\|}}{C}$ —— $(CH_2)_{18}CH_3$ H_2C —— OH

16.2 KEY QUESTIONS

1 C. Hydrolysis is a reaction in which molecules are split by water. *Lysis* means splitting, e.g. electrolysis is the splitting of a substance using electricity. *Hydro* means the agent is water.

2 acidic, basic, saponification, salts, glycerol

3 Hard water is water that contains significant concentrations (>120 ppm) of metal ions, such as calcium and magnesium.

4 Soap forms an insoluble scum. Scum is the insoluble salts of calcium and magnesium. They are off-white in colour. Because these salts are insoluble, this reduces the concentration of soap in the water, meaning more soap must be added in hard water areas to achieve the same result. The insoluble scum can deposit on laundry, leaving it stiff and discoloured.

5 Similarities: both contain both ionic and covalent bonds, have a cleaning action; both have a long hydrocarbon chain section in their molecules

Differences: starting materials are obtained from different sources, detergents from petrochemicals and soaps from natural fats and oils. Detergents are unaffected by the presence of calcium and magnesium ions and do not form scum as soaps do.

Section 16.3 The cleaning action of soaps and detergents

16.3 KEY QUESTIONS

1 A, non-polar tail; B, hydrophobic; C, hydrophilic; D, charged end

2 micelles, hydrophobic/non-polar, polar/hydrophilic

3 a Broken: the ionic bonds break between the metal cation and the organic anion, dispersion forces between molecules of soap
Formed: ion–dipole forces between the anions and cations from the dissociated soap molecule, dispersion forces between non-polar portion of anion and water
   b Broken: dispersion forces between non-polar portion of anion and water
Formed: dispersion forces between non-polar portions of anions
   c Broken: dispersion forces between the grease and the fabric
Formed: dispersion forces between the grease and micelles
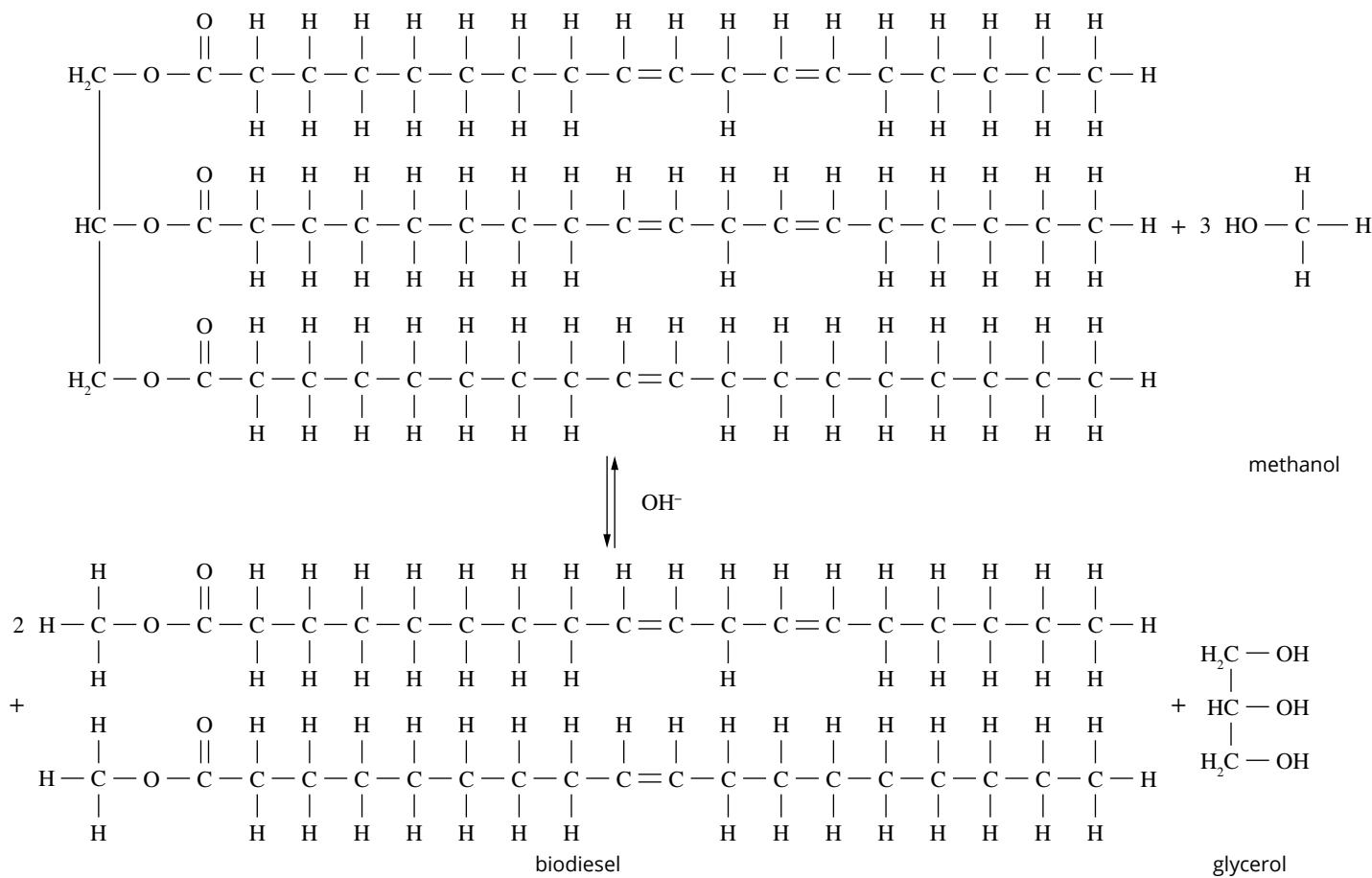
Section 16.4 **Production of biodiesel**

16.4 KEY QUESTIONS

1   Transesterification

2   **a** true
    b true
    c false
    d true
    e false
    f true

3   CO_2 is absorbed from the atmosphere during the growth of plants used as raw materials in the production of biodiesel.

4   Advantages: lipase catalyst may be used more than once; requires lower temperature, meaning less energy is used in the process; can be carried out at a lower pressure

    Disadvantages: longer time for reaction to complete; yield is typically much lower
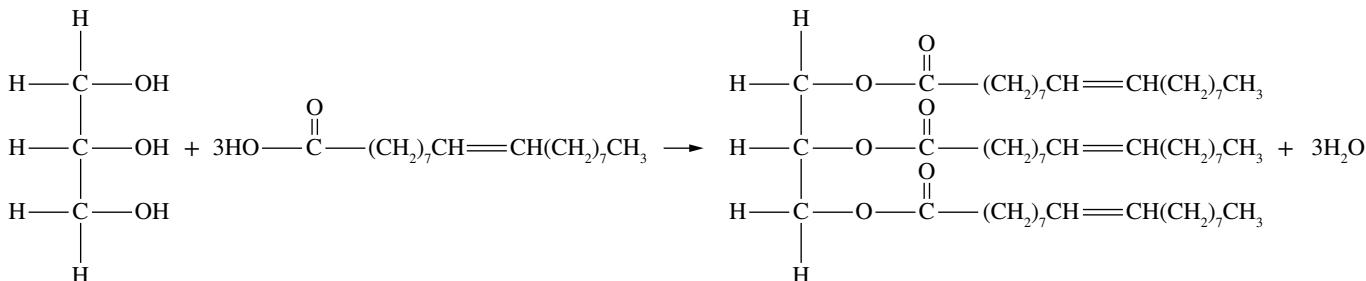
5
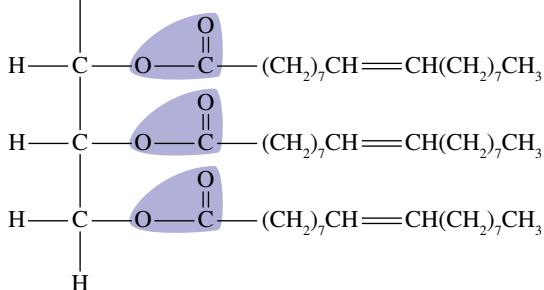
CHAPTER 16 **REVIEW**

