Unit 3 **Area of Study 1 Review**

Multiple-choice questions

1 B A fuel is a chemical that undergoes reaction in a way that provides useful energy. This includes chemical fuels and nuclear fuels. Instead, a wind turbine converts the kinetic energy of wind.

2 C Reactions involving fuels release energy to the surroundings, so the enthalpy stored in the products will always be lower than that in the reactants.

3 D Carbon dioxide and water are the products of complete combustion of any carbon-based fuel.

4 B Hydrogen combustion produces no carbon dioxide (hence I) and the energies per unit mass are, for hydrogen $\frac{242}{2}$ = 141 kJ g^{-1}, and for methane $\frac{802}{16}$ = 50 kJ g^{-1} (hence II). The energy per unit volume will be proportional to the molar energies, which favour methane.

5 A Biodiesel molecules possess a slightly polar ester group that can bond to water. Also, biodiesel can contain glycerol and partially converted triglycerides possessing hydroxy and carboxy groups.

6 D Biodiesel molecules contain polar ester groups, allowing for stronger intermolecular attractions between them than exist between the purely hydrocarbon petrodiesel molecules. At low temperatures this causes the viscosity of biodiesel to increase significantly.

7 A The carbon released by combustion of fossil fuels derives from underground deposits and adds to the existing levels of CO_2. The carbon released by combustion of biodiesel derives from carbon dioxide absorbed by plants during photosynthesis so there is no net addition to existing levels from the combustion.

8 C The negative ΔH value indicates an exothermic reaction. Bond breaking absorbs energy and bond forming releases energy, and in an exothermic reaction there is a net release of energy.

9 C An exothermic reaction involves an energy conversion from enthalpy (chemical energy) into heat, but no energy is created or destroyed.

10 C The negative ΔH value indicates a decrease in enthalpy overall, but bond breaking is necessary for initiation so there will be an initial increase (i.e. an activation energy barrier).

11 B $n(C_3H_8) = \frac{100}{44.0} = 2.27$ mol

energy released (exothermic) = $\frac{2220}{1} \times 2.27 = 5.05 \times 10^3$ kJ

12 B 1 MJ = 1000 kJ

$n(CO_2) = \frac{1000}{2200} \times 3 = 1.35$ mol

$V(CO_2) = n \times V_m = 1.35 \times 24.8 = 33.5$ L

13 D $d = \frac{m}{V} = \frac{n \times M}{V}$

$pV = nRT \Rightarrow \frac{n}{V} = \frac{p}{R \times T}$ hence $d = \frac{n \times M}{V} = \frac{p}{R \times T} \times M = \frac{p \times M}{R \times T}$

14 A $\overset{-3}{N}H_4^+$, $\overset{0}{N}_2$, $\overset{+2}{N}O$, $\overset{+5}{N}O_3^-$

15 D This is the only case where the oxidant (Pb^{2+}, $E° = -0.13$ V) has a lower $E°$ than the reductant (I^-, $E° = +0.54$ V).

16 C A spontaneous reaction will occur with the half-equations $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ and $H_2(g) \rightarrow 2H^+(aq) + 2e^-$. The products of the reaction include $H^+(aq)$, which will increase the acidity of the mixture (lower pH).

17 A The strongest oxidant will be the species gaining electrons (i.e. on the left-hand side) with the highest $E°$ value. The strongest reductant will be the species losing electrons (i.e. on the right-hand side) with the lowest $E°$ value.

18 C The anode is, by definition, the site of oxidation in any cell. In a galvanic cell this is the electrode labelled negative.

19 D The half-cell reactions will be as follows.

At the positive cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. Hence, $Cu^{2+}(aq)$ is consumed and the blue colour of the solution will fade.

At the negative anode: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$. Hence, Ni(s) is consumed and mass of the nickel electrode will decrease.

20 D The source of energy in both cases is the high enthalpy stored in the fuel/oxygen combination. Direct combustion converts the available enthalpy into heat, whereas the reaction in a fuel cell converts it directly into electrical energy.

21 A No catalyst affects the energy output or product composition of a chemical reaction (except by changing the balance of side reactions that may occur). Fuel cells are efficient energy converters but if the reactions do not occur at an adequate rate, then current and power output are limited compared to, say, combustion reactions where the energy is converted very quickly.

Short-answer questions

22 **a** A fuel is a chemical that undergoes reaction in a way that provides useful energy. This includes chemical fuels and nuclear fuels.

b The methane found in natural gas, like all fossil fuels, derives from the decomposition of ancient biomass largely as a result of the action of heat and pressure in the Earth's crust and is tapped from underground reserves where it is normally associated with coal and oil. It is non-renewable because it takes millions of years to form by natural processes. Since its carbon comes from underground reserves, its combustion adds to current levels of atmospheric carbon dioxide.

The methane found in biogas derives from the anaerobic digestion of biomass by microorganisms. It is renewable because the biomass can be produced as needed. Because the carbon in the source biomass is absorbed from the atmosphere during photosynthesis, its re-release upon combustion of the biogas has relatively little net effect of atmospheric carbon dioxide levels.

23 **a** Petrol, petrodiesel, LNG, LPG

b Methanol, ethanol, biodiesel

c Generally, the higher the proportion of oxygen in a fuel, the lower the available energy. The presence of oxygen means that the fuel is already partially oxidised.

d Methanol and ethanol are renewable fuels that are relatively easy to produce, store and transport in large quantities. As fossil fuel reserves diminish, they are becoming increasingly cost-effective.

e For example, air transport

f For most forms of ground-based transport, the storage volume is more limiting than mass considerations.

24 **a** $75.6 \times 9.82 = 742$ MJ

b Heat losses occur in the boiler due to imperfect insulation. Heat is also lost through friction in moving parts within the turbines and generator.

c A non-renewable energy resource is one that cannot be replaced or regenerated as fast as it is consumed. Thus non-renewable resources are eventually exhausted.

d Biogas is a renewable energy source, whereas existing coal supplies (which remain large) are non-renewable and would eventually be consumed. Because biogas carbon is derived from absorption of atmospheric CO_2 in photosynthesis, its use as a fuel has relatively little effect on net levels of atmospheric CO_2. Biogas can be produced from waste biomass that would otherwise require disposal.

25 **a** Equation 1 doubled. Hence, $\Delta H = 2 \times (+181) = +362$ kJ mol^{-1}

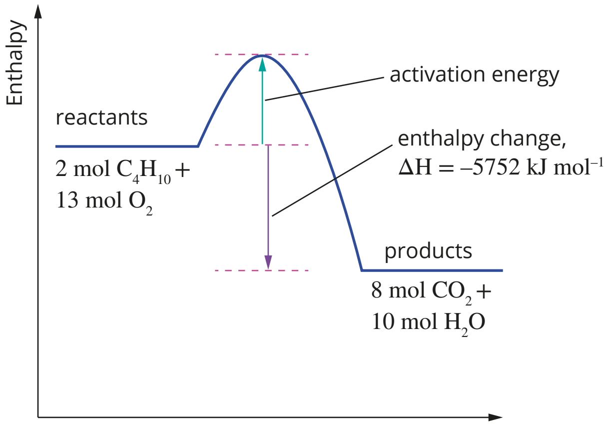
b Equation 1 reversed. Hence, $\Delta H = -181$ kJ mol^{-1}

c Equation 2 halved and reversed. Hence, $\Delta H = \frac{1}{2} \times (+114) = +57$ kJ mol^{-1}

d Equation 1 + Equation 2. Hence, $\Delta H = (+181) + (-114) = +67$ kJ mol^{-1}

26 **a** The equation has combustion of 2 mol of butane, hence $\Delta H = 2 \times (-2876) = -5752$ kJ mol^{-1}

b



c Some initial input of energy is required to allow some reactants to overcome the activation energy barrier (associated with breaking bonds in reactants) to initiate the rapid reaction.

d Heat of combustion = $\frac{2876}{58.0}$ = 49.6 kJ g^{-1}

e Energy released = 3.00 × 49.6 = 149 kJ

⇒ energy absorbed by water = $\frac{30}{100} \times 149 = 44.6$ kJ $= 4.46 \times 10^4$ J

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

$\Delta T = \frac{q}{mc} = \frac{4.46 \times 10^4}{150 \times 4.18} = 71.2°\text{C}$

⇒ final temperature = 20.0 + 71.2 = 91.2°C

27 **a** $n(CH_4) = \frac{m}{M} = \frac{1000}{16} = 62.5$ mol

⇒ energy released = $62.5 \times \frac{802}{1} = 5.01 \times 10^4$ kJ = 50.1 MJ

b $n(CO_2) = \frac{1000}{802} \times 1 = 1.25$ mol

⇒ $V(CO_2) = nV_m = 1.25 \times 24.8 = 30.9$ L

c $2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g) \qquad \Delta H = -1042$ kJ mol^{-1}

OR

$CH_4(g) + \frac{3}{2}O_2(g) \rightarrow CO(g) + 2H_2O(g) \qquad \Delta H = -521$ kJ mol^{-1}

(ΔH is calculated as follows: energy released when 1 mol CO is formed = 18.6 × 28 = 521 kJ, etc.)

d **i** 802 kJ

ii $\left(\frac{20}{100} \times 521\right) + \left(\frac{80}{100} \times 802\right) = 746$ kJ

iii 521 kJ

28 **a** Heat energy absorbed = $m \times c \times \Delta T = (224 \times 1000) \times 4.18 \times (70 - 14) = 5.24 \times 10^7$ J = 52.4 MJ

energy from fuel = $\frac{52.4}{1.25}$ = 41.9 MJ kg^{-1}

b Imperfect insulation may allow some heat losses; some of the energy released is absorbed by the container; incomplete combustion of the fuel will reduce energy released

29 a i $p = \frac{16\,500}{101.3} = 163$ atm

ii $p = 163 \times 760 = 1.24 \times 10^5$ mmHg

b $n(\text{He}) = \frac{pV}{RT} = \frac{16\,500 \times 25.0}{8.314 \times 288} = 172$ mol

$m(\text{He}) = nM = 172 \times 4.0 = 689$ g

c $V(\text{He}) = nV_m = 172 \times 24.8 = 4.27 \times 10^3\ \text{L} = 4.27\ \text{m}^3$

d total $V(\text{He}) = \frac{nRT}{p} = \frac{172 \times 8.314 \times 303}{108} = 4.02 \times 10^3$ L

$\Rightarrow$ number of balloons $= \frac{4.02 \times 10^3}{6.5} = 618$

30 a Advantages include: very high energy per unit mass; water is the only product of combustion; renewable

Disadvantages include: hydrogen is difficult and dangerous to transport and store; requires energy for production; relatively expensive

b Advantages include: no recharge time; range is potentially greater; one of the reactants (oxygen/air) doesn't need to be carried with the cell; doesn't incorporate toxic materials such as heavy metals

Disadvantages include: hydrogen is difficult and dangerous to transport and store; relatively expensive; lower power output

c Advantages include: greater efficiency of energy conversion so potentially longer range; quieter

Disadvantages include: lower power output; expensive

31 a Anode: $CH_3OH(g) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

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

b $n(CH_3OH) = \frac{m}{M} = \frac{1.00}{32.0} = 0.0313$ mol

$\Rightarrow$ maximum energy $= 0.0313 \times \frac{1453}{2} = 22.7$ kJ

c $V(CH_3OH) = \frac{1.00}{0.79} = 1.27$ mL

900 mL produces 1 kWh = 3600 kJ

$\Rightarrow$ energy obtained from fuel cell $= \frac{1.27}{900} \times 3600 = 5.1$ kJ

d Percentage efficiency $= \frac{5.1}{22.7} \times \frac{100}{1} = 22\%$

e Incomplete reaction of the fuel (methanol) is likely. Some may be incompletely oxidised or pass into the electrolyte waste without reacting at all. Also, a significant amount of heat is generated in most fuel cells, further reducing efficiency.

32 a Oxidation number changes: I (+5 → −1) and S (+4 → +6).

The oxidant is HIO_3. The reductant is SO_2.

b Not redox

c Oxidation number changes: Fe (+2 → +3) and O (0 → −2).

The oxidant is O_2. The reductant is $Fe(OH)_2$ (or Fe^{2+}).

d Oxidation number changes: H (−1 → 0) and H (+1 → 0).

The oxidant is H_2O. The reductant is NaH.

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

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

Overall: $2Al(s) + 3Br_2(aq) \rightarrow 2Al^{3+}(aq) + 6Br^-(aq)$

b Oxidation: $S_2O_3^{2-}(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8e^-$

Reduction: $ClO^-(aq) + 2H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$

Overall: $4ClO^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 4Cl^-(aq) + 2H^+(aq)$

c Oxidation: $H_2O_2(aq) \rightarrow O_2(aq) + 2H^+(aq) + 2e^-$

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

Overall: $3H_2O_2(aq) + 2MnO_4^-(aq) + 2H^+(aq) \rightarrow 3O_2(aq) + 2MnO_2(s) + 4H_2O(l)$

34 a Cadmium; the anode is the site of oxidation (the negative electrode in a galvanic cell)

b The equations indicate alkaline conditions in the cell, hence a hydroxide compound such as KOH or NaOH

c For effective recharging of a cell, the discharge products must remain in electrical contact with the electrodes. Because the products in this cell are solids, they remain on the respective electrode surfaces allowing the cell reactions to be reversed.

d These are simply the reverse of the reactions occurring during discharge.

At the positive electrode (the anode during recharging):

$Ni(OH)_2(s) + OH^-(aq) \rightarrow NiOOH(s) + H_2O(l) + e^-$

At the negative electrode (the cathode during recharging):

$Cd(OH)_2(s) + 2e^-(aq) \rightarrow Cd(s) + 2OH^-(aq)$

Overall:

$2Ni(OH)_2(s) + Cd(OH)_2(s) \rightarrow 2NiOOH(s) + Cd(s) + 2H_2O(l)$

e Enthalpy (chemical energy) → electrical energy

35 a $E°(Sn^{2+}/Sn) = -0.14$ V and $E°(Fe^{2+}/Fe) = -0.41$ V

i cell voltage = $(-0.14) - (-0.41) = 0.27$ V

ii Fe^{2+}/Fe

iii $Sn^{2+}(aq) + Fe(s) \rightarrow Sn(s) + Fe^{2+}(aq)$

b $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V and $E°(Al^{3+}/Al) = -1.71$ V

i cell voltage = $(+0.77) - (-1.71) = 2.48$ V

ii Al^{3+}/Al

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

c $E°(H^+/H_2) = 0$ V and $E°(I_2/I^-) = +0.54$ V

i cell voltage = $(+0.54) - (0) = 0.54$ V

ii H^+/H_2

iii $I_2(aq) + H_2(g) \rightarrow 2I^-(aq) + 2H^+(aq)$

36 **a** A

b O_2 is the oxidant, which enters the 'air space' from outside.

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

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

e From the electrochemical series:

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

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

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

Since $E°(Zn^{2+}/Zn) < E°(O_2,H_2O/OH^-)$ a spontaneous cell reaction will occur.

Since $E°(Ag^+/Ag) > E°(O_2,H_2O/OH^-)$ a spontaneous cell reaction will not occur.

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

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

$E°(O_2,H_2O/OH^-) - E°(Al^{3+}/Al) = (+0.40) - (-1.71) = 2.10$ V

g With an acidic electrolyte the cathode reaction becomes:

cathode reaction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E° = +1.23$ V

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

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

Since $E°(Zn^{2+}/Zn) < E°(O_2,H^+/H_2O)$ a spontaneous cell reaction will occur.

Since $E°(Ag^+/Ag) < E°(O_2,H^+/H_2O)$ a spontaneous cell reaction will occur.

Essentially, O_2 becomes a stronger oxidant in acidic conditions, and is capable of spontaneous reaction with the relatively weak reductant, Ag.

Area of study 2 How can the yield of a chemical product be optimised?

Multiple-choice questions

1 C The recharging of a secondary cell involves reversing the spontaneous reactions that occur during discharge.

2 D The ΔH is the difference between the initial enthalpy (reactants) and the final enthalpy (products). The value is positive here because there is a net increase (endothermic).

3 B The activation energy is the difference between the initial enthalpy (on the right for the reverse reaction) and the maximum enthalpy on the curve. It is always positive.

4 D There is no consistent connection between the enthalpy changes in a reaction and the activation energy.

5 B The activation energy represents the minimum energy required for a 'fruitful' collision to occur between reactant particles. The area under the curve represents the total number of particles and the shaded area represents the number of particles with energy higher than the activation energy.

6 A Increasing the temperature raises the average speed/energy of the particles, increasing the numbers of particles with higher energies. A catalyst reduces the activation energy, lowering the energy required for fruitful collisions.

7 C A catalyst does not affect either the initial or the final states in a chemical reaction. It provides an alternative intermediate pathway with a lower activation energy threshold.

8 D For $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$ $K = 4.0 \times 10^{-4}$ M

For the equation

$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$

reversing the reaction inverts K $\Rightarrow K = \frac{1}{(4.0 \times 10^{-4})} = 2.5 \times 10^3\ \mathrm{M}^{-1}$

For the equation $2HCl(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$

halving coefficients gives square root of K $\Rightarrow K = \sqrt{2.5 \times 10^3} = 50\ \mathrm{M}^{-\frac{1}{2}}$

9 B For any chemical reaction $aA + bB + \ldots \rightarrow xX + yY + \ldots$ the equilibrium constant $K = \frac{[X]^x\,[Y]^y\ldots}{[A]^a\,[B]^b\ldots}$

10 D For this reaction $K = \frac{[Y]^2 \times [Z]^n}{[W]^2 \times [X]^2}$ and has the unit M^2. Hence $(2 + n) - (2 + 2) = 2 \Rightarrow n = 4$.

11 C In the normal course of a reaction, the concentrations of the products increase and the concentrations of the reactants decrease as the reaction approaches equilibrium. In this instance the ratio: $\frac{\text{increase in [products]}}{\text{decrease in [reactants]}} = \frac{0.4}{0.8} = \frac{1}{2}$.

12 B Lower temperatures give higher *K* values, and hence higher yields, for exothermic reactions (negative Δ*H*).

Higher pressures will drive an equilibrium towards the side with fewer particles, so higher pressures will increase the yield of NO_2 here.

13 C The reduction in volume will increase concentrations of all species and hence increase the net concentration of particles, inducing an equilibrium shift to the side with fewer particles. Hence a net back reaction occurs, reducing the amount of products NO and Cl_2. However, this loss of Cl_2 does not completely offset the increase in concentration resulting from the initial volume change, so there is a net increase in the concentration of Cl_2.

14 C The equilibrium constant gives us information only about the extent of a reaction. It tells us nothing about the activation energy and hence tells us nothing about the rate of a reaction. All we know about this reaction from the extremely high *K* value is that when equilibrium is reached the mixture will comprise almost exclusively products, but we cannot say whether this will take milliseconds or millions of years.

15 A Since these equations share a common species, $H_2CO_3(aq)$, changes that affect one will have a consequent effect on the other. Decreasing the pH means raising $[H_3O^+(aq)]$, which will induce a shift left in the second reaction. The consequent increase in $[H_2CO_3(aq)]$ will induce a shift left in the first reaction also, resulting in the loss of CO_2 from the solution.

All other changes listed will induce a shift right in the first equation and lead to more dissolved CO_2.

16 C The very small value of the equilibrium constant K_w implies a very low ratio of products to reactants so that the products will generally be in a very small minority.

17 A In an electrolytic cell, the negative terminal of the external power supply sends electrons to the cathode, causing reduction of the strongest available oxidant, in this case Ag^+.

18 A $n(\text{Ag}) = \frac{\text{m}}{\text{M}} = \frac{0.055}{107.9} = 5.1 \times 10^{-4}$ mol

$\Rightarrow n(e^-) = \frac{1}{1} \times n(\text{Ag}) = 5.1 \times 10^{-4}$ mol

$\Rightarrow Q = (5.1 \times 10^{-4}) \times 96\,500 = 49$ C

$\Rightarrow I = \frac{Q}{t} = \frac{49}{7.0 \times 60} = 0.12$ A

19 B $n(\text{metal}) = \frac{n(e^-)}{\text{charge on metal ion}}$ ⇒ amount of metal deposited will be greatest for corresponding ion with smallest charge.

20 B I: Zinc is a stronger reductant than tin and so will displace Sn^{2+} from solution.

II: Copper is a weaker reductant than tin and so will not displace Sn^{2+} from solution.

III, IV: Sn^{2+} ions will be the strongest oxidant in both cases and so will undergo reduction at the cathode.

Short-answer questions

21 **a** 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 fruitful is unchanged, the higher frequency of collisions overall will increase the frequency of fruitful collisions and hence the rate of reaction.

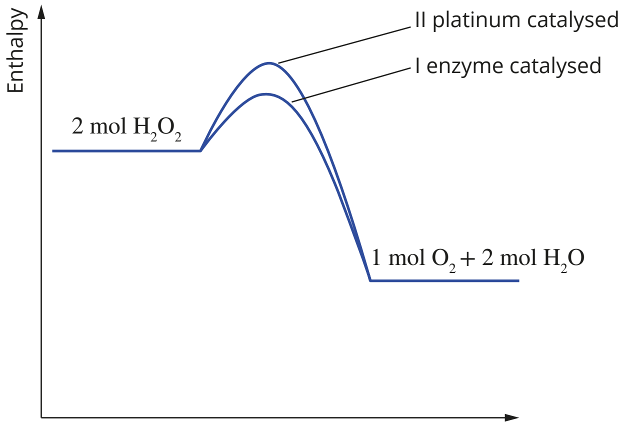
b The higher temperature means the particles in the mixture will be moving faster and hence colliding more frequently. Also, and more significantly, having faster-moving particles means there will be a higher proportion of collisions that are fruitful, since there is a greater chance of a collision having energy greater than the activation energy. These two factors combine to give a higher frequency of fruitful collisions and hence a higher rate of reaction.

c Apart from changing concentration and temperature, reaction rates can be affected by:

- changing reactant pressures for gases
- the presence of a catalyst
- changing the available surface area for reactions involving solids or for non-homogenous mixtures.

22 **a** The function is to act as a catalyst and lower the activation energy, giving a higher reaction rate.

b



c System I would be faster. The lower activation energy requirement means that there is a greater probability of any given collision having sufficient energy to meet it, so fruitful collisions will occur more frequently.

23 **a** The rates are equal up until time *T*.

b The addition of reactant W increases the frequency of collisions between left-hand side particles so the rate of the forward reaction increases initially.

Because the forward reaction is now the faster, there will be a net forward reaction. This will consume the left-hand side particles so the forward reaction will slow down, and generate right-hand side particles so the reverse reaction speeds up. When the two rates become equal again, equilibrium has been re-established and no further change occurs.

c **i** Adding Y: This accounts for the initial increase in the rate of the reverse reaction; the subsequent changes reflect the inevitable re-establishment of equilibrium.

ii Adding a catalyst: Both rates increase equally and this is the characteristic effect of a catalyst.

Note: It doesn't apply here, but another case that would produce this change is that where a gas-phase reaction is compressed (volume decreased) and there are equal number of reactant (left-hand side) and product (right-hand side) particles in the equation.

iii Adding an inert gas: This does not affect the concentrations of reactants or products and so affects neither the frequency of collisions between reacting particles, nor the probability of a collision meeting the activation energy requirement. Hence, it does not affect the rate of either reaction.

d Lowering the temperature means the particles in the mixture will be moving slower and hence colliding less frequently, and there will be a lower proportion of collisions that meet the activation energy requirement and are fruitful. Hence, there will be a lower frequency of fruitful collisions and a lower rate. This is true for both forward and reverse reactions.

e Because the forward reaction is faster (the reverse reaction has slowed to a greater extent), there will be a net forward reaction.

f Exothermic. Lowering the temperature will always induce a shift in the exothermic direction, which in this case must be the forward reaction since that is the direction of the shift.

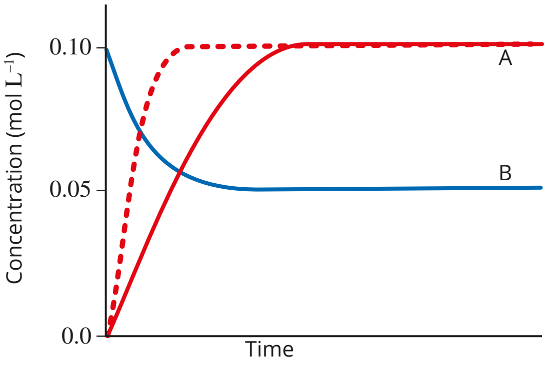
Because there is a net forward reaction, the equilibrium constant, *K*, has increased. An increase in *K* resulting from a decrease in temperature is characteristic of an exothermic reaction.

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

From the equation: $\frac{\text{change in } [N_2O_4]}{\text{change in } [NO_2]} = \frac{1}{2}$ and from the graph: $\frac{\text{change in [B]}}{\text{change in [A]}} = \frac{1}{2}$

b $K = \frac{[NO_2]^2}{[N_2O_4]}$

c Final concentration will be unchanged but reached in less time.



d $[NO_2] = 0.100\text{ M}; [N_2O_4] = 0.050\text{ M} \Rightarrow K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.100^2}{0.050} = 0.20\text{ M}$

25 **a** exothermic reaction ⇒ decrease *K*

b shift right ⇒ decrease amount of I_2O_5

c no temperature change ⇒ no change to *K*

d shift left ⇒ decrease amount of I_2

e shift right (to side with more gas particles) ⇒ increase amount of CO_2

f initial volume increase ⇒ decrease concentration of CO_2 (not offset by increased amount)

g shift left ⇒ decrease amount of CO_2

h catalyst does not affect equilibrium ⇒ no change

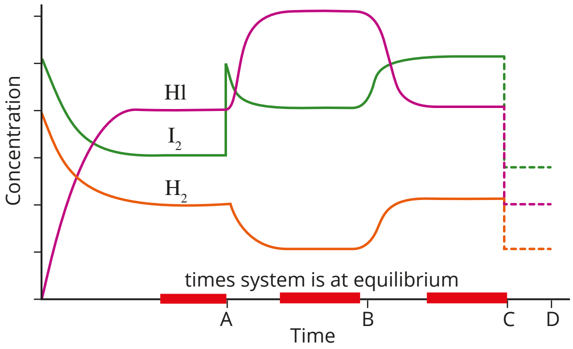
i no temperature change ⇒ no change to *K*

26 **a** Iodine (I_2) has been added, followed by a net forward reaction to re-establish equilibrium.

b The temperature has been increased, resulting in a net back reaction (because the forward reaction is exothermic).

c Equilibrium exists when the concentrations are constant (see diagram).

d Doubling the volume will halve all concentrations. Because there are equal numbers of reactant (left-hand side) and product (right-hand side) particles, the mixture remains at equilibrium and there is no shift (see diagram).