1 hydroxyl and carboxyl
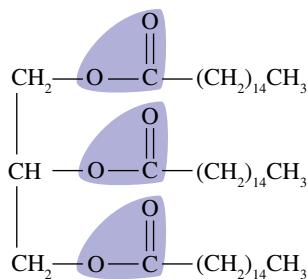
2 **a**

b

3 **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.
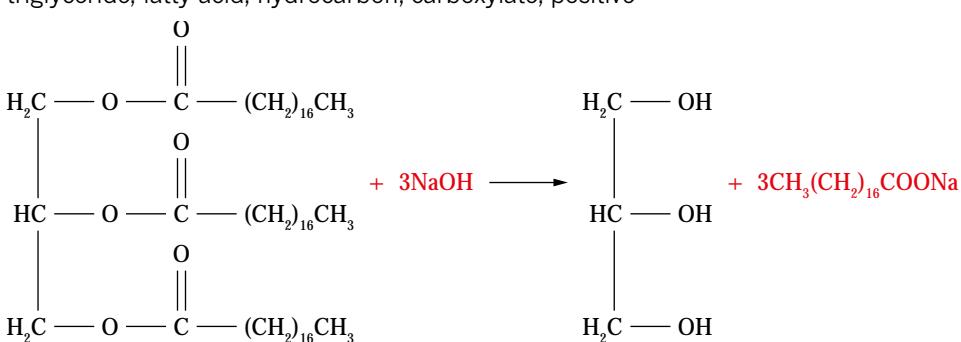
4 B. This is a soap because it has a fatty acid ion and a metal ion, Li^+.

5 **a** 0.6 mol
   b 0.2 mol

6 triglyceride, fatty acid, hydrocarbon, carboxylate, positive

7

8 **a** glycerol
   b a fat
   c a fatty acid
   d a detergent
   e a soap

9 In unsaturated soap molecules, the double bonds present mean that the hydrocarbon chain of the soap occupies more space than a similar, but saturated, hydrocarbon chain.
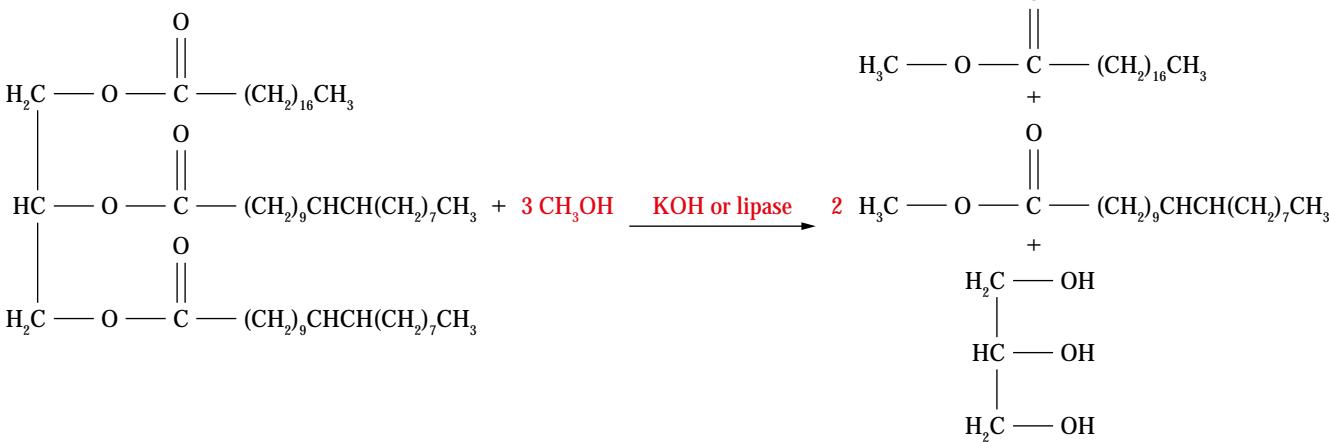
The effectiveness of the soap micelles relies on the formation of dispersion forces between the hydrocarbon ends of the soap. As the unsaturated chains cannot get as close to one another, the dispersion forces will be weaker and this results in the soap micelle not being as stable.

The C=C double bond is more reactive than the single bonds in the hydrocarbon chain from the saturated fat. The soap will more likely be oxidised to form products that have an unpleasant odour.

As the unsaturated soap molecules occupy more space, molecules cannot get as close to one another and hence the dispersion forces would be anticipated to be weaker in these soaps. The soap will be soft, or may even be a liquid soap.

10 Petrodiesel comes from crude oil, which is a non-renewable resource. Most scientists think there is a link between the carbon dioxide released into the atmosphere from burning fossil fuels and climate change. Biodiesel is made from oil that comes from plants that capture atmospheric carbon dioxide as they grow. This serves to offset the carbon dioxide produced from burning biodiesel.

11
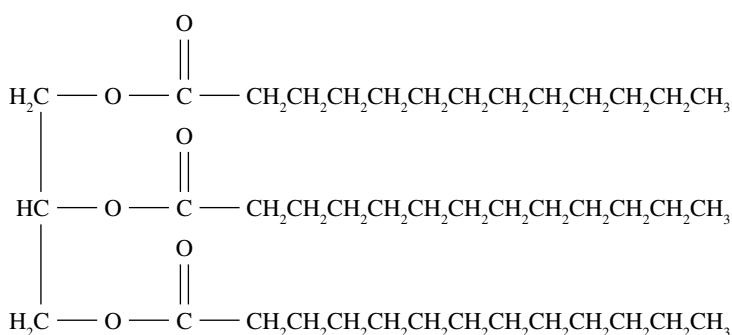
12 The term 'renewable feedstock' means the main reactant or reactants used in a chemical process come from sources that can be regenerated in a relatively short time period.

13 A catalyst is a substance that provides an alternative reaction pathway with a lower activation energy. This increases the rate of reaction because more molecules collide with energy greater than or equal to the activation energy for this different pathway.
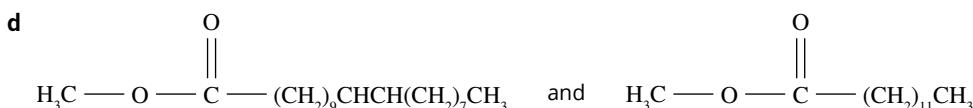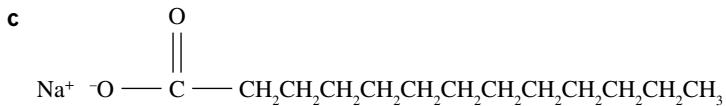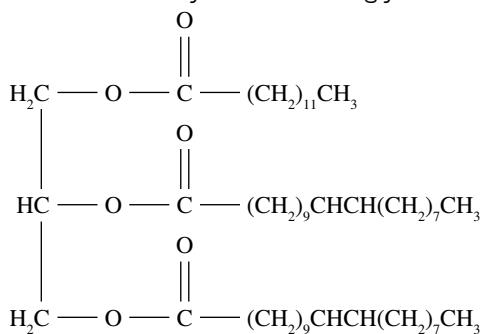
14 a methanol

   b glycerol

15 By increasing the concentration of the methanol, the rate of the forward reaction will increase, pushing the equilibrium position to the right (towards the products). This has the effect of maximising the yield for the reaction.

16 a

b At least one 'fatty acid' in the triglyceride must be unsaturated.

$$H_2C \!-\! O \!-\! \underset{\displaystyle \overset{\displaystyle O}{\|}}{C} \!-\! (CH_2)_{11}CH_3$$

$$HC \!-\! O \!-\! \underset{\displaystyle \overset{\displaystyle O}{\|}}{C} \!-\! (CH_2)_9CHCH(CH_2)_7CH_3$$

$$H_2C \!-\! O \!-\! \underset{\displaystyle \overset{\displaystyle O}{\|}}{C} \!-\! (CH_2)_9CHCH(CH_2)_7CH_3$$

c

$$Na^+\ {}^-O \!-\! \underset{\displaystyle \overset{\displaystyle O}{\|}}{C} \!-\! CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

d

$$H_3C \!-\! O \!-\! \underset{\displaystyle \overset{\displaystyle O}{\|}}{C} \!-\! (CH_2)_9CHCH(CH_2)_7CH_3 \quad \text{and} \quad H_3C \!-\! O \!-\! \underset{\displaystyle \overset{\displaystyle O}{\|}}{C} \!-\! (CH_2)_{11}CH_3$$

Biodiesel is a mixture of the constituent fatty acids of the triglyceride used. As there are both saturated and unsaturated constituent fatty acids, some of each must be present in the biodiesel.

17 At a ratio approaching 3:1, a competing saponification reaction can occur. This produces soap molecules. The purification of biodiesel relies on two steps. The first of these is separation, where the differences in the polarity of the glycerol, which is polar, and the biodiesel, which is relatively non-polar, ensure that the two substances do not dissolve in one another. The intermolecular forces capable of forming between the glycerol and the biodiesel do not release a sufficient amount of energy to compensate for the energy required to break apart the intermolecular forces between molecules of the same type. This results in two separate layers being formed.

When soap molecules are present in the reaction mixture, this allows for micelles to stabilise each substance in the other and, as a result, the two liquids will mix and form an emulsion. This would significantly increase the amount of time necessary for the mixture to be distilled and would certainly affect yield adversely.

18 Both saponification and transesterification can rely on the use of a base to break the ester bonds present in the triglyceride.

In saponification, the resulting hydrolysis introduces three hydrogen atoms to form glycerol and water while the carboxylate ions will produce a metal fatty acid salt, once glycerol and sufficient water are removed. In transesterification, the ester bond is broken, splitting the alcohol and fatty acid, but these then form methyl esters (as well as water and glycerol).

Overall, saponification starts with an ester (the triglyceride) and ends with three fatty acids and an alcohol (glycerol). Transesterification starts with one ester (the triglyceride) and three alcohols (three methanol molecules) and ends with three esters (from each of the fatty acids) and one alcohol (glycerol).
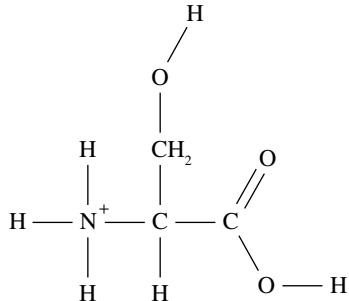
Chapter 17 **From amino acids to proteins**

Section 17.1 **Amino acids**
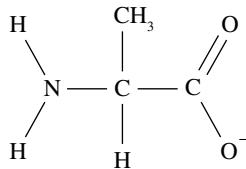
17.1 KEY QUESTIONS

1 A. A is the only amino acid in which the carboxyl and amino groups are not attached to the same carbon atom.

2 Nine out the 20 amino acids required by the body cannot be manufactured in the body. They must be provided by the food we eat. These are called essential amino acids.
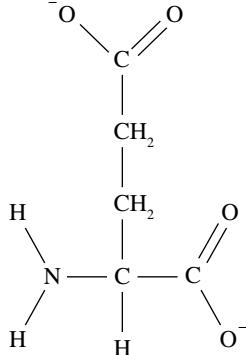
3 **a**

b

c

4
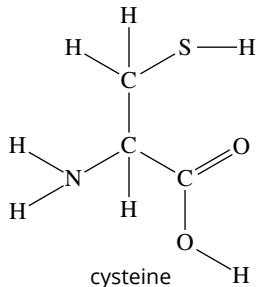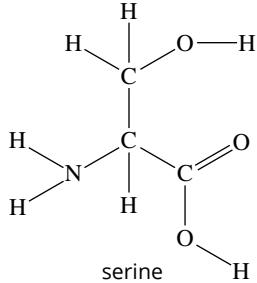
Structure of R group	Is the R group polar or non-polar?	Is the R group acidic, basic or neutral?
$-CH(CH_3)_2$	Non-polar	Neutral
$-CH_2COOH$	Polar	Acidic
$-CH_2C_6H_5$	Non-polar	Neutral
$-(CH_2)_4NH_2$	Polar	Basic

Section 17.2 **The formation of proteins**

17.2 KEY QUESTIONS

1   Tripeptide   Three amino acids joined by peptide links in a polypeptide chain
    Side chain   Variable part of an amino acid
    Polypeptide   Several amino acids that are joined by peptide links
    Amino group   Functional group present in all amino acids
    Water   By-product of the reaction that produces polypeptides

2   **a** A: amino group, B: amide group, C; side chain, D: carboxyl group
    b alanine, serine, leucine

3   B. B is correct because five peptide bonds (–CONH–) can be seen. C is incorrect because this polypeptide contains six amino acid units, but two of the units are the same amino acid.

    A is incorrect because there are two R groups that contain a carboxyl group plus the carboxyl group on the terminal amino acid. Therefore, there are three carboxyl groups.

    D is incorrect because the reaction to produce polypeptides is known as condensation polymerisation.

4   **a**

serine

cysteine

b $H_2NCH(CH_2OH)COOH + H_2NCH(CH_2SH)COOH \rightarrow H_2NCH(CH_2OH)CONHCH(CH_2SH)COOH + H_2O$
c $H_2NCH(CH_2SH)CONHCH(CH_2OH)COOH$
d condensation

Section 17.3 Primary and secondary structures of proteins

17.3 KEY QUESTIONS

1 **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.

2 The sequence of amino acids gives proteins their unique shape based on interactions of functional groups in different regions of the sequence. As protein shape is related to function, determining this sequence allows scientists to understand more about the role of specific proteins.

3 nine, peptide/amide, condensation polymerisation, alanine, lysine, glycine, valine, methionine

4 α-Helices result from interaction between the hydrogen on the amino group and the oxygen of the carbonyl group of a peptide link, specifically four amino acids along in the chain, causing a hydrogen bond to form. This results in this section of the protein coiling into an α-helix. β-Pleated sheets are also formed from hydrogen bonds between peptide links in regions where two or more parts of the polypeptide chain line up parallel to each other. The resulting structure is similar to a pleat.

Section 17.4 Tertiary structure of proteins

KEY QUESTIONS

1 B and C. 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 α-helix and β-pleated sheets that make up the secondary structure. Hydrogen bonds can also form between side chains that contain –OH, –NH or –C=O functional groups that make up the tertiary structure.

2

Bond type	Required components in R group	Amino acid examples
Hydrogen bond	Contains –O–H, –N–H and –C=O	Serine, threonine, histidine
Dipole–dipole interaction	Any polar group such as those containing –S–H, –O–H or –N–H	Cysteine, asparagine
Ionic interaction	Contains $-NH_3^+$ and another group that contains $-COO^-$	Aspartic acid, glutamic acid, lysine, arginine
Covalent cross-link	Cysteine side groups react to form a disulfide bridge (–S–S–)	Cysteine
Dispersion force	Any non-polar group	Alanine, leucine, phenylalanine
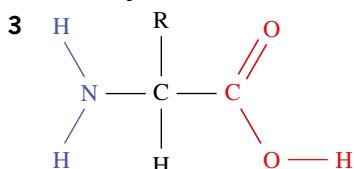
3 **a** dispersion forces
   b ionic bonding
   c hydrogen bonding
   d covalent bonding

CHAPTER 17 **REVIEW**

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 there are nine essential amino acids. Because humans do not have the capacity to produce them, they need to be included in the diet.

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.
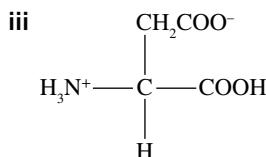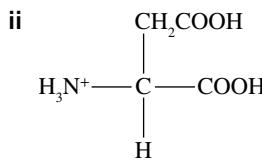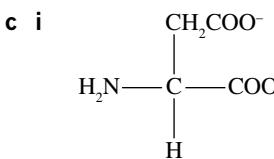
2   carboxyl and amino functional groups

3

4   **a**   **i**   carboxyl

   ii   amino

b   A zwitterion is a molecule that contains positive and negative charges, but has no charge overall.

c   **i**

   ii

   iii
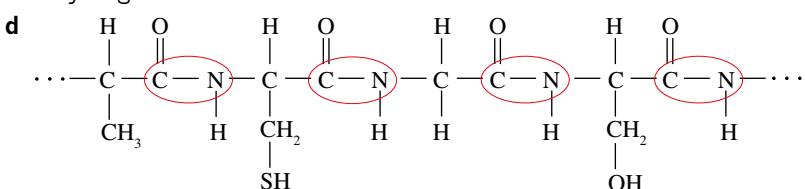
   Either carboxyl protons may be lost.