27 **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** It is a catalyst, to allow the reaction mixture to reach equilibrium more quickly.

ii The yield would be poorer. Because the reaction is exothermic, increasing the temperature would 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 **i** 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 $Hb_4.O_2$.

ii High O_2 pressure will drive the second reaction to the right. This lowers the concentration of free haemoglobin, Hb_4, which drives the first reaction to the left, removing $Hb_4.CO$.

d $CH_3OH(g) + O_2(g) \rightarrow CO(g) + 2H_2O(g)$

28 a i Positive electrode (anode): $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Negative electrode (cathode): $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

ii Brown I_2 forming at the positive electrode; bubbles forming at the negative electrode and increasing pH of electrolyte if tested with indicator

b i Positive electrode (anode): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

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

ii Bubbles forming at the positive electrode and decreasing pH of electrolyte if tested with indicator; lead solid/crystals deposited at the negative electrode

c i Positive electrode (anode): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Negative electrode (cathode): $2H_2O(l) + 2e- \rightarrow H_2(g) + 2OH^-(aq)$

ii Copper positive electrode getting smaller, and appearance of blue colour (Cu^{2+}) in the electrolyte solution; bubbles forming at the negative electrode and increasing pH of electrolyte if tested with indicator

29 a i Anode: reductant strength is $H_2O > Cl^-$, so

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

ii Cathode: oxidant strength is $Sn^{2+} > H_2O > Mg^{2+}$, so

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

b When Sn^{2+} is consumed, oxidant strength is $H_2O > Mg^{2+}$, so

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c At high concentrations of Cl^- ions, chlorine gas is usually formed as it is able to effectively compete with water to react at the anode:

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

30 a The coating will appear at the spatula. Nickel metal is produced by a reduction reaction:

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

and reduction always occurs at the cathode (negative electrode in electrolysis).

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

Negative electrode (cathode): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

c $Q = It = 2.5 \times (15 \times 60) = 2250\ \text{C}$

$\Rightarrow n(e^-) = \frac{Q}{F} = \frac{2250}{96\,500} = 0.0233\ \text{mol}$

$\Rightarrow n(Ni) = \frac{1}{2} \times n(e^-) = 0.0117\ \text{mol}$

$\Rightarrow m(Ni) = nM = 0.0177 \times 58.7 = 0.68\ \text{g}$

31 **a** $Li^+(l) + e^- \rightarrow Li(l)$

b $2Cl^-(l) \rightarrow Cl_2(l) + 2e^-$

c Water (H_2O) is a stronger oxidant than Li^+ and would be preferentially reduced at the cathode, producing hydrogen gas rather than lithium metal.

d A mixed electrolyte will have a lower melting temperature, making the process safer and less expensive. Potassium chloride is appropriate because K^+ will not be reduced in preference to Li^+.

e Like sodium, lithium is a very reactive metal. It must not be allowed to come into contact with air because it will be spontaneously re-oxidised. Also, it will react very quickly with water to produce hydrogen gas with the potential for explosion, so it must not be allowed to come in contact with water.

32 **a** Both types of cell contain a pair of electrodes (anode and cathode) and an electrolyte.

b In a galvanic cell, high-energy reactants undergo spontaneous reaction to generate electricity. The energy transformation is:

chemical energy → electrical energy.

Heat energy is also produced, reducing the efficiency of the cell.

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 → chemical energy.

Heat energy is also produced, reducing the efficiency of the cell.

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 oxidant–reductant 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 oxidant–reductant 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.

33 **a** **i** For example, sodium (and other group 1 metals), magnesium, aluminium

ii For example, NaOH, H_2, Cl_2

b The following is an example of the answers for aluminium.

i $C(s) + 2O^{2-}(l) \rightarrow CO_2(g) + 4e^-$

ii $Al^{3+}(l) + 2e^- \rightarrow Al(l)$

iii For example, molten cryolite (Na_3AlF_6) is used as a solvent; graphite electrodes are used; anodes are consumed as cell operates; molten aluminium collects beneath the electrolyte

The following is an example of the answers for NaOH.

i $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

ii $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

iii For example, high NaCl(aq) concentration are used so $Cl^-(aq)$ oxidised at anode; semipermeable membrane prevents mixing of Cl^- and OH^- ions in electrolyte while still allowing Na^+ ions to migrate

c Water can itself act either as an oxidant or a reductant. Electrolysis from an aqueous solution is only possible when the desired reaction involves a stronger oxidant or reductant than water, otherwise water will react preferentially. In that case, the desired reaction can only be achieved in the absence of water, either in an alternative solvent or in a molten electrolyte.

d Graphite is a good electrical conductor, relatively inexpensive, relatively inert and has a high melting temperature.

e Metallic cathodes are always inert as the electrolytic process ensures only reduction can occur at their surface. However, the iron in a steel anode would likely be a better reductant than the target species so that the outcome would be the oxidation, and hence the consumption, of the electrode itself rather than the desired electrode reaction.

34 a Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

b Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Cathode: $Na^+(l) + e^- \rightarrow Na(l)$

35 a (+) electrode: $2Ni(OH)_2(s) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2NiOOH(s) + 2e^-$

(−) electrode: $Zn(OH)_2(s) + 2e^- \rightarrow 2OH^-(aq) + Zn(s)$

b As in all forms of electrolysis, an external power source is used to drive a current through the cell to force non-spontaneous reactions to occur. In a secondary cell, the non-spontaneous reactions are the reverse of the spontaneous reactions that occur during discharge.

c For recharging to be possible, the discharge products must remain in electrical contact with the electrodes. Any discharge products that migrate away from the electrode will not be available to participate in the reaction reversal during recharging, so that less reactant will be available on the next discharge cycle.

d Likely explanations include the following.

- Discharge products are more soluble and mobile at higher temperatures, and hence more readily migrate away from the electrodes.
- At higher temperatures, side-reactions are more likely to occur, reducing the amount of active material.

e Apart from the two points mentioned in part **d**, the following are other possibilities.

- Some of the discharge products become coarse and resist current flow.
- Impurities may be present in electrodes or half-cell chemicals.
- Build-up of products may reduce contact between the electrolyte and the electrodes.
- Mechanical vibration can dislodge reactive materials from the electrodes over time.

Unit 4 **Area of Study 1 Review**

Multiple-choice questions

1 D Higher flashpoint reflects lower volatility due to stronger intermolecular bonding, which in turn implies the likelihood of higher viscosity. At room temperature each is below its flash point, which represents the minimum temperature required for ignition.

2 D There are no C—C or Si—Si bonds in TMS, and C—H bonds are relatively strong.

3 A The C—C bond energy (348 kJ mol^{-1}) is higher than that for C—Si bonds, implying that C—C bonds are stronger. Hence, more energy will be required to break the C—C bonds in diamond than the C—Si bonds in silicon carbide.

4 C Ethene is the smallest alkene; there is no such thing as 'methene'.

5 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) substituent is attached at carbon 2.

6 D Non-polar alkanes have only weak dispersion forces, which are weaker for smaller alkanes as the presence of functional groups such as —Cl and —OH introduce some additional dipole–dipole attractions. Smaller alkanes have weaker dispersion forces, and hence lower boiling points, than larger ones.

7 C Hydroxyl groups are not significantly acidic or basic.

8 A CH_2CH_2 (ethene) is unsaturated and undergoes an addition reaction with bromine, where one Br atom adds to each side of the double bond.

9 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*.

10 C Acidified dichromate ($Cr_2O_7^{2-}/H^+$) is an oxidant typically used to convert a primary alcohol into a carboxylic acid. Heating ensures that conditions are forcing enough to ensure that the intermediate aldehyde, ethanal, is completely oxidised.

11 D The '-oate' component of an ester derives from the carboxylic acid used, so this ester derives from ethanoic acid. The '-yl' component derives from the alcohol used, which must be methanol.

12 C IV is the only structure where the hydroxy group is not highest ranked, because of the carboxy group.

13 D The fingerprint region of the IR spectrum is typically unique to a particular compound. Small differences between structural isomers affect the energies of bond vibration.

14 C The base peak in a mass spectrum corresponds to the strongest signal, and therefore arises from the most commonly detected fragment. The peak corresponding to the unfragmented molecule is called the molecular ion (or parent ion) peak.

15 C More surface area means more frequent adsorption–desorption and leads to better separation.

16 A The retention time results from the interactions of individual component molecules with the stationary and mobile phases. It depends on the nature of the particles, not on how many of them there are.

17 A Peak height can give a reasonable estimate provided the peaks are very sharp, but peak area is the true measure of quantity.

18 C All H atoms are in an oxidation state of +1 throughout.

19 B Generally, smaller atoms bond more strongly and require higher frequency/energy for vibration. Multiple bonds are stronger than single bonds and likewise require higher frequency/energy.

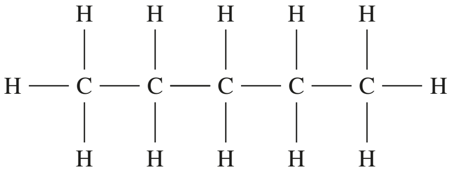
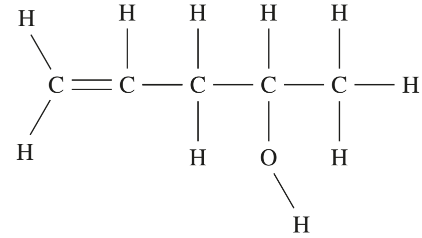
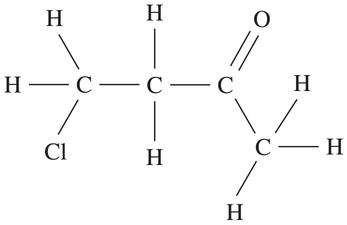
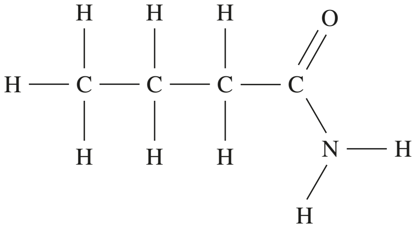
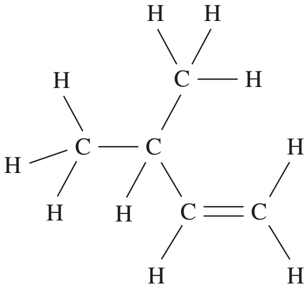
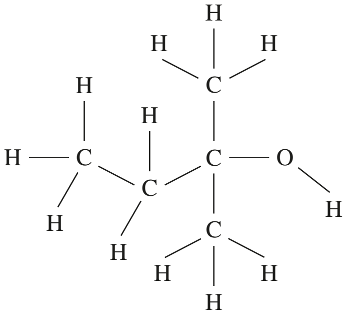
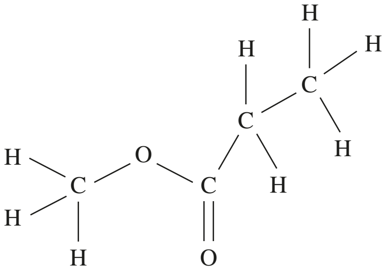
20 A The expected peaks are two hydrogen environments and three carbon environments.

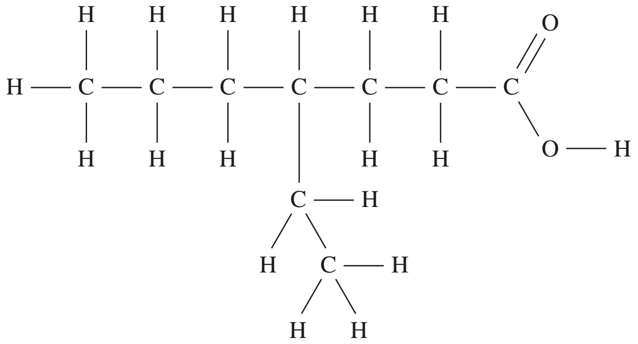
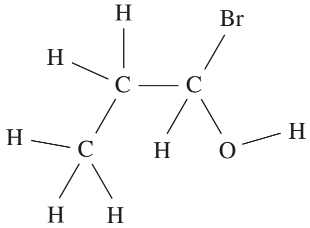
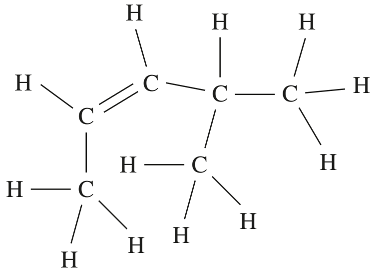
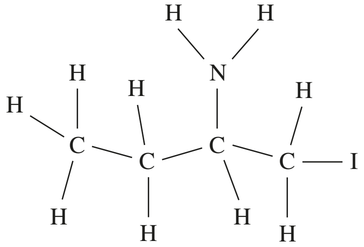
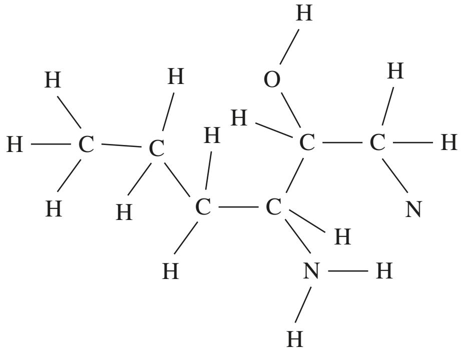
Short-answer questions

21	**a**	**i**	C_7H_{16}	**ii**	e.g. $CH_3CH_2CH_2CH(CH_3)CH_2CH_3$
	b	**i**	$C_4H_{10}O$	**ii**	e.g. $CH_3CH_2CHOHCH_3$
	c	**i**	$C_3H_6O_2$	**ii**	e.g. CH_3CH_2COOH
	d	**i**	$C_5H_{11}OCl$	**ii**	e.g. $CH_2Cl(CH_2)_4OH$
	e	**i**	C_8H_{16}	**ii**	e.g. $CH_3CH_2CHCHCH_2CH(CH_3)_2$
	f	**i**	$C_6H_{12}O$	**ii**	e.g. $CH_3CH_2CH(CH_3)CH_2CHO$
	g	**i**	C_8H_{12}	**ii**	e.g. $CH_3CCCH_2CH_2CHCHCH_3$
	h	**i**	$C_6H_{12}O$	**ii**	e.g. $CH_3CHCHC(OH)(CH_3)CH_3$
	i	**i**	$C_4H_7NO_2$	**ii**	e.g. $CH_3COCH_2CONH_2$