5   The carboxyl and amino groups react to form amide links between amino acids

6   B. There are two peptide bonds that link three different amino acids in this tripeptide. When hydrolysed, the peptide bonds are broken and the three amino acids are re-formed.

7   **a** $H_2NCHCH_3CONHCH_2COOH$, $H_2NCH_2CONHCHCH_3COOH$

   b   6 (using each amino acid once in each peptide)

   c   very large numbers

   d
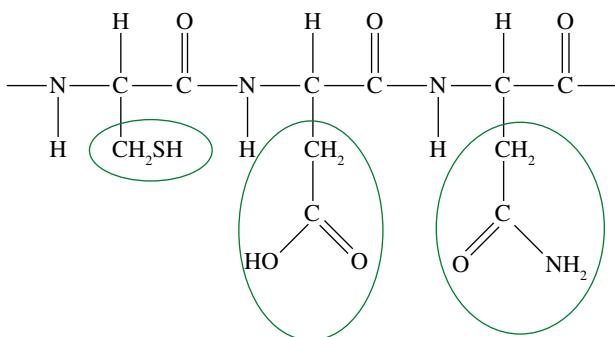
   e   alanine, cysteine, glycine, serine

8   **a**   covalent bond/peptide bond/amide bond

   b   hydrogen bond

   c   α-helix

9 β-Pleated sheets are formed when two adjacent strands of peptide lie in a plane and form hydrogen bonds between their respective backbones.

10

11 The activity of an enzyme, which is a type of protein, depends on its three-dimensional shape. The tertiary structure results from a combination of hydrogen bonding, electrostatic attraction between polar groups and disulfide linkages. If the wrong amino acid is introduced into the chain, these bonds may not form and the tertiary structure may be distorted. In some instances, the enzyme becomes inactive, depending upon how the tertiary structure is altered.

12 Primary structure refers to the sequence of amino acids in a protein.

Secondary structure refers to the folding of a section due to, for example, hydrogen bonding between peptide links.

Tertiary structure refers to the overall three-dimensional shape of a protein.

Three-dimensional structure of a protein
Source: Alfred Pasieka/Science Photo Library

13 a ionic interactions
b dipole–dipole interactions
c dispersion forces

14 Nearby cysteine residues are capable of forming covalent bonds with each other between the sulfur atoms. These covalent bonds are strong and help to stabilise the tertiary structure (three-dimensional shape) of the keratin protein.

15 Replacing leucine with serine would have a greater effect on the tertiary structure than replacing with isoleucine. This is because isoleucine and leucine both have non-polar amino acid side chains and would therefore form similar strength interactions with nearby amino acid side chains. Serine is a polar amino acid with a side chain capable of forming hydrogen bonds with other amino acid side chains. This may result in the protein changing its three-dimensional shape.

16 C, low
D
A

17 a Leucine has a non-polar side chain and is therefore hydrophobic. It would tend to be found hidden inside the protein structure, away from the surrounding water.

b Lysine has a polar, hydrophilic side chain. It would tend to be found on the outside of the protein structure, forming hydrogen bonds or ion–dipole interactions with water molecules (depending on the pH).

c Phenylalanine has a non-polar side chain and is therefore hydrophobic. It would tend to be found hidden inside the protein structure, away from the surrounding water.

d Aspartic acid has a polar, hydrophilic side chain. It would tend to be found on the outside of the protein structure, forming hydrogen bonds or ion–dipole interactions with water molecules (depending on the pH).

18 The primary structure of a protein is the sequence of amino acids. These amino acids are joined together by amide groups, formed from the condensation reaction between the carboxyl and amino groups on two amino acids. The amide groups are therefore integral to the primary structure of the protein in that they link the sequence of amino acids together. The secondary structure of the protein also depends on these amide groups. Hydrogen bonds form between the oxygen in the C=O of one amide group and the hydrogen in the N–H of another amide group. These hydrogen bonds help to stabilise the α-helices and β-sheets that make up the secondary structure of the protein.

Chapter 18 **Uses of proteins**

Section 18.1 **Investigating proteins**

18.1 KEY QUESTIONS

1 When the primary structure is known, scientists are able to search the Protein Data Bank (PDB) for proteins with similar primary structures. Depending on the level of similarity, the function of these similar proteins may provide a good estimate of the function of the protein of interest. This is because proteins with similar primary structures usually have similar three-dimensional shapes, and therefore similar biological functions.

2 The PDB is an invaluable resource to scientists. It provides them with the means to share information about protein structure, function and known interactions between them. It is important that it remain freely available so that all scientists are able to benefit equally from the information.

3 A polypeptide consists of amino acid units that are joined by peptide bonds, –CONH–. B is a peptide bond. All of the bonds between atoms in the polypeptide chain are covalent bonds, such as A. The sequence of amino acids in the polypeptide chain is known as its primary structure.
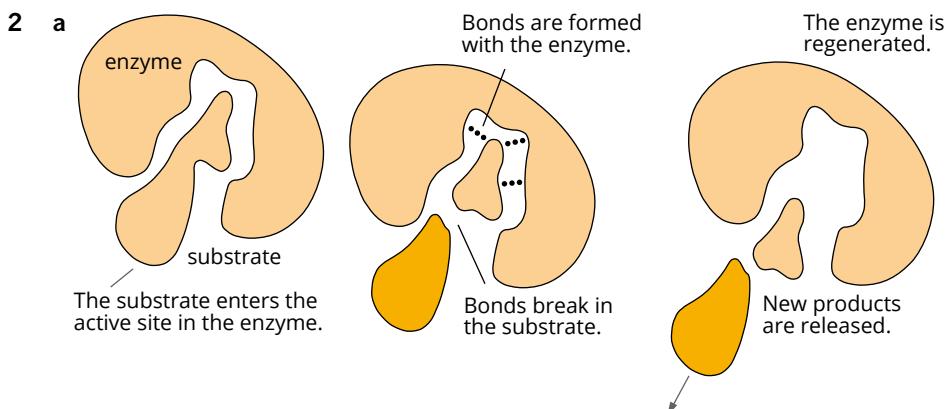
Each amino acid unit has a side chain (or R group) that distinguishes it from other amino acids. For example, the group labelled D is the side chain of tyrosine.

Interactions between the side chains are responsible for producing the tertiary structure of the polypeptide and its overall three-dimensional shape. A covalent bond, known as a disulfide bridge, can form when the side chains of two cysteine units interact, labelled C in the model.

Section 18.2 **Enzymes**

18.2 KEY QUESTIONS

1 D. Enzymes are biological catalysts. They provide an alternative reaction pathway with a lower activation energy. Each enzyme is specific to a particular reaction.

2 a

b Hydrogen bonds, ion–dipole interaction, dipole–dipole interactions, ionic interactions

3 a True
  b True
  c False
  d True

Section 18.3 Enzymes: dependence on pH and temperature

18.3 KEY QUESTIONS

1 During hydrolysis, covalent bonds between carbon atoms and nitrogen atoms are broken. This breaks the protein into its component amino acids. Denaturation is a result of the disruption of interactions between the side chains of the amino acids and the amide links that form the peptide chain. These interactions are responsible for the three-dimensional shape of the enzyme. When the shape is altered, the enzyme ceases to function but the primary structure remains intact.

2 In a solution of pH 11, the concentration of OH^- ions is high. The $-COOH$ group will donate a proton to become a $-COO^-$ group. In a solution of pH 2, the concentration of H^+ ions is high. The $-NH_2$ group will accept a proton to become a $-NH_3^+$ group. Neither the methyl group nor the hydroxyl group is affected by changing pH.

Structure of side chain	Is the side chain acidic or basic or neither?	Is the side chain positively charged, negatively charged or neutral?	
		In a solution of pH 2	In a solution of pH 11
$-CH_2COOH$	Acidic	Neutral	Negative
$-CH_2CH(CH_3)_2$	Neither	Neutral	Neutral
$-CH_2OH$	Neither	Neutral	Neutral
$-(CH_2)_4NH_2$	Basic	Positive	Neutral

3 a Denaturation occurs when there is a change to the structure and shape of an enzyme that 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, in a process called coagulation.
   c no
   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.

4 a Changes to the pH of the solution can change the charge of acidic or basic side groups on the amino acids of the protein. These changes can cause the protein to denature, disrupting the three-dimensional shape of the active site and reducing enzyme activity.
   b A decrease in temperature reduces the frequency and energy of the collisions between reactants. This reduces the rate of reaction observed as a reduction in enzyme activity. It can also reduce the flexibility of the enzyme structure, reducing its effectiveness as a catalyst according to the induced fit model.

Section 18.4 Enzymes in industry

18.4 KEY QUESTIONS

1 91.3%
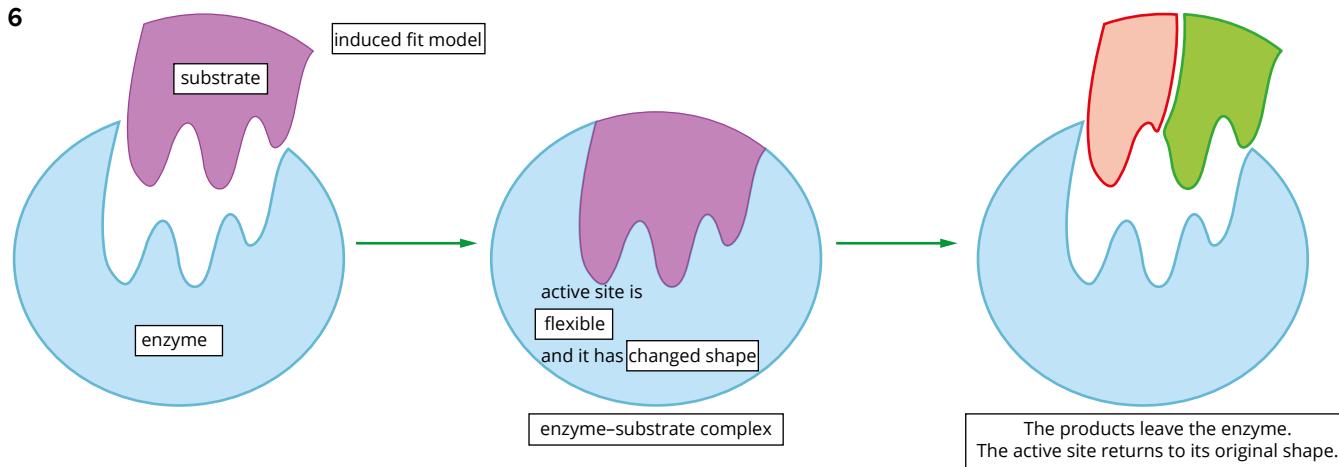
2 A high temperature would produce a high reaction rate, but would also result in a lower yield because the forward reaction is exothermic. A moderate temperature is used as a compromise between rate and yield.

3 A high pressure favours both the production of ethanol and a high rate of reaction. As there are 2 moles of gaseous reactants and 1 mole of gaseous products, a high pressure favours the forward reaction (formation of ethanol), in that the system responds to try and partially counteract the imposed change.

CHAPTER 18 REVIEW

1 a true
   b true
   c False; a mutation will not necessarily cause a loss in protein function. If the mutation is far away from the active site of the protein, then its activity may not be affected at all. Similarly, if the mutation results in exchanging an amino acid with similar characteristics, then it may not have a large effect on the protein's secondary and tertiary structure. For example, exchanging aspartic acid for glutamic acid may not have a large impact on the protein.
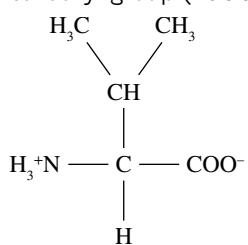
2 When a protein is being synthesised, secondary structures such as α-helices and β-pleated sheets form as a result of hydrogen bonds between the amide groups on adjacent regions of the polypeptide chain. The protein chain then folds further and interactions such as hydrogen bonds, dipole–dipole interactions, dispersion forces and disulfide bridges can form between amino acid side chains. This can result in amino acid units that are far apart in the protein's primary structure ending up adjacent to one other in the protein's three-dimensional shape.

3 **a** 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.

b 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.

4 **a** true

b true

c false

d false

e true

f true

g true

5 If the substituted amino acid lies within the active site of the protein, it may not have a significant effect on the overall three-dimensional shape of the protein, yet have a large impact on the strength of the interactions that hold the enzyme–substrate complex together. For example, if a serine amino acid unit is substituted for an alanine within the active site of the protein, the alanine side chain will only be able to form dispersion forces with the substrate, rather than hydrogen bonds. This alteration to the strength of the enzyme–substrate interactions may alter the activity of the enzyme.

6

7 Insulin is a protein that is released into the bloodstream in response to rising blood sugar levels. As a result, it has an optimal pH of ~7, the pH of blood. If it were ingested and entered the acidic environment of the stomach, it would be exposed to low pH conditions and may become irreversibly denatured and lose its function. Side chains, such as aspartic acid and glutamic acid, which would be negatively charged at pH 7, would become neutral at lower pH levels. This would affect the types of interactions they are able to have with other side chains, altering the three-dimensional shape of insulin and ultimately its function.

8 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.

9 A. Under highly acidic conditions, an amino acid is protonated at the amino group ($-NH_3^+$) and protonated at the carboxyl group ($-COOH$).

10

11 A, optimum temperature, fastest reaction rate. B, less frequent collisions, lower energy reactants. C, enzyme denatures, tertiary structure changes, three-dimensional shape of active site alters and enzyme activity drops.

12 $C_6H_{12}O_6 \rightarrow 2CO_2 + 2CH_3CH_2OH$

13 Fermentation: uses conditions of low temperatures and normal pressures. Grain or other plant materials are used as a starting material. The ethanol requires many distillation steps to purify it.

Hydration of ethene: uses conditions of moderate temperatures and high pressures. Crude oil is used as a starting material. The ethanol produced does not require as many distillation steps to purify it.

14 a Increasing pressure would increase both the yield and the rate of reaction. According to Le Châtelier's principle, the system would respond to reduce the overall pressure by favouring the products, the side with fewer moles of gaseous particles, shifting the equilibrium position to the right. In terms of collision theory, increasing the pressure would increase the frequency of collisions, thereby increasing the rate of the reaction.

b Decreasing the temperature would increase the yield of ethanol, but would decrease the rate of reaction. According to Le Châtelier's principle, the equilibrium position shifts in the direction of the exothermic reaction when the temperature is decreased and the yield would increase. The rate of reaction would decrease because not only are there less frequent collisions, but a lower proportion of particles would have sufficient energy to react.

15 Advantages: enzymes are highly specific and reactions can be conducted at atmospheric temperature and pressure. They are also biodegradable.

Disadvantages: enzymes are highly sensitive to changes in temperature and pH. They can also be more expensive to produce.

16 Distillation can separate liquids in a mixture based on differences in their boiling points. When an ethanol–water mixture is heated, the ethanol will boil first and enter the gaseous phase, separating it from the water. The ethanol vapour is then cooled down (condensed) and collected as a liquid.

17 A biological washing powder has the advantage of being biodegradable. It also does not require high temperatures, so clothes can be washed in colder water, resulting in lower energy costs. The disadvantages are that the enzymes are very sensitive to changes in temperature or pH, meaning that if the water temperature is too hot, the enzymes will not function as well. Some individuals are also sensitive to the enzymes in biological detergents and they can cause skin irritation.

18 Ethanol is a solvent that is capable of forming hydrogen bonds (as well as dispersion forces) with the amino acid side chains and amide groups in the protein backbone. As the ethanol concentration increases, it will form a greater number of these interactions with the protein. These interactions may interfere with the existing dipole-dipole interactions, dispersion forces, hydrogen bonds and disulfide bonds that are maintaining the three-dimensional shape of the enzymes and cause the protein to denature. If the shape of the enzyme is lost, its ability to catalyse the fermentation process will also be lost.

Chapter 19 Science inquiry skills in chemistry

Section 1.1 Questioning

Worked example: Try yourself 19.1.1

DEVELOPING A HYPOTHESIS

Develop a hypothesis and identify variables for investigating how the voltage of the galvanic cell is affected by the concentration of the silver ions in the silver nitrate solution.	
Thinking	**Working**
Write an inquiry question.	What is the relationship between the concentration of the silver ions and the voltage of the galvanic cell?
Identify the independent variable.	Concentration of the silver ions in the silver nitrate solution
Identify the dependent variable.	Voltage of the galvanic cell
Identify the controlled variables.	Concentration of Fe^{2+} ions in the anode half-cell Same silver cathode Temperature
Write a potential hypothesis.	The voltage of the galvanic cell is directly proportional to the concentration of the silver ions.