22 **a** Heptan-3-ol, 1 chiral centre
b 3-Fluorobutanoic acid, 1 chiral centre
c *trans*-Pent-2-ene, no chiral centres
d 4-Ethylhexan-3-amine, 1 chiral centre
e 1-Aminopropan-2-ol, 1 chiral centre
f 5-Chlorohexan-3-ol, 2 chiral centres
g 6-Hydroxyoctanoic acid, 1 chiral centre
h 2-Bromo-3-methylpentane, 2 chiral centres
i Methyl butanoate, no chiral centres

23

a	
b	
c	
d	
e	
f	
g	

h	
i	
j	
k	
l	

24 **a** Acidified dichromate ($Cr_2O_7^{2-}/H^+$) or acidified permanganate (MnO_4^-/H^+)

b Warm with hydroxide (eg KOH, NaOH), or H_2O/catalyst

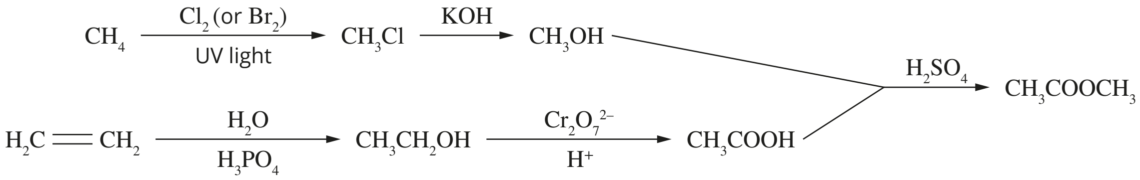
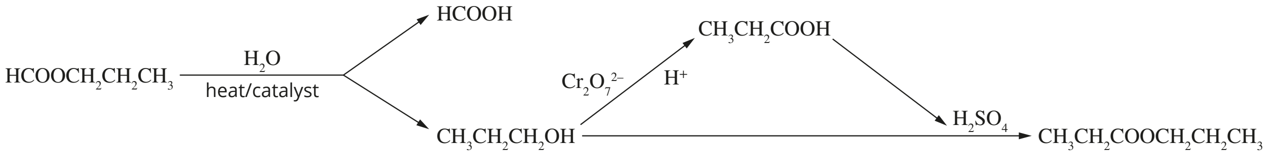
c H_2O and acid catalyst (eg H_3PO_4)

d Acidified dichromate ($Cr_2O_7^{2-}/H^+$) or acidified permanganate (MnO_4^-/H^+)

e H_2 and Ni catalyst (other metals sometimes used)

f NH_3

25

a	$CH_3CH_2CH_3 \xrightarrow[\text{UV light}]{Cl_2\text{ (or }Br_2)} CH_3CH_2CH_2Cl \xrightarrow{KOH} CH_3CH_2CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3CH_2COOH$
b	
c	

26 **a** $CH_3CH_2COOH + NaHCO_3 \rightarrow CH_3CH_2COONa + CO_2 + H_2O$

b $CH_3CH_2CH_2OH + H_2O \rightarrow CH_3CH_2COOH + 4H^+ + 4e^-$

c $CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$

d $CH_3CH_2COOH + CH_3CH_2NH_2 \rightarrow CH_3CH_2COO^- + CH_3CH_2NH_3^+$

e $2CH_3CH_2COOH + 7O_2 \rightarrow 6CO_2 + 6H_2O$

27 **a** Viscosity is a measure of the resistance to flow. Low viscosity liquids are 'runnier'.

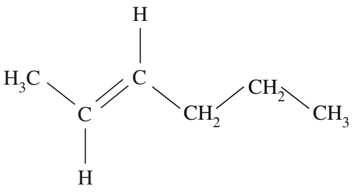
b **i** Viscosity increases from methanol to ethanol to propan-1-ol because larger molecules have stronger dispersion forces between them, tending to restrict movement.

ii Water solubility decreases from butan-1-ol to hexan-1-ol because additional $—CH_2—$ groups reduce the polarity of the molecules, increasing the effect of the hydrophobic part that cannot form hydrogen bonds to water molecules.

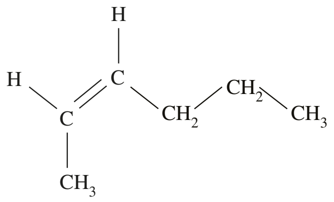
iii Ethane-1,2-diol has one more hydroxyl group than ethanol. The additional hydrogen bonding that this allows accounts for the higher viscosity and boiling point of ethane-1,2-diol.

iv Benzene has a comparable molecular mass to butan-1-ol but is non-polar and can only form relatively weak intermolecular dispersion forces. Weak bonding between benzene molecules results in low viscosity, and the inability to form strong bonds to water molecules results in relatively low water solubility. A comparison of propanone and propan-1-ol also illustrates the point.

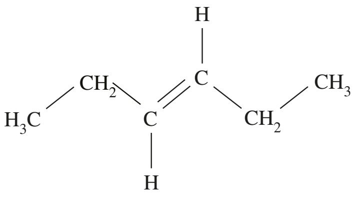
28



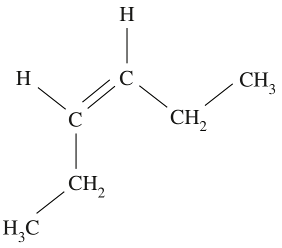
trans-hex-2-ene



cis-hex-2-ene



trans-hex-3-ene



cis-hex-3-ene

29 **a** Radiowaves (radio frequencies)

b The changes associated with this are nuclear magnetic dipoles switching between low and high energy states corresponding to alignment with the external magnetic field.

c It is used as an internal standard for determination of chemical shifts.

d **i** B. High chemical shift is characteristic of an aldehyde and the quartet results from three adjacent H atoms.

ii D. Singlet suggests no neighbouring H atoms. Chemical shift is consistent with an adjacent C═O group.

iii E. Quartet shows three neighbouring H atoms. Moderately high chemical shift is consistent with an adjacent O atom.

iv C. Singlet because all H atoms in the molecule are equivalent so no splitting is observed. Chemical shift is consistent with an adjacent halogen (Cl) atom.

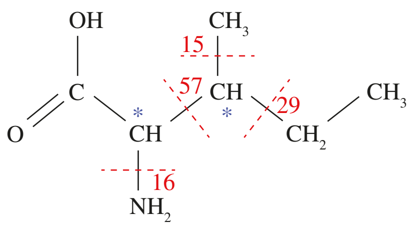
v F. Triplet shows two neighbouring H atoms and low chemical shift is consistent with no adjacent heteroatoms.

vi A. Doublet shows one neighbouring H atom and chemical shift is consistent with an adjacent C═O group.

30 **a** $C_6H_{13}NO_2$

b 131

c



d **i** CH_3^+

ii $C_2H_5^+$

iii $C_4H_9^+$

e **i** The base peak is the strongest signal in the mass spectrum, that is, the most abundant fragment ion.

ii 131 − 86 = 45 mass units lost. This is most likely to be CO_2H.

31 **a** $M(CHCl_3) = 119.4\ g\ mol^{-1}$ $M(CH_4) = 16.0\ g\ mol^{-1}$ $M(Cl_2) = 70.9\ g\ mol^{-1}$

$$\text{Atom economy} = \frac{\text{molar mass of product}}{\text{total molar mass of reactants}} \times 100 = \frac{119.4}{16.0 + 3 \times 70.9} \times 100 = 52.2\%$$

b $n(CH_4) = \frac{m}{M} = \frac{1000}{16.0} = 62.5\ mol$

$n_{max}(CHCl_3) = n(CH_4) = 62.5$ mol; this is the maximum yield

$m_{max}(CHCl_3) = nM = 62.5 \times 119.4 = 7.46 \times 10^3\ g = 7.46\ kg$

$m_{yield}(CHCl_3) = \frac{75}{100} \times 7.46\ kg = 5.60\ kg$

c Sodium hydroxide and sodium ethanoate

d $M(CHCl_3) = 119.4\ g\ mol^{-1}$ $M(CH_3COCH_3) = 58.1\ g\ mol^{-1}$ $M(NaOCl) = 74.4\ g\ mol^{-1}$

$$\text{Atom economy} = \frac{\text{molar mass of product}}{\text{total molar mass of reactants}} \times 100 = \frac{119.4}{58.1 + 3 \times 74.4} \times 100 = 42.4\%$$; slightly lower

e Addition reactions of alkenes have an atom economy of 100%, since in addition reactions the atoms of a small molecule add across a C═C double bond and there are no other products formed.

32 **a** Spectrum A: ~3000 cm^{-1} is C—H, ~1700 cm^{-1} is C═O

Spectrum B: ~3000 cm^{-1} is C—H, ~3400 cm^{-1} is O—H

b Spectrum A is propanone; spectrum B is propan-2-ol.

c Because of the symmetry of the molecule, all six hydrogens are in the same bonding environment and are 'equivalent'.

d Again, because of the symmetry of the molecule the two terminal carbon atoms are in identical environments and hence absorb and emit the same frequency.

e ^1H NMR: three peaks as there are three different H environments ($—C\underline{H}_3$, $—C\underline{H}(OH)—$ and $—CH(O\underline{H})—$)

^{13}C NMR: two peaks as there are two different C environments ($—\underline{C}H_3$, $—\underline{C}H(OH)—$)

f **i** 58

ii It provides the molecular mass from which the molecular formula can be deduced.

iii $[CH_3CO]^+$

33 **a** Taurine, glycine

b Viewing under UV light or applying a stain

c $R_f = \frac{\text{distance travelled by spot}}{\text{distance travelled by solvent}} = \frac{6}{50} = 0.12$

d Taurine is bonded least strongly. Strong interactions with the mobile phase will favour desorption and result in higher R_f values since molecules will spend less time adsorbed to the stationary phase. Taurine has the lowest R_f value and so does not desorb readily into the mobile phase.

34 **a** Sorbic acid adsorbs most strongly. Its longer retention time indicates that it spends a relatively long time adsorbed onto the stationary phase.

b Only benzoic acid, for which there is a peak in the sample spectrum with the same retention time. There are no peaks in the sample with retention times corresponding to the other two.

c 4.74 mg/100 mL

d Mass of preservative in 10.0 mL solution = $\frac{4.74}{100} \times 10.0 = 0.474$ mg

Concentration of preservative in sauce = $\frac{0.474}{1.50} \times 100 = 31.6$ mg/100 g

35 $n(NaOH) = cV = 0.350 \times 0.017\,48 = 0.006\,12$ mol

$n(C_8H_6O_4) = \frac{1}{2} \times n(NaOH) = 0.003\,06$ mol in 10 mL aliquots

$n_{total}(C_8H_6O_4) = \frac{100}{10} \times 0.003\,06 = 0.0306$ mol in original sample.

$m(C_8H_6O_4) = nM = 0.0306 \times 166.1 = 5.08$ g

Percentage = $\frac{0.508}{5.26} \times 100 = 96.6\%$

Unit 4 **Area of Study 2 Review**

Multiple-choice questions

1 B Two amino acids are required to form a dipeptide.

2 A VI is glycerol; V and VIII are fatty acids but only VIII is saturated ($C_nH_{2n+1}COOH$).

3 B A glycosidic link forms from two hydroxyl groups.

4 B A saturated fatty acid has the formula $C_nH_{2n+1}COOH$, or $C_xH_{2x}O_2$; in this case $C_{18}H_{36}O_2$ would be the formula of the saturated fatty acid. Each double bond reduces the number of hydrogen atoms by two; hence $C_{18}H_{34}O_2$ must possess one double bond.

5 A The reaction involves formation of peptide links between the carboxy group of one amino acid and the amino group of another.

6 A The bond between C═O and N—H groups on nearby, regularly spaced peptide links causes the helical shape.

7 A Acid disrupts the weaker bonding maintaining secondary and tertiary structure of the protein. Harsher conditions result in the acid hydrolysis of the peptide links, destroying the primary structure.

8 C Aerobic respiration requires oxygen and results in complete oxidation of the glucose to produce carbon dioxide (and water), releasing the maximum available energy. Aerobic respiration does not require oxygen; instead the glucose is partially decomposed to release a small portion of its available energy.

9 B $(165 + 131 + 149) - (2 \times 18) = 409$. Two water molecules are formed as by-products of the condensation.

10 B $3x + 92(\text{glycerol}) = 878 + 54$. Three water molecules are incorporated in the hydrolysis step.

11 D Links between monosaccharides result from condensation of hydroxyl (—OH) groups. This results in a type of ether linkage (—O—), which when it occurs between carbohydrate units is called a glycosidic link.

12 B All are composed of glucose. Differences are in the stereochemistry of C-1 (α- in starch and glycogen, β- in cellulose) and the chain size and extent of branching.

13 A Essential nutrients (fatty acids or amino acids) are those that must be obtained from external sources in the diet because the body is unable to synthesise them biochemically.

14 A Antioxidants act as ‘sacrificial reductants’, intercepting and reacting with oxidising agents.

15 B High GI foods are digested quickly, leading to a more rapid and early increase in blood sugar; typically, this means higher levels of amylopectin which is more quickly digested than amylose.

16 B Carbohydrates (mainly glucose) provide the bulk of the body's day-to-day energy needs. Fats store more energy per gram and so are ideal for longer term energy storage. The energy content of fats is higher as their oxygen content is lower; this makes them ideal for longer term energy storage but not for rapid turnover. Carbohydrates, with more oxygen, are already partially oxidised so their further oxidation yields less energy, but glucose respiration is the fundamental source of energy for the body.

17 A Vitamins do not contribute directly to the energy value of food but need to be present in small amounts for the normal progress of a variety of essential processes (such as the normal function of many enzymes). Because they cannot be synthesised in the body (except for vitamin D) they must be obtained in the diet.