19.1 KEY QUESTIONS

1 **a** A hypothesis is a statement that can be tested. This involves making a prediction based on previous observations.
   b A theory is a hypothesis that is supported by a great deal of evidence from a wide variety of sources. A principle is a theory that is so strongly supported by evidence that it is unlikely to be shown to be untrue in the future.

2 **a** amount of sodium hypochlorite
   b time
   c temperature
   d pH

3 qualitative

4 C. Using a calibrated pH meter at a particular temperature

5 **a** valid
   b reliable
   c accurate

Section 19.2 Planning investigations

19.2 KEY QUESTIONS

1 B. Repeating experiments and presenting results support the reliability of an experiment.

2 **a** In a control experiment, two groups of subjects are tested; the groups, or the tests performed on them, are identical except for a single factor (the variable), which is not changed in the control experiment.
   b The dependent variable is the variable that is measured to determine the effect of changes in the independent variable. The independent (experimental) variable is the variable that is changed in an experiment. For example, in an experiment testing the effect of soil pH on flower colour, the independent variable would be soil pH and the dependent variable would be flower colour.

3 **a** source/location of water

    b pH

    c temperature of solutions

4 **a** Litmus paper and universal indicator give qualitative information about pH through colour.

    b A calibrated pH meter will give quantitative information and is more accurate than using litmus paper or universal indicator

Section 19.3 Reducing uncertainty in data

19.3 KEY QUESTIONS

1 **a** systematic errors

    b random errors

2 **a** Systematic (the solution then placed in the burette will always have a lower concentration, so the volume (titre) measured will always be higher than the 'true' value)

    b Random (the inaccuracy of the measuring cylinder will lead to some measurements being greater, and some measurements being smaller than the true value of the volume)

    c mistake

3 There could be many reasons that the same experimental results cannot be obtained. The experimental design may be poor because of a:

- lack of objectivity
- lack of clear and simple instructions
- lack of appropriate equipment
- failure to control variables.

Other problems not specifically related to the experiment could be:
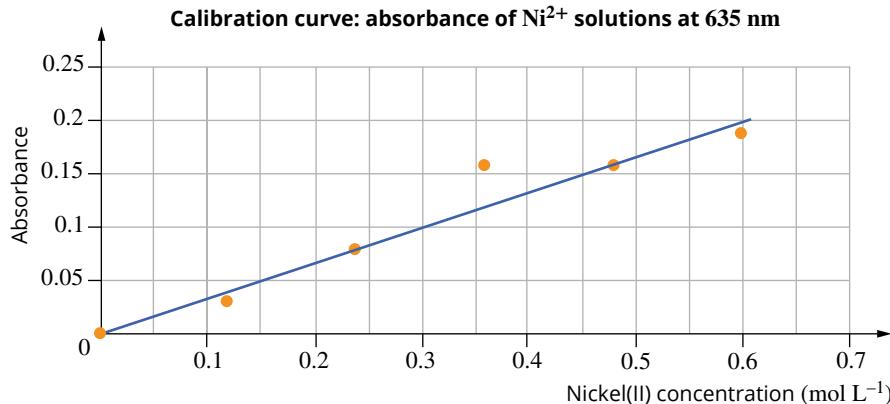
- a poor hypothesis that could not be tested objectively
- conclusions that do not agree with the results
- interpretations that are subjective.

Section 19.4 Processing data and information

19.4 KEY QUESTIONS

1 Add a trend line or line of best fit.

2 **a**

Calibration curve: absorbance of Ni^{2+} solutions at 635 nm

    b Data point 4 (0.36, 0.159) is an outlier.

    c An outlier is a point in the data that does not fit the trend.

Section 19.5 **Analysing data and information**

19.5 KEY QUESTIONS

1   A linear graph shows the proportional relationship between two variables.
2   An inversely proportional relationship
3   Directly proportional
4   Time restraints and limited resources

Section 19.6 **Conclusions**

19.6 KEY QUESTIONS

1   B. A scientific article should always be written using objective language. A concluding paragraph must summarise the information presented in the article and connect it with the title. It should also include limitations, possible applications of the research and potential future research.
2   The statement 'Many repeats of the procedure were conducted' is unquantified. 'The procedure was repeated 30 times' is better because the number of trials is quantified.

Section 19.7 **Communicating**

19.7 KEY QUESTIONS

1   **a** g mol^{-1}
    b mol L^{-1}
2   **a** Divide the value in mL by 1000.
    b To make the numbers easier to comprehend; to use the units that match the units on the measuring device (e.g. volumes on pipettes are given in mL).

CHAPTER 19 REVIEW

1   **a** dependent variable
    b controlled variable
    c independent variable
2   **a** reflect
    b create
    c analyse
    d investigate
    e apply
    f identify
    g describe
3   Independent variable, source of the water; dependent variable, calcium ion concentration; controlled variables, temperature, time of testing, method of testing
4   **a** It can dissolve or eat away at substances, including tissues such as your skin or lungs.
    b It Is toxic (poisonous) if inhaled.
    c It is a highly combustible liquid that could catch fire.
5   Accuracy refers to the ability of the method to obtain the correct measurement close to a true or accepted value.
    Validity refers to whether an experiment or investigation is, in fact, testing the set hypothesis and aims.
6   **a** mistake
    b random error
    c systematic error

7 A linear (or directly proportional) relationship

8 Evaluate the method; identify issues that could affect validity, accuracy, precision and reliability of data; state systematic sources of error and uncertainty; and recommend improvements to the investigation if it is to be repeated

9 A trend is a pattern or relationship that can be seen between the dependent and independent variables. It may be linear, in which the variables change in direct proportion to each other to produce a straight trend line. The relationship may be in proportion but non-linear, giving a curved trend line. The relationship may also be inverse, in which one variable decreases in response to the other variable increasing. This could be linear or non-linear.

10 Any issues that could have affected the validity, accuracy, precision or reliability of the data plus any sources of error or uncertainty

11 The purpose of referencing and acknowledgments is to avoid plagiarism and ensure creators and sources are properly credited for their work.

12 A. In APA style, the in-text citation should list the first author's last name and the year of publication.

13 0.0230 L or 2.30×10^{-2} L (ensure that you keep the same number of significant figures)

14 a Independent variable—concentration of the electrolyte
   Dependent variable—cell voltage
   Controlled variables—type of electrolyte, distance between the electrodes, temperature, supply of oxygen and hydrogen

   b The data collected would be the cell potential, measured in volts, it would be quantitative.

   c Voltmeter that reads to two decimal places,
   Accurate volumetric glassware, such as burettes and pipettes, to measure out the concentrations of the solutions, which measure to the nearest 0.1 of a millilitre.

   d Raw data is data collected in the field and recorded as measurements are taken. Processed data tabulates this into a form in which the reader can clearly see the concentration of the electrolyte and the measured voltage generated by the cell. This can also then be processed and graphed with the independent variable on the *x*-axis (concentration) and dependent variable on the *y*-axis (voltage).
   If the hypothesis is correct, the graph would show an increase in voltage as the concentration increases, i.e. a line with a positive gradient. If this line was a straight line, it would indicate a linear (directly proportional) relationship between the voltage and the concentration.

Unit 4 **Review**

SECTION 1: MULTIPLE CHOICE

1 B. The longest continuous chain is 5 carbons and there are no double bonds present, so the molecule is a derivative of pentane. An additional methyl (CH_3) side group is attached at carbon 2.

2 B. Oxidation of a secondary alcohol produces a ketone. Oxidation of primary alcohols produces either an aldehyde or a carboxylic acid, depending on the conditions used.

3 A. Non-polar alkanes have only weak dispersion forces, which become stronger as the molecular size increases. The presence of functional groups such as Cl and OH introduces some additional dipole–dipole attractions, and so increases the boiling point. An OH group allows for stronger hydrogen bonding between molecules, and so raises the boiling point.