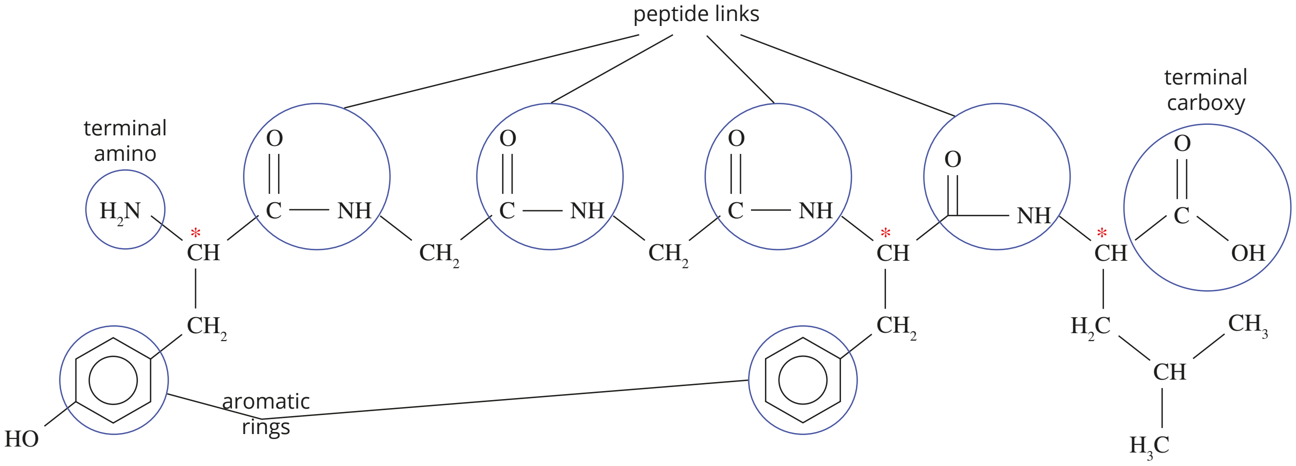
18 C Artificial sweeteners work because their shape and the spatial arrangement of certain key atom groups allows them to interact with taste receptors in the same way that sugar molecules naturally do.

19 C The only benefit of artificial sweeteners is that their higher sweetness means that less needs to be used (compared to natural sugars).

20 A Energy released = $(\frac{0.0015}{2} \times 3120) = 2.34\ \text{kJ} = 2340\ \text{J}$; calibration constant = $\frac{2340}{\Delta T} = \frac{2340}{2.0}$

Short-answer questions

21 a, c, d See diagram.



b Tyrosine, glycine (× 2), phenylalanine

22 a i A, C

i B

ii D

b All of them

c Energy

d Starch in food undergoes hydrolysis (A) during digestion to form glucose, which is absorbed into the bloodstream. Some glucose is used to derive energy in cellular respiration (D). Some excess glucose undergoes condensation (B) to form glycogen for temporary storage, which is later hydrolysed (C) to release its stored glucose when needed.

e Humans lack the enzyme necessary for hydrolysis of cellulose to glucose (cellulase), so cellulose passes though the digestive tract mostly unreacted. The different spatial orientation of atoms on the glycosidic links in cellulose compared to starch means that no strong interaction can form between the active site of amylase (the enzyme that catalyses starch hydrolysis) and cellulose.

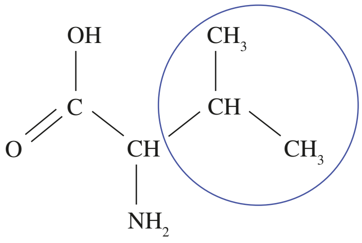
f i Fatty acids (and glycerol)

ii Amino acids

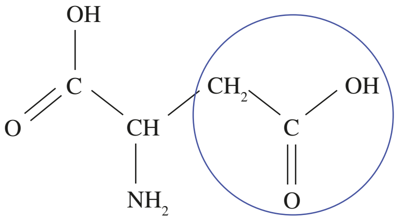
23 a Essential amino acids cannot be synthesised in the body and must therefore be obtained from the diet.

b Histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine

c, d

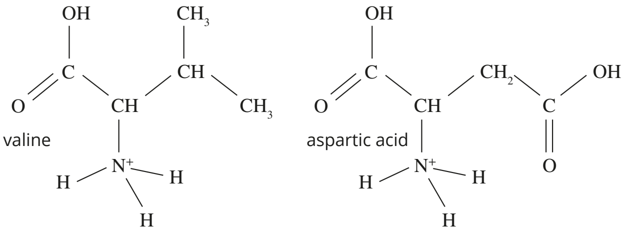


valine

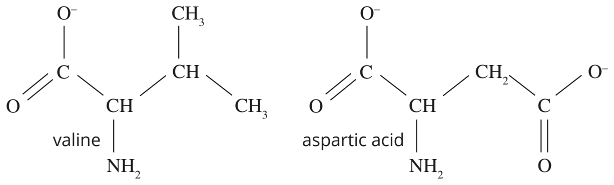


aspartic acid

e At low pH (acidic) the amino group becomes protonated and hence positively charged. At high pH (basic) the acidic carboxyl groups become deprotonated and gain a negative charge. Aspartic acid possesses two carboxyl groups, and at sufficiently high pH both can become deprotonated.

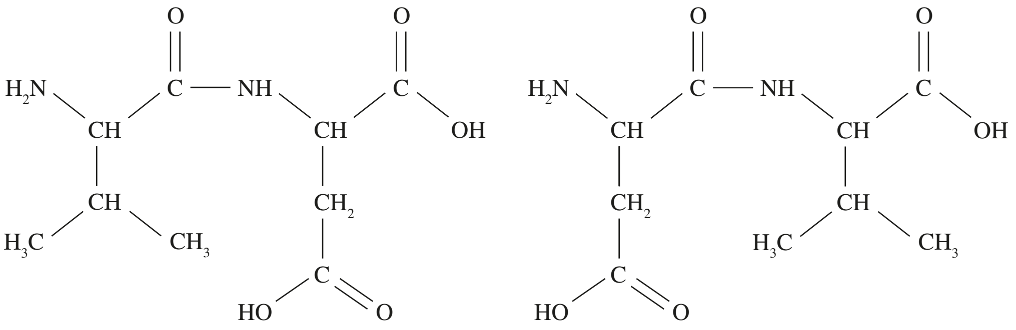


at low pH



at high pH

f



24 a The primary structure of a protein relates to the formation of peptide linkages between the amino acids as they are linked together in a specific sequence; 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.

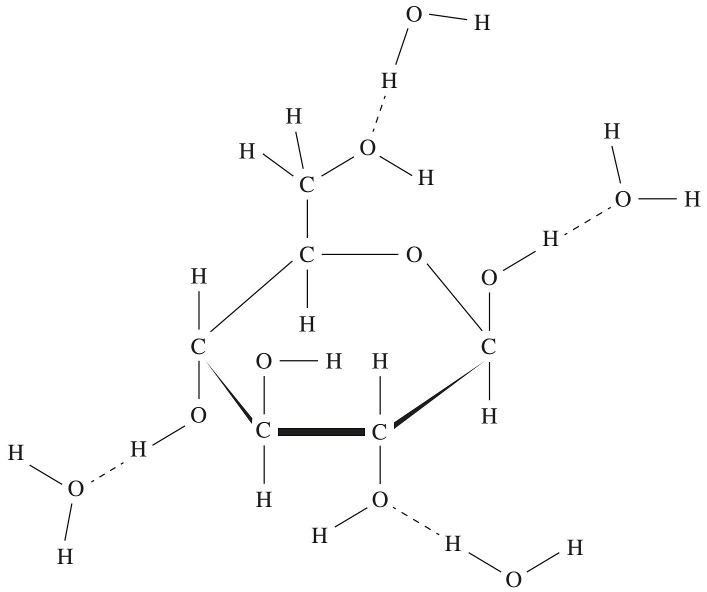
b These are features of the secondary structure of proteins, maintained by hydrogen bonding between the regularly spaced peptide linkages along the backbone of all protein chains.

c The secondary and tertiary structures of proteins are largely maintained by non-covalent bonding interactions such as hydrogen bonding, ion–ion/ion–dipole attractions, and dispersion forces, which are generally weaker than the covalent bonding in the peptide linkages maintaining the primary structure.

d 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.

e Even before the disruption to bonding becomes sufficient to permanently denature an enzyme, changes that affect the functional groups at the active site can significantly interfere with the substrate interactions and reduce activity.

25 a, b See diagram. Other bonding locations are possible. H atoms on water molecules can bond to any of the six oxygen atoms in glucose. O atoms on water molecules will only bond to the hydroxyl (−OH) hydrogen atoms in glucose.



26 a $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H = -2.83\ \text{MJ mol}^{-1} = -2.83 \times 10^3\ \text{KJ mol}^{-1}$

b $M(C_6H_{12}O_6) = 180\ \text{g mol}^{-1}$

$n(C_6H_{12}O_6) = \frac{m}{M} = \frac{10.0}{180} = 0.0556\ \text{mol}$

Energy = 0.0556 × 2.83 = 0.157 MJ = 157 kJ

c $n(O_2)\ \frac{0.500}{2.83} \times 6 = 1.06\ \text{mol}$

$V(O_2)\ nV_m = 1.06 \times 24.8 = 26.3\ \text{L}$

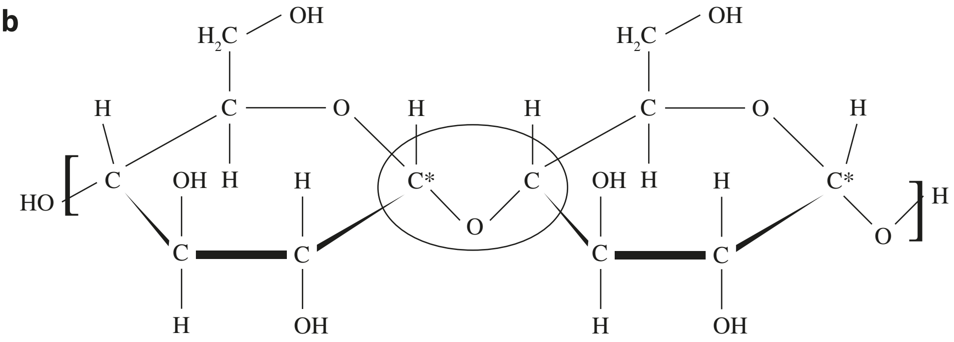
27 a Disaccharides

b Yes, both have the molecular formula $C_{12}H_{22}O_{11}$ but clearly have different structures.

c Glucose and fructose

d Some humans lose the ability to produce lactase and so are unable to digest/hydrolyse lactose, which results in irritation in the gut, among other symptoms.

28 a, b



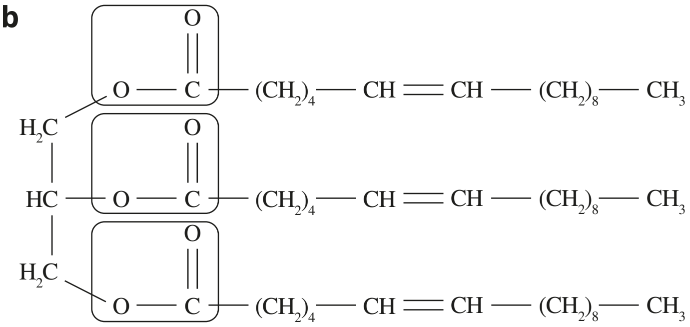
c The hydrolysis of starch (amylose) is catalysed by the enzyme amylase, whose active site is specific for binding to the amylose structure. Altering the stereochemistry on even one atom, as in the case of cellulose, changes the spatial configuration of key atoms and groups and prevents binding to the enzyme's active site.

d Normal chain formation involves formation of glycosidic links at carbons 1 and 4 as shown in the diagram. Branching results when glycosidic links form via hydroxyl groups at other centres on the glucose molecule.

e Starch is the primary form of storage of excess glucose in plants, while glycogen performs a similar function in animals. Cellulose is a structural material produced by plants for making cell walls.

29 I	**a**	$C_{22}H_{40}O_2$; $C_{21}H_{39}COOH$	**b**	Polyunsaturated	**c**	Omega-6
II	**a**	$C_{18}H_{28}O_2$; $C_{17}H_{27}COOH$	**b**	Polyunsaturated	**c**	Omega-3
III	**a**	$C_{20}H_{42}O_2$; $C_{19}H_{39}COOH$	**b**	Saturated	**c**	Neither
IV	**a**	$C_{16}H_{30}O_2$; $C_{15}H_{29}COOH$	**b**	Monounsaturated	**c**	Neither

30 a, b



c Fatty acid III. The double bonds in unsaturated fats cause kinks in the hydrocarbon 'tails' that tend to prevent them from packing tightly and forming strong intermolecular attractions. Saturated fats tend to have higher melting temperatures.

d Fatty acid III. The double bonds in unsaturated fats are reactive and susceptible to attack by oxidants such as oxygen.

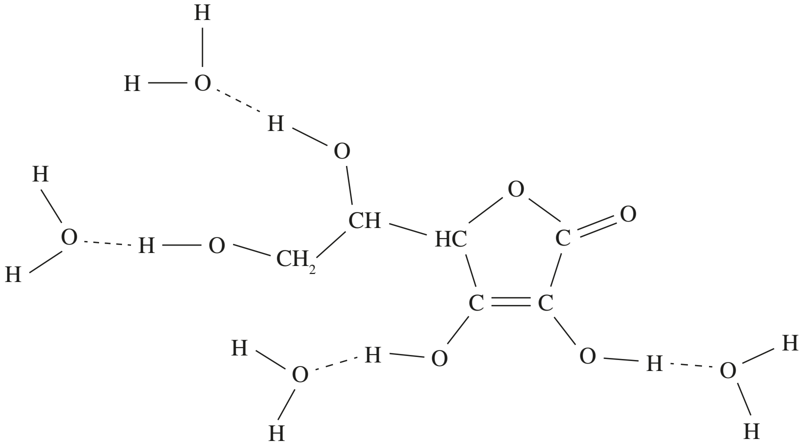
31 **a** $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

b $C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2C_6O_{12}O_6(aq)$

c $3C_{11}H_{23}COOH(l) + C_3H_8O_3(aq) \rightarrow C_{39}H_{74}O_6(l) + 3H_2O(l)$

d $C_{11}H_{23}COOH(l) + 17O_2(g) \rightarrow 12CO_2(g) + 12H_2O(l)$

32 **a** Water molecules should only be bonded to hydroxyl (−OH) hydrogens.



b Vitamin C has several polar hydroxyl groups that allow it to form strong hydrogen bonds to water molecules. Vitamins A and D lack these and are non-polar, allowing them to dissolve only in non-polar solvents such as oils.