4 C. The hydroxyl group in alcohols is not significantly acidic or basic. II is not true.

5 C

$$n(CHCl_3) = \frac{m}{M} = \frac{1000}{119.368}$$

$$n(CH_4) = n(CHCl_3) = \frac{1000}{119.368}$$

$$m(CH_4) = n \times M = \frac{1000}{119.368} \times 16.042$$

$$m(CH_4)\text{needed} = \frac{1000}{119.368} \times 16.042 \times \frac{100}{75} = 179\,g$$

6 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.

7 C

$$n(C_2H_6) = \frac{m}{M} = \frac{6.32}{30.068}$$

$$n(CO_2) = 2 \times n(C_2H_6)$$

$$V(CO_2) = n \times V_m = 2 \times \frac{6.32}{30.068} \times 22.71 = 9.55\,L$$

8 C. Addition polymerisation requires the presence of a carbon–carbon double bond in the molecule.

9 B. Aldehyde groups occur at the end of the molecule because they are terminal groups. Ketones have carbon atoms on either side of the carbonyl group. Secondary and tertiary amides have carbon atoms on either side of the amide group.

10 C. 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.

11 B. $3x + 92$(glycerol) $= 878 + 54$ (three water molecules incorporated in the hydrolysis step).

12 C. The graph indicates that the yield of Z decreases with increasing temperature. This is characteristic of an exothermic reaction. The graph indicates that the yield of Z increases with increasing pressure. This indicates that the forward reaction is pressure reducing, and so z is less than 3 (3 mol of reactant gases).
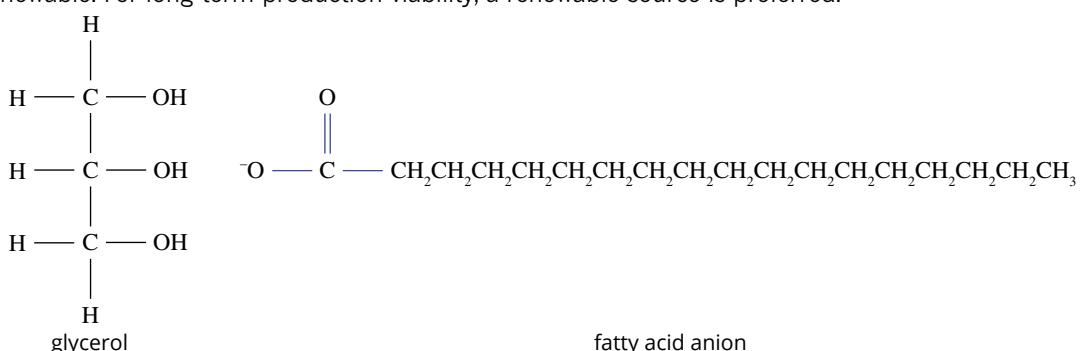
SECTION 2: SHORT ANSWER

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

  b **i** $CH_2CH_2(g) + H_2O(g) \xrightarrow{H_3PO_4} CH_3CH_2OH(g)$
   **ii** addition
    iii The forward reaction reduces pressure in the system because there are fewer moles of gaseous products than reactants. Use of a high pressure will move the equilibrium to the right to lower the pressure, according to Le Chatelier's principle. Use of high pressure increases reaction rate because the frequency 12 collisions between particles is increased.

c Use of the enzyme catalyst allows the reaction to take place at a much lower, more economical temperature and pressure.

Glucose, obtained from plants, is a renewable raw material, while ethene, obtained from fossil fuels, is not renewable. For long-term production viability, a renewable source is preferred.

2 a i

glycerol   fatty acid anion

ii Carboxylate

b i Anionic ($-SO_3^-$)
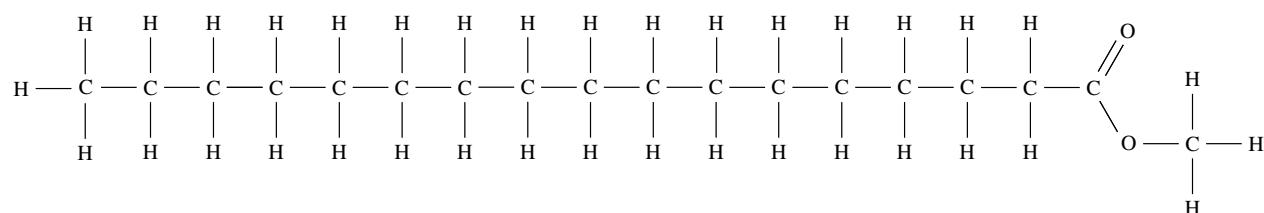
ii Ion–dipole

iii Dispersion forces

c i Detergents lather in hard water whereas soaps do not.

ii Many detergents are produced from a non-renewable resource (petroleum) or many detergents are non-biodegradable.

d i

ii Dipole–dipole bonds and dispersion forces

3 a i $(CH_3)_2CHCH_2CHCHCH_2CH_3$

ii $CH_3CH_2CH(CH_3)CH_2CHO$

iii $CH_3COCH_2CONH_2$

b i *trans*-pent-2-ene

ii 3-ethylhexan-3-amine

iii methyl butanoate

c i Acidified dichromate ($Cr_2O_7^{2-}/H^+$) or acidified permanganate (MnO_4^-/H^+)

ii H_2 and Ni catalyst (other metals sometimes used)

d i $CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$

ii $CH_3CH_2COOH + CH_3CH_2NH_2 \rightarrow CH_3CH_2COO^- + CH_3CH_2NH_3^+$

4 a i -1

ii $CH_3CH_2OH(l) \rightarrow CH_3CHO(l) + 2H^+(aq) + 2e^-$

b i $n(\text{ethanol}) = \dfrac{m}{M} = \dfrac{3.00}{46.068} = 0.0651\,\text{mol}$

$n(\text{dichromate}) = cV = 1.00 \times 0.025 = 0.0250\,\text{mol}$

0.0651 mol of ethanol will react with 0.0217 mol of dichromate
Hence dichromate is in excess.
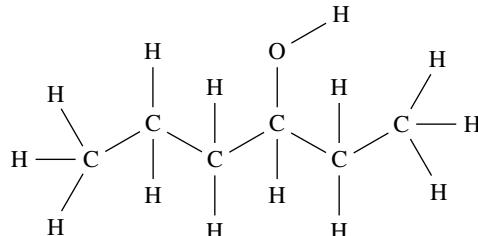
$n(\text{ethanal}) = n(\text{ethanol})$

$n(\text{ethanal})_{\text{expected}} = nM = \dfrac{3.00}{46.068} \times 44.052 = 2.869\,\text{g}$

$\% \text{ yield} = \dfrac{2.42}{2.869} \times 100 = 84.3\%$

    ii Ethanol and ethanal may evaporate from the reaction vessel, or the reaction is a reversible reaction and so does not go to completion, or some ethanal is lost in the collection process, or some ethanal was oxidised further to produce ethanoic acid.
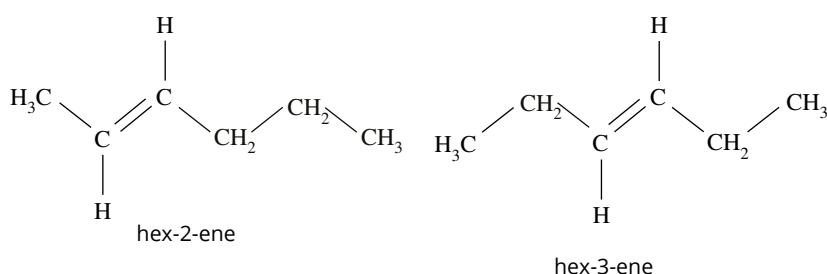
5 a i
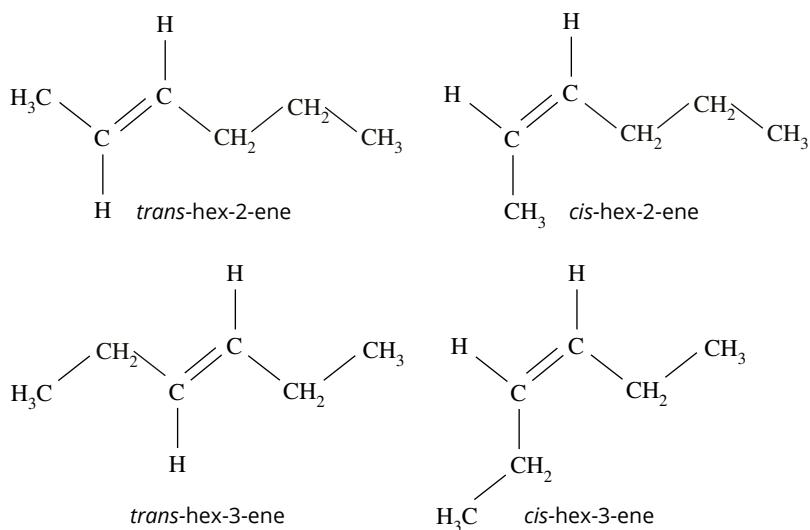
    ii secondary

    iii Both ethanol and hexan-3-ol can hydrogen bond with water to allow some solubility. In the alcohol homologous series, water solubility decreases from ethanol to hexanol because each additional CH_2 group reduces the polarity of the molecules, increasing the effect of the non-polar, hydrocarbon part that cannot form hydrogen bonds to water molecules. Thus the larger hexan-3-ol molecule is almost insoluble.