33 **a** Coenzyme (or cofactor)

b The ‘active site’ of an enzyme is the region on its surface responsible for its catalytic activity. This region has the ability to bind to a specific molecule, or part of a molecule. This molecule is called the ‘substrate’ and binding to the active site of the enzyme alters the substrate in a way that lowers the activation energy of a reaction in which the substrate participates.

c Like all catalysts, enzymes increase the rate of reaction but are unchanged after the reaction is complete, so that a single enzyme molecule can catalyse a reaction many times over. A reactant is changed and consumed in the course of a reaction.

d In the lock-and-key model the active site has a fixed shape that only the substrate, or a close mimic, can fit into and bind. The induced fit model holds that the enzyme and the substrate are altered by the binding process, with the enzyme’s active site undergoing some deformation that helps maximise the bonding interaction.

e Coenzymes usually attach to the active site of the enzyme (or sometimes the substrate) and are necessary for the ‘fit’ between substrate and active site that allows effective binding to occur.

34 a 70 s

b Exothermic (temperature increases)

c The temperature decreases due to loss of heat to the surroundings. Better insulation for the calorimeter would reduce this loss.

d ~21.7 – 16.0 = 5.7°C

e Energy released = 5.7 × 486 = 2.77×10^3 J = 2.77 kJ

$n(\text{Zn}) = \frac{0.833}{65.4} = 0.0127$ mol

Heat released per mole of Zn = $\frac{2.77}{0.0127}$ = 218 kJ

Hence $\Delta H = -218$ kJ mol^{-1}

35 a $E = VIt = 5.00 \times 3.00 \times 120 = 1800$ J

Calorimeter constant = $\frac{1800}{1.85}$ = 973 J $°\text{C}^{-1}$

b $E = 973 \times 2.68 = 2.61 \times 10^3$ J = 2.61 kJ

Energy content = $\frac{2.61}{0.220}$ = 11.9 kJ g^{-1}

c Generally, the energy measured by calorimetry is higher because the food is completely combusted, whereas in human metabolism some parts of the food are not completely digested or converted into products that can be completely oxidised for energy.

Chapter 1 Fuels

Section 1.1 Types of fuels

1.1 Key questions

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

2 Renewable: bioethanol, biogas, biodiesel. Non-renewable: coal, oil, LPG, natural gas, coal seam gas.

3 Coal has the longest expected lifespan based on reserves and current rates of use. Carbon dioxide emission issues may reduce long-term dependence on coal.

4 **a** The rate of global energy use is more than can be supplied by wood. Wood has a relatively low energy density and is unsuitable for many portable/transport applications.

b Using a non-renewable energy source cannot be sustained indefinitely but moderate and careful use now can increase the likelihood that it will meet the needs of future generations.

5 Crude oil consists of a range of hydrocarbons with different boiling temperatures. The use to which a fraction is put is influenced by its boiling temperature and so fractional distillation is needed to separate them.

Section 1.2 Fossil fuels and biofuels

1.2 Key questions

1 Coal is excavated, crushed and dried. Coal is added to a furnace. Energy released from coal is transferred to water. Steam is produced. Steam turns a turbine. Electricity is generated.

2 **a** Advantage
b Disadvantage
c Advantage
d Advantage
e Disadvantage

3

Source	**Composition of source**	**Extraction process**
Crude oil	Mixture of alkanes	Fractional distillation
Coal seam gas	Gas adsorbed on solid	Fracking
Sewage	Organic matter	Anaerobic digester
Gas well	Mainly small alkanes	Drilling

4 **a** Energy will be absorbed by the evaporation of the water. The energy content per gram will be less than that for coal with a lower water content.

b Removal of some water by drying and/or crushing

c Use of off-peak (e.g. night time) electricity to dry the coal would reduce the cost.

d Potential atmospheric pollution from oxides of sulfur require either pre-treatment and/or post-treatment to remove or reduce sulfur from the brown coal and post-treatment to remove or reduce it from exhaust gases.

Section 1.3 Petrodiesel and biodiesel

1.3 Key questions

1 D. Petrodiesel is about 75% alkanes and 25% aromatic compounds. Most molecules contain 10–15 carbon atoms.

2 Transesterification

3 **a** True
  b True
  c False
  d True
  e False
  f True

4 Some CO_2 is consumed in the production of the triglycerides that biodiesel is made from.

CHAPTER 1 REVIEW

TYPES OF FUELS

1 Apart from the difficulties in daily travel, lack of crude oil and natural gas will make transport of manufactured goods difficult and costly. It will also stop the production of all the products that are derived from crude oil—plastics, synthetic fibres, dyes, paints, solvents, detergents and pharmaceuticals.

2 **a** Coal
  b Coal, oil, natural gas, nuclear energy, hydraulic power, new technologies, hydroelectricity

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

4 **a** Black coal
  b Peat
  c Black coal

5 **a** Methane and carbon dioxide
  b The composition of biogas depends on the original material from which it is sourced and the method of decomposition.

6 Soybean, canola and palm oil

7 When coal is burnt, energy is used to vaporise this water, reducing the amount of heat released.

FOSSIL FUELS AND BIOFUELS

8 Natural gas. Australia has a large supply of natural gas, but globally other fuel resources will last longer based on current patterns of usage.

9 The term ‘energy efficiency’ is used to describe the percentage of energy from a source that is converted to the form of energy desired.

10 Heat losses to the surroundings, friction, release of light and sound.

11 **a** Petrol, bioethanol, biogas
  b B

12 Photosynthesis uses six molecules of carbon dioxide to produce one molecule of glucose:

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

Fermentation of glucose produces ethanol and two molecules of CO_2:

$C_6H_{12}O_6(aq) \rightarrow 2CO_2(g) + 2CH_3CH_2OH(aq)$

Combustion of ethanol releases heat and four molecules of CO_2:

$2CH_3CH_2OH(l) + 3O_2(g) \rightarrow 3H_2O(g) + 2CO_2(g)$

Therefore, all of the carbon dioxide released into the atmosphere by the fermentation and combustion of ethanol has been taken in by plants in the process of photosynthesis.

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

14 **a** E10 petrol is a mixture of 10% ethanol and 90% conventional petrol.

b Use of E10 petrol will extend the availability of petrol as a fuel and will allow more of the larger fractions from crude oil to be used as a feedstock for other uses rather than being burnt as a fuel.

15 All of the points are inter-related. Many other valid responses are possible.

a Polar ice caps are shrinking, causing sea levels to rise worldwide. Local effects on the wildlife adapted to polar conditions. Melting ice adds cold, fresh water to the ocean with the possibility of altering the major ocean currents, resulting in climate changes, e.g. to Western Europe.

b Changed weather patterns causing droughts, floods, hurricanes and resulting in changed growth patterns in plants that might lead to both plant and animal extinctions.

c The changed weather patterns can result in crops failing, affecting the economy and driving some people to starvation.

d Some plants and animals that are dependent on particular weather conditions for propagation or for key parts of their life cycle may become extinct.

PETRODIESEL AND BIODIESEL

16 C. The general formula of an alkane is C_nH_{2n+2}. $C_{11}H_{24}$ can be identified as an alkane from its formula. It has 11 carbon atoms in the molecule, placing it in the diesel fraction.

17 Advantages = a, b, c, e, f, g; disadvantages = d, h

18 **a** Biodiesel

b Petrodiesel

c Biodiesel

d Biodiesel

Biodiesel has stronger intermolecular forces due to the presence of dipoles within biodiesel molecules. This leads to the cold flow issues and the higher absorption of water. Its shelf life is also shorter due to its higher biodegradability than petrodiesel.

CONNECTING THE MAIN IDEAS

19 **a** Biochemical fuels are derived from renewable resources such as plants. Ethene, the feedstock used for the industrial production of ethanol, is derived from the distillation and cracking of crude oil, a non-renewable resource.

b Ethanol can be produced from the fermentation of sugar by yeasts. Sugar may be derived from sugar cane or by the hydrolysis of starch from grains such as maize.

20 Individual student response required.

21 **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 Biofuels could potentially be carbon neutral—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 2 Energy from fuels

Section 2.1 Exothermic and endothermic reactions

2.1 Key questions

1 D. Combustion reactions result in a production of heat; therefore, energy is lost to the surroundings and the reaction is exothermic.

2 **a** 180 kJ
  b 1.5×10^3 kJ
  c 0.0100 kJ or 1.00×10^{-2} kJ
  d 2.0×10^{-6} kJ

3 In chemistry, the system is usually the chemical reaction, whereas the surroundings refer to everything else; for example, the beaker or test tube in which the reaction takes place.

4 In any reaction, the total amount of chemical energy of the reactants is made up of the bonds between atoms within the reactants. If the total amount of chemical energy within the reactants is less than the total amount of chemical energy within the products, energy must be supplied to the system, the reaction is said to be endothermic.

Section 2.2 Thermochemical equations and energy profile diagrams

Worked example: Try yourself 2.2.1

CALCULATING ΔH FOR ANOTHER EQUATION

Carbon reacts with hydrogen according to the equation:

$6C(s) + 3H_2(g) \rightarrow C_6H_6(g) \quad \Delta H = +49 \text{ kJ mol}^{-1}$

Calculate ΔH for the reaction represented by the equation:

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

Thinking	**Working**
The reaction has been reversed in the second equation, so the sign for ΔH is changed to the opposite sign.	ΔH for the second equation will be negative
Identify how the mole amounts in the equation have changed.	The mole amount for C_6H_6 has changed from 1 to 3, H_2 has changed from 3 to 9 and C has changed from 6 to 18. They have all tripled.
Identify how the magnitude of ΔH will have changed for the second equation.	The mole amounts of the chemicals have all tripled, so ΔH will also have tripled.
Calculate the new magnitude of ΔH. (You will write the sign of ΔH in the next step.)	3×49 $= 147$
Write ΔH for the second equation, including the sign.	$\Delta H = -147 \text{ kJ mol}^{-1}$

2.2 Key questions

1 A negative ΔH value indicates a reaction is *exothermic*. This is because the enthalpy of the reactants is *greater than* the enthalpy of the products. Energy is being *released to* the surroundings.

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

3 It would be lower because the change of state of the H_2O from liquid to gas will require energy to be absorbed.

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

5 $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g) \quad \Delta H = +2803 \text{ kJ mol}^{-1}$

Section 2.3 Energy from combustion

Worked example: Try yourself 2.3.1

WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

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

Worked example: Try yourself 2.3.2

WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

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

Worked example: Try yourself 2.3.3

WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

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

Worked example: Try yourself 2.3.4

CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the amount of energy released when 5.40 kg of propane (C_3H_8) is burnt in an unlimited supply of oxygen.	
Thinking	**Working**
Calculate the number of moles of the compound using: $n = \frac{m \text{ (in grams)}}{M}$	$n(C_3H_8) = \frac{m}{M}$ $= \frac{5.40\times10^3}{44.0}$ $= 122.7$ mol
Multiply the number of moles by the heat of combustion per mole.	Energy $= n \times \Delta H_c$ $= 122.7 \times 2220$ $= 2.72 \times 10^5$ kJ

2.3 Key questions

1 $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$

2 Propane: heat of combustion $= \frac{-2220}{44.0} = -50.5$ kJ g^{-1}

Octane: heat of combustion $= \frac{-5450}{114.0} = -47.8$ kJ g^{-1}

Propane releases more energy per gram; therefore, propane releases more energy per kilogram.