b

hex-2-ene

hex-3-ene

c

trans-hex-2-ene

cis-hex-2-ene

trans-hex-3-ene

cis-hex-3-ene

6 a i O

    ii L or N

    iii N

  b i Lowered. Lowering the temperature will favour the forward exothermic reaction.

    ii Lowering the temperature will decrease the rate of the reaction.

    iii High pressure equipment is expensive, and the use of high pressures for harmful gases such as sulfur dioxide is potentially dangerous. With the use of a catalyst, satisfactory yields are achieved at the safer, cost-effective lower pressure.

  c i not change

    ii not change

    iii increase

SECTION 3: EXTENDED ANSWER

1 **a** m(C in the sample) = m(C in the CO_2) = $\frac{12.01}{44.01} \times 11.60 = 3.166\,g$

m(H in the sample) = m(H in the H_2O) = $\frac{2.016}{18.016} \times 4.74 = 0.530\,g$

m(O in sample) = 6.500 – 3.166 – 0.530 = 2.804 g

C:H:O = $\frac{3.166}{12.01} : \frac{0.530}{1.008} : \frac{2.804}{16.00}$ = 0.264:0.526:0.175 = 1.5:3.0:1.0 = 3:6:2

Empirical formula is $C_3H_6O_2$

$pV = nRT = \frac{mRT}{M}$

$M = \frac{mRT}{pV} = \frac{5.01 \times 8.314 \times 473}{120 \times 2.22} = 74.0\,g\,mol^{-1}$
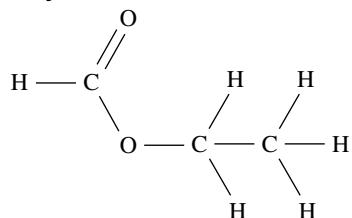
This is the same value as the empirical formula mass

∴ Molecular formula is $C_3H_6O_2$.
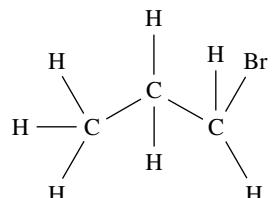
b **i** methyl ethanoate

ii Add sodium carbonate to samples of the two isomers. Isomer I (an ester) will show no reaction. Isomer II (a carboxylic acid) will react to evolve carbon dioxide (colourless, odourless gas produced).

iii ethyl methanoate

c **i**
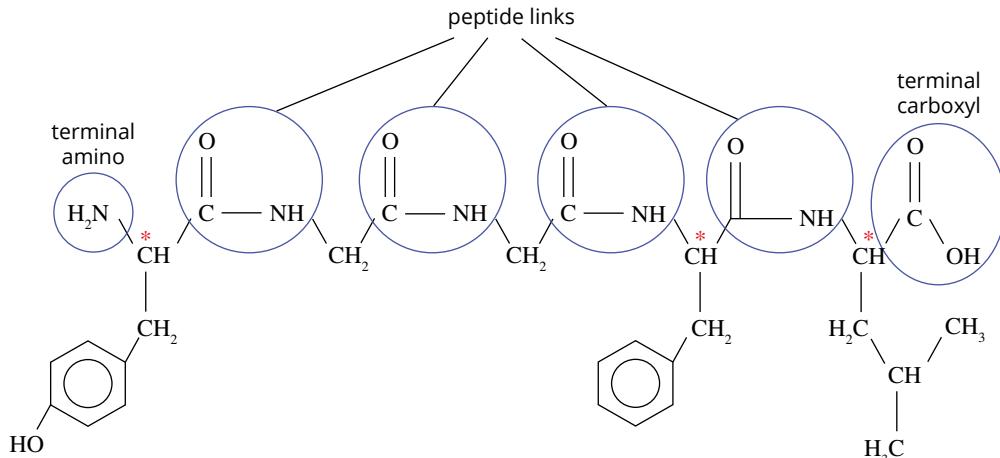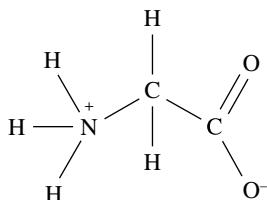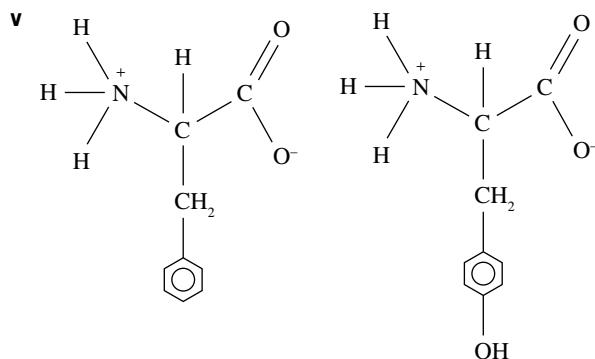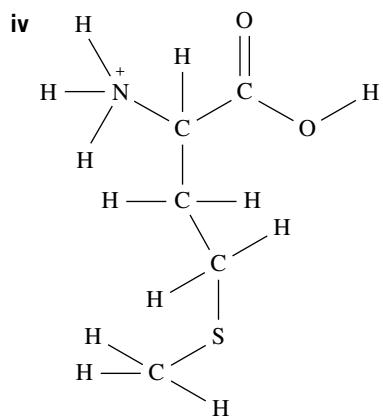
ii Dispersion forces will be similar in both molecules as they are very similar in molar mass. Compound C, propan-1-ol, contains a hydroxyl group which can form hydrogen bonds between the molecules. This bonding is stronger than the dipole–dipole bonding between propanone molecules. The stronger bonding leads to the higher boiling point.

iii The purple permanganate solution, when mixed with the colourless propanol, will decolorise. The products, including the manganese(II) ion and propanoic acid (isomer II), are colourless.
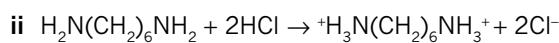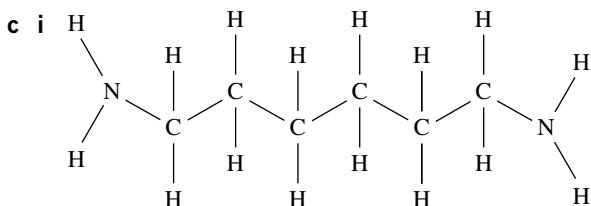
2 **a** **i** glycine, tyrosine, phenylalanine

ii and **iii**

iv

v

b i The primary structure of a protein relates to the formation of peptide linkages between the amino acids because they are linked together in a specific sequence; because this is a condensation reaction between carboxyl and amino functional groups, water is produced as a by-product. Secondary and tertiary structures do not involve condensation reactions.

ii These are features of the secondary structure of proteins, maintained by hydrogen bonding between the regularly spaced peptide linkages along the backbone of all protein chains.

iii Even before the disruption to bonding becomes sufficient to permanently denature an enzyme, changes in pH that affect the functional groups at the active site can significantly interfere with the substrate interactions and reduce activity.

iv 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 to heat.

c i

ii $H_2N(CH_2)_6NH_2 + 2HCl \rightarrow \,^+H_3N(CH_2)_6NH_3^+ + 2Cl^-$

iii Both have amide links between the monomer residues.

iv Nylon is a copolymer with only two alternating monomers. Proteins have 20 different monomers with a wide range of combinations and sequences.