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

4 **a** $n = \frac{m}{M} = \frac{250}{16.0} = 15.6$ mol

Energy $= n \times \Delta H_c = 15.6 \times 890 = 1.39 \times 10^4$ kJ

b $n = \frac{m}{M} = \frac{9.64\times10^3}{44.0} = 219$ mol

Energy $= n \times \Delta H_c = 219 \times 2220 = 4.86 \times 10^5$ kJ

c $n = \frac{m}{M} = \frac{403\times10^3}{46.0} = 8.76 \times 10^3$ mol

Energy $= n \times \Delta H_c = 8.76 \times 10^3 \times 1367 = 1.20 \times 10^7$ kJ

d Energy $= m \times \Delta H_c = 573 \times 10^6 \times 30 = 1.7 \times 10^{10}$ kJ

Section 2.4 Determining the heat of combustion of fuels

Worked example: Try yourself 2.4.1

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

<table>
<tr><td colspan="2">Calculate the heat energy, in kJ, needed to increase the temperature of 375 mL of water by 45°C.</td></tr>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Change the volume of water, in mL, to mass of water, in g. Remember that 1 mL of water has a mass of 1 g.</td><td>1 mL of water has a mass of 1 g, so 375 mL of water has a mass of 375 g.</td></tr>
<tr><td>Find the specific heat capacity of water from the Table 2.4.1.</td><td>The specific heat capacity of water is 4.18 J g^{-1} $°C^{-1}$.</td></tr>
<tr><td>To calculate the quantity of heat energy in joules, use the formula:
$q = C$ (J g^{-1} $°C^{-1}$) $\times m$ (g) $\times \Delta T$ (°C)</td><td>$q = 4.18 \times 375 \times 45$
$= 7.05 \times 10^4$ J</td></tr>
<tr><td>Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10^{-3}.</td><td>$q = 7.05 \times 10^4 \times 10^{-3}$
$= 70.5$ kJ</td></tr>
</table>

Worked example: Try yourself 2.4.2

CALCULATING THE HEAT OF COMBUSTION OF A FUEL FROM EXPERIMENTAL DATA

<table>
<tr><td colspan="2">0.295 g of ethanol (C_2H_5OH) undergoes complete combustion in a spirit burner. The heat energy released is used to heat 100 mL of water. The temperature of the water rose from 19.56°C to 38.85°C. Calculate the heat of combustion of ethanol in kJ mol^{-1}.</td></tr>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Calculate the temperature change of the water.</td><td>$\Delta T = 38.85 - 19.56$
$= 19.29°C$</td></tr>
<tr><td>Use the specific heat capacity of water to determine the energy used to heat the water. Use the formula:
$q = C \times m \times \Delta T$
(m in this formula is the mass of water.)</td><td>$q = 4.18 \times 100 \times 19.29$
$= 8063$ J</td></tr>
<tr><td>Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10^{-3}.</td><td>$q = 8063 \times 10^{-3}$
$= 8.063$ kJ</td></tr>
<tr><td>Calculate the amount, in moles, of methanol using the formula:
$n = \frac{m}{M}$</td><td>$n = \frac{0.295}{46.0}$
$= 0.00641$ mol</td></tr>
<tr><td>Determine the heat of combustion of methanol, in kJ mol^{-1}.
Heat of combustion $= \frac{\text{heat released by sample}}{\text{amount of sample (in mol)}}$</td><td>Heat of combustion combustion $= \frac{8.063}{0.00641}$
$= -1.26 \times 10^3$ kJ mol^{-1}
(Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)</td></tr>
</table>

Worked example: Try yourself 2.4.3

WRITING A THERMOCHEMICAL EQUATION USING HEAT OF COMBUSTION DATA

Write a thermochemical equation for the complete combustion of ethane (C_2H_6).	
Thinking	**Working**
Add oxygen as a reactant and carbon dioxide and water as the products in the equation.	$C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
Balance the carbon, hydrogen then oxygen atoms. Add states.	$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$
Obtain the heat of combustion, in kJ mol^{-1}, from the data in Table 2.4.2.	The heat of combustion of ethane is 1560 kJ mol^{-1}.
Determine ΔH for the thermochemical equation by multiplying the heat of combustion by the coefficient of the fuel in the balanced equation.	$\Delta H = 2 \times -1560 = -3120$ kJ mol^{-1}
Write the thermochemical equation.	$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$ $\Delta H = -3120$ kJ mol^{-1}

2.4 Key questions

1 $q = C \times m \times \Delta T$

$= 4.18 \times 1000 \times 25.0$

$= 1.0 \times 10^5$ J

$= 1.05 \times 10^2$ kJ

2 It is assumed that all of the energy released by the combustion of the fuel is used to heat the water. In reality, some of the energy will be used to heat the steel can as well as being lost to the surroundings.

3 $q = C \times m \times \Delta T$

$= 4.18 \times 300 \times 1.78$

$= 2.23 \times 10^3$ J

$= 2.23$ kJ

$$\Delta H_c = \frac{q}{n}$$

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

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

(Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)

4 $q = C \times m \times \Delta T$

$= 4.18 \times 500 \times 11.5$

$= 24\,035$ J

$= 24.035$ kJ

$$\Delta H_c = \frac{q}{n}$$

$$= \frac{24.035}{0.500}$$

$$= -48.1 \text{ kJ g}^{-1}$$

(Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)

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

b $q = C \times m \times \Delta T$

$= 4.18 \times 500 \times 80.0$

$= 167\,200 \text{ J}$

$= 167.2 \text{ kJ}$

$\Delta H_c = \frac{q}{n}$

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

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

$= 0.1879 \text{ mol}$

$m = n \times M$

$= 0.1879 \times 16.0$

$= 3.01 \text{ g}$

CHAPTER 2 REVIEW

EXOTHERMIC AND ENDOTHERMIC REACTIONS

1 **a** 2.21 kJ
b 152 J
c 1.89 MJ
d 12.5 kJ

2 **a** Exothermic, because heat and light energy are released to the surrounding environment by the combustion of wood.
b Endothermic, because thermal energy is absorbed from the surrounding environment to melt the ice.
c Endothermic, because electrical energy is consumed from a power supply as the battery is recharged.
d Exothermic, because heat energy is released to the surrounding environment as organisms in the compost heap decompose the plant material. The temperature of the heap rises as a consequence.

3 Luminescence is the ability of chemicals to give off light, or glow. Chemiluminescence results from exothermic reactions where the energy given off to the surroundings is in the form of light energy. Glow sticks are produced when two chemicals are mixed together once a reaction vessel is broken, allowing them to mix. When they mix, the energy is released to the surroundings as light energy. Bioluminescence describes living things that are luminescent. Glow-worms are able to control the amount of luminescence they give off by taking in more or less oxygen for the reaction system in which light energy is released.

THERMOCHEMICAL EQUATIONS AND ENERGY PROFILE DIAGRAMS

4 C. Some energy is always absorbed to break bonds in the reactants.

5 **a** True
b False
c False
d True

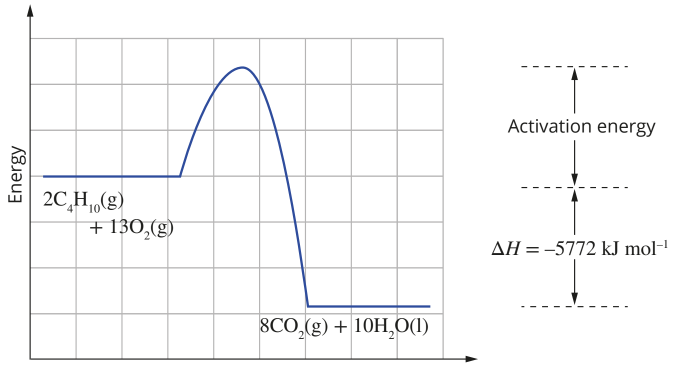
6 **a** Exothermic because ΔH is negative.
b The value of ΔH would now be doubled as the amount of all of the reactants and products is also doubled.
$\Delta H = -5238 \text{ kJ mol}^{-1}$

7 If a chemical equation is written for an endothermic reaction, ΔH is positive, telling you that energy is absorbed as the reaction proceeds. The enthalpy of the products must be higher than the enthalpy of the reactants.

If this reaction is reversed, the enthalpy of the reactants is now higher than the enthalpy of the products. The reaction releases energy as the reaction proceeds, so is exothermic. ΔH becomes negative.

8 a Higher energy in bonds of reactants

b



ENERGY FROM COMBUSTION

9 $C_4H_9OH(g) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

10 $2C_4H_{10}(g) + 9O_2(g) \rightarrow 8CO(g) + 10H_2O(l)$

11 $n = \frac{m}{M}$

$= \frac{5000}{16.0}$

$= 312.5$ mol

Energy $= n \times \Delta H_c$

$= 312.5 \times 890$

$= 278\ 125$ kJ

$= 278\ 125 \times 10^{-3} = 278$ MJ

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

$= \frac{1000}{114.0}$

$= 8.772$ mol

Energy $= 8.772 \times 5450$

$= 4.781 \times 10^4$ kJ

ii $n(C_4H_{10}) = \frac{m}{M}$

$= \frac{1000}{58}$

$= 17.241$ mol

Energy $= 17.241 \times 2886$

$= 4.98 \times 10^4$ kJ

iii $n(H_2) = \frac{m}{M}$

$= \frac{1000}{2.00}$

$= 500$ mol

Energy $= 500 \times 286$

$= 1.43 \times 10^5$ kJ

b H_2, C_4H_{10}, C_8H_{18}

DETERMINING THE HEAT OF COMBUSTION OF FUELS

13 These questions use the formula relating specific heat capacity and energy. It is important to use the correct units. As the density of water is 1 g mL^{-1}, 1 mL of water weighs 1 g. Remember to convert kg to g. As the temperature is only a difference, the unit is not important.

The formula is: energy = specific heat capacity × mass of water × temperature rise, which can be rewritten for water as:

$E = 4.184 \times m \times \Delta T$

a $E = 4.184 \times 100 \text{ g} \times 60.0°\text{C}$
$= 25\,104 \text{ J}$
$= 25.1 \text{ kJ}$

b $E = 4.184 \times 250 \text{ g} \times 75.0°\text{C}$
$= 78\,450 \text{ J}$
$= 78.5 \text{ kJ}$

c $E = 4.184 \times 1500 \text{ g} \times 10.0°\text{C}$
$= 62\,760 \text{ J}$
$= 62.8 \text{ kJ}$

d $E = 4.184 \times 2300 \times 82.0$
$= 789\,000 \text{ J}$
$= 789 \text{ kJ}$

e $E = 2.2 \times 300 \text{ g} \times 82.0°\text{C}$
$= 54\,120 \text{ J}$
$= 54.1 \text{ kJ}$

14 $q = C \times m \times \Delta T$. Therefore, $\Delta T = \frac{q}{C \times m}$

$$= \frac{10\,000}{4.18 \times 200}$$

$$= 12.0°\text{C}$$

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

15 $q = C \times m \times \Delta T$
$= 4.18 \times 300 \times 6.67$
$= 8364 \text{ J}$
$= 8.36 \text{ kJ}$

$$\Delta H_c = \frac{q}{m}$$

$$= \frac{8.36}{0.254}$$

$$= -32.9 \text{ kJ g}^{-1}$$

(Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)

16 $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ mol}^{-1}$

Or

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta H = -572 \text{ kJ mol}^{-1}$

CONNECTING THE MAIN IDEAS

17 **a** 1 mol of CO(g) and 0.5 mol of $O_2(g)$

b **i** As the coefficients are twice those in the given equation, ΔH will also be doubled.
$\Delta H = 2 \times (-283) \text{ kJ mol}^{-1}$
$= -566 \text{ kJ mol}^{-1}$

ii As the coefficients are twice those in the given equation and the equation is reversed, ΔH will also be doubled, and have the opposite sign. $\Delta H = +566 \text{ kJ mol}^{-1}$.

18 $q = C \times m \times \Delta T$

$= 4.18 \times 100.0 \times 5.52$

$= 2307$ J

$= 2.307$ kJ

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

$= \frac{0.0450}{30.0}$

$= 0.00150$ mol

$\Delta H = \frac{q}{n(C_2H_6)}$

$= \frac{2.307}{0.00150}$

$= 1.54 \times 10^3$ kJ mol^{-1}

(Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)

$C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H = -1.54 \times 10^3$ kJ mol^{-1}

Or

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$ $\Delta H = -3.08 \times 10^3$ kJ mol^{-1}

19 a $q = C \times m \times \Delta T$

$= 4.18 \times 500 \times 22.9$

$= 47\,861$ J

$= 47.9$ kJ

$\Delta H_c = \frac{47.9}{3.00}$

$= -16.0 \times 10^3$ kJ g^{-1}

$= -16.0 \times 10^6$ MJ t^{-1}

(Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)

b The heat of combustion calculated would be lower.

Some of the heat released by the burning wood would be used to heat the beaker holding the water and to heat the air surrounding the beaker. Not all of the energy will be used to heat the water so the temperature rise will be lower than it should be, making the heat of combustion of the fuel seem lower than the actual value.

Also, the combustion of the wood may have been incomplete, with some carbon and carbon monoxide formed instead of carbon dioxide. As a consequence, less energy would have been released and the temperature rise would be lower.

Chapter 3 Combustion of fuels

Section 3.1 Introducing gases

Worked example: Try yourself 3.1.1

CONVERTING VOLUME UNITS

A gas has a volume of 700 mL.

What is its volume in:

- **a** cubic centimetres (cm^3)?
- **b** litres (L)?
- **c** cubic metres (m^3)?

Thinking	**Working**
Recall the conversion factors for each of the units of volume. Apply the correct conversion to each situation.	**a** The units of mL and cm^3 are equivalent. 1 mL = 1 cm^3 700 mL = 700 cm^3 **b** 1000 mL = 1 L Divide volume in mL by 1000 to convert to L. $700\text{ mL} = \frac{700}{1000}$ $= 0.700\text{ L}$ **c** 1×10^6 mL = 1 m^3 Divide volume in mL by 1×10^6 to convert to m^3. $700\text{ mL} = \frac{700}{1 \times 10^6}$ $= 0.000700\text{ m}^3$

Worked example: Try yourself 3.1.2

CONVERTING PRESSURE UNITS

Cyclone Yasi was one of the biggest cyclones in Australian history.

- **a** The atmospheric pressure in the eye of Cyclone Yasi was measured as 0.902 bar. What was the pressure in kilopascals (kPa)?
- **b** What was the pressure in the eye of Cyclone Yasi in atmospheres (atm) if it is known to be 677 mmHg?
- **c** If the atmospheric pressure in the eye of Cyclone Yasi was 0.891 atm, what was the pressure in kilopascals (kPa)?
- **d** The atmospheric pressure in the eye of Cyclone Yasi was 677 mmHg. What was the pressure in bars?

Thinking	**Working**
a To convert bars to kilopascals, use the conversion relationship: 1 bar = 100 kPa To change bar to kPa, multiply the value by 100.	$0.902\text{ bar} = 0.902 \times 100$ $= 90.2\text{ kPa}$
b To convert millimetres of mercury to atmospheres, use the relationship: 1 atm = 760 mmHg To change mmHg to atm, divide the value by 760.	$677\text{ mmHg} = \frac{677}{760}$ $= 0.891\text{ atm}$
c To convert atmospheres to kilopascals, use the conversion relationship: 1 atm = 101.3 kPa To change atm to kPa, multiply the value by 101.3.	$0.891\text{ atm} = 0.891 \times 101.3$ $= 90.2\text{ kPa}$

d This can be done in two steps. First, convert millimetres of mercury to atmospheres. Use the conversion relationship: 760 mmHg = 1 atm To change mmHg to atm, divide the value by 760. Keep the answer in your calculator and proceed to the next step. Next, convert atmospheres to bar. Use the conversion relationship: 1 atm = 1.013 bar To change atm to bar, multiply the quotient from the previous step by 1.013.	677 mmHg $= \frac{677}{760}$ 677 mmHg $= \frac{677}{760} \times 101.3$ = 0.902 bar

3.1 Key questions

1 **a** Molecules of gases are in constant, rapid, random motion and the forces between molecules are negligible. They continue to move outwards until stopped by the walls of the container, filling all the space available.

b Most of the volume occupied by a gas is space, so compression can be achieved by reducing the space between the particles.

c The molecules in a gas are spread much further apart than those of a liquid. A given mass of gas would occupy a much greater volume than the same mass of the liquid phase. Therefore, the density of the gas is less.

d Gases mix easily together because of the large amount of space between the molecules.

e The pressure exerted by a gas depends on the number of collisions of gas particles and the wall of the container. The pressure is independent of the type of gas involved. The total pressure exerted by a mixture of gases will depend on the total number of collisions each gas has with the container.

2 **a** Tyres have a recommended maximum pressure to give a comfortable ride as well as good traction on the road. If the pressure in a tyre is too high, the gas inside cannot be compressed as easily and passengers will be more aware of bumps on the road.

b During a long journey on a hot day, the air in a tyre warms up. This means the air molecules have increased kinetic energy, and collisions with the walls of the tyres will increase in frequency and exert more force, and so the pressure will increase.

c Particles from the cooking food escape the pot and move randomly through the house. If the food has an odour, and if there are enough particles in the air, you will detect the odour as you enter the house.

d As air is pumped into a balloon, air molecules collide with the rubber of the balloon, forcing it to expand. If too much air is pumped in, the balloon reaches a stage where it cannot stretch any further. If the number of collisions by molecules per given surface area is increased still further, the rubber will break.

3 **a** As temperature increases, the average kinetic energy of gas molecules in the can will increase. This will lead to an increase in the frequency and force of collisions of gas molecules with the inside walls of the aerosol cans. This will cause an increase in pressure.

b As the syringe is compressed, the inside surface area of the syringe will decrease. The number of collisions of molecules per unit area per second with the inside walls of the syringe will increase. This will cause a pressure increase.

4 These conversions should be applied as needed: 1.00 atm = 760 mmHg = 101.3 kPa = 1.013×10^5 Pa = 1.013 bar

a 140 kPa = 140 × 1000 Pa = 1.40×10^5 Pa

b 92 000 Pa = $\frac{92000}{1000}$ kPa = 92 kPa

c 1.00 atm = 760 mmHg
So 4.24 atm = 760 × 4.24 mmHg = 3.22×10^3 mmHg
1.00 atm = 1.013×10^5 Pa
So 4.24 atm = $1.013 \times 10^5 \times 4.24$ Pa = 4.30×10^5 Pa

d 101.3 kPa = 760 mmHg

So 120 kPa = $\frac{760}{101.3} \times 120$ kPa = 900 mmHg

101.3 kPa = 1.00 atm

So 120 kPa = $\frac{1.00}{101.3} \times 120$ atm = 1.18 atm

101.3 kPa = 1.013 bar

So 120 kPa = $\frac{1.013}{101.3} \times 120$ atm = 1.20 bar

e 760 mmHg = 1.00 atm

So 1400 mmHg = 1.00 × $\frac{1400}{760}$ = 1.84 atm

760 mmHg = 1.013 × 10^5 Pa

So 1400 mmHg = 1.013 × 10^5 × $\frac{1400}{760}$ Pa = 1.87 × 10^5 Pa

760 mmHg = 1.013 bar

So 1400 mmHg = 1.013 × $\frac{1400}{760}$ bar = 1.87 bar

f 1.013 × 10^5 Pa = 1.00 atm

So 80 000 Pa = 1.00 × $\frac{80\,000}{1.013 \times 10^5}$ atm = 0.790 atm

1.013 × 10^5 Pa = 760 mmHg

So 80 000 Pa = 760 × $\frac{80\,000}{1.013 \times 10^5}$ mmHg = 600 mmHg

1.013 × 10^5 Pa = 1.013 bar

So 80 000 Pa = 1.013 × $\frac{80\,000}{1.013 \times 10^5}$ bar = 0.800 bar

5 These conversions should be applied as needed: 1 mL = 1 cm^3, 1 L = 1000 mL = 1000 cm^3, 1 m^3 = 1 × 10^6 cm^3 = 1 × 10^6 mL = 1000 L

a 2 L = 2 × 1000 mL = 2 × 10^3 mL

b 4.5 L = $\frac{4.5}{1000}$ = 4.5 × 10^{-3} m^3

c 2250 mL = $\frac{2250}{1000}$ = 2.250 L

d 120 mL = $\frac{120}{1000}$ = 0.120 L

e 5.6 mL = $\frac{5.6}{1000}$ = 5.6 × 10^{-3} L

f 3.7 m^3 = 3.7 × 1000 = 3.7 × 10^3 L

g 285 mL = 285 cm^3 = $\frac{285}{1 \times 10^6}$ = 2.85 × 10^{-4} m^3

h 4.70 × 10^{-3} m^3 = 4.70 × 10^{-3} × 1000
= 4.70 L
= 4.70 × 1000
= 4.70 × 10^3 cm^3

Section 3.2 Universal gas equation

Worked example: Try yourself 3.2.1

CONVERTING TEMPERATURES FROM CELSIUS TO KELVIN

What is 100°C on the kelvin temperature scale?	
Thinking	**Working**
T (in K) = T (in °C) + 273	T (in K) = T (in °C) + 273 = 100 + 273 = 373 K

Worked example: Try yourself 3.2.2

CALCULATING THE VOLUME OF A GAS FROM ITS AMOUNT (IN MOL)

Calculate the volume, in L, occupied by 3.5 mol of oxygen gas at SLC. Assume that oxygen behaves like an ideal gas.	
Thinking	**Working**
Rearrange $n = \frac{V}{V_m}$ to make volume the subject.	$n = \frac{V}{V_m}$ $V = n \times V_m$
Substitute in the known values where V_m = 24.8 L mol^{-1} (at SLC) and solve.	$V = n \times V_m$ $= 3.5 \times 24.8$ $= 86.8$ L
Consider the units and significant figures. The answer should be given to the smallest number of significant figures in the measurement.	$V = 87$ L

Worked example: Try yourself 3.2.3

CALCULATING THE VOLUME OF A GAS USING THE UNIVERSAL GAS EQUATION

Calculate the volume, in L, occupied by 13.0 mol of carbon dioxide gas (CO_2) if the pressure is 250 kPa at 75.0°C.	
Thinking	**Working**
Convert units, if necessary. Pressure is in kPa and temperature in K.	$P = 250$ kPa (no conversion required) $T = 75.0 + 273 = 348$ K
Rearrange the universal gas equation so that volume, V, is the subject.	$PV = nRT$ $V = \frac{nRT}{P}$
Substitute values for pressure, amount, temperature and the gas constant, R, then solve for V. Express the answer to the correct number of significant figures.	$V = \frac{13.0 \times 8.31 \times 348}{250}$ $= 150$ L

3.2 Key questions

1 Remember to convert temperatures by using: $T = t + 273$, where T is the absolute temperature (in kelvin), and t is the temperature on the Celsius scale. It is also conventional not to use the degree symbol when writing the absolute temperature. For example, 25°C would be written as 298 K.

- **a** $T = 100 + 273 = 373$ K
- **b** $T = 175 + 273 = 448$ K
- **c** $T = -145 + 273 = 128$ K

2 Remember that, under standard laboratory conditions (SLC), 1 mol of any gas has a volume of 24.8 L.

Use the formula $n = \frac{V}{V_m}$, where n is the amount, in mol, V is the volume, in L, and V_m is the molar volume in, L mol^{-1}.

To calculate V, the formula is rearranged to $V = n \times V_m$.

- **a** $V(Cl_2) = 24.8 \times 1.4 = 34.72$ L $= 34$ L
- **b** $V(H_2) = 24.8 \times 1.0 \times 10^{-3}$ L $= 0.0248$ L $= 25$ mL
- **c** Since $n = \frac{m}{M}$ and the molar mass of nitrogen is 28.0 g mol^{-1}:

  $V(N_2) = \frac{24.8 \times 1.4}{28.0} = 1.24$ L $= 1.2$ L

3 Remember, that under standard laboratory conditions (SLC), 1 mol of any gas has a volume of 24.8 L.
These questions involve three steps:

1 Calculate the amount, in mol, of gas at SLC.

2 Find the molar mass (M) of the gas.

3 Use $n = \frac{m}{M}$ to find the mass by reorganising as $m = n \times M$.

a $n(\text{Ne}) = \frac{2.80}{24.8} = 0.113 \text{ mol}$

$m(\text{Ne}) = 0.113 \times 20.2 = 2.28 \text{ g}$

b $n(\text{O}_2) = \frac{50.0}{24.8} = 2.016 \text{ mol}$

$m(\text{O}_2) = 2.016 \times 32.0 = 64.5 \text{ g}$

c $V = 140 \text{ mL} = 0.140 \text{ L}$

$n(\text{CO}_2) = \frac{0.140}{24.8} = 0.005645 \text{ mol}$

$m(\text{CO}_2) = 0.005645 \times 44.0 = 0.248 \text{ g}$

4 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

$P = \frac{nRT}{V} = \frac{0.25 \times 8.31 \times (5 + 273)}{5.0}$

$= 115.5 \text{ kPa}$

$= 1.2 \times 10^2 \text{ kPa}$

5 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

a $V = \frac{nRT}{P} = \frac{0.20 \times 8.31 \times (40 + 273)}{115} = 4.5 \text{ L}$

b $V = \frac{nRT}{P} = \frac{12.5 \times 8.31 \times (150 + 273)}{5 \times 101.3} = 86.8 \text{ L}$

c Since $n = \frac{m}{M}$ and the molar mass of hydrogen sulfide is 34.1 g mol^{-1}:

$V = \frac{nRT}{P} = \frac{8.50 \times 8.31 \times (27 + 273)}{34.1 \times 100} = 6.21 \text{ L}$

6 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

The second step involves use of $n = \frac{m}{M}$.

The molar mass of helium is 4.0 g mol^{-1}.

$n(\text{He}) = \frac{PV}{RT} = \frac{95 \times 100}{8.31 \times (273 + 0)}$

$= 4.19 \text{ mol}$

$m(\text{He}) = 4.19 \times 4.0$

$= 17 \text{ g}$

7 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

Since $n = \frac{m}{M}$ and the molar mass of nitrogen is 28.0 g mol^{-1}:

$T = \frac{PV}{nR} = \frac{102 \times 10.0 \times 28.0}{11.3 \times 8.31}$

$= 304 \text{ K}$

$= 31°\text{C}$

8 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

These conversions should be applied as needed: 1.00 atm = 101.3 kPa = 1.013 bar.

$n(\text{N}_2) = \frac{PV}{RT} = \frac{1.2 \times 10^2 \times 3.2}{8.31 \times (25 + 273)} = 0.16 \text{ mol}$

$n(\text{He}) = \frac{PV}{RT} = \frac{1.2 \times 101.3 \times 2.5}{8.31 \times (23 + 273)} = 0.12 \text{ mol}$

$\therefore$ There is a greater amount of nitrogen.

Section 3.3 Calculations involving combustion of fuels—Part 1

Worked example 3.3.1: Try yourself

USING MOLE RATIOS

How many moles of carbon dioxide are generated when 0.50 moles of butane (C_4H_{10}) are burned completely in oxygen?	
Thinking	**Working**
Write a balanced equation for the reaction.	$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$
Note the number of moles of the known substance.	$n(C_4H_{10}) = 0.50$ mol
Write a mole ratio for: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(CO_2) = \frac{8}{2} \times 0.50$ $= 2.0$ mol

Worked example: Try yourself 3.3.2

SOLVING MASS–MASS STOICHIOMETRIC PROBLEMS

Calculate the mass of carbon dioxide produced when 3.60 kg of butane (C_4H_{10}) are burned completely in oxygen.	
Thinking	**Working**
Write a balanced equation for the reaction.	$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$
Calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_4H_{10}) = \frac{3.60 \times 10^3}{58.0}$ $= 62.07$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$
Calculate the number of moles of the unknown substance using: $n(\text{unknown}) = \text{mole ratio} \times n(\text{known})$	$n(CO_2) = \frac{8}{2} \times 62.07$ $= 248.3$
Calculate the mass of the unknown substance using: $m = n \times M$	$m(CO_2) = 248.3 \times 44.0$ $= 10924$ g $= 10.9$ kg

3.3 Key questions

1 **a** $\frac{n(CH_3OH)}{n(O_2)} = \frac{2}{3}$

b $\frac{n(O_2)}{n(H_2O)} = \frac{3}{4}$

c $\frac{n(CH_3OH)}{n(CO_2)} = \frac{2}{2} = 1$

2
- Write a balanced equation for the reaction.
- Identify the known and unknown substances in the question.
- Calculate the amount, in mol, of the known substance using $n = \frac{m}{M}$.
- Use mole ratios from the equation to calculate the amount of the unknown.
- Calculate the mass of the unknown substance using $m = n \times M$.

3 The balanced equation shows that 25 mol of oxygen reacts with 2 mol of octane, producing 16 mol of carbon dioxide. The amount of each is found using $n = \frac{m}{M}$, where m is the mass in grams and M is the molar mass. A periodic table is used to calculate the molar masses of CO_2 = 44.0 g mol^{-1}, O_2 = 32.0 g mol^{-1} and C_8H_{18} = 114.0 g mol^{-1}.

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

$n(C_8H_{18}) = \frac{200}{114.0} = 1.754$ mol

$\therefore n(O_2) = \frac{25}{2} \times 1.754 = 21.93$ mol

$\therefore m(O_2) = 21.93 \times 32.0 = 702$ g

b $\therefore \frac{n(CO_2)}{n(C_8H_{18})} = \frac{16}{2} = 8$

$n(C_8H_{18}) = \frac{200}{114.0} = 1.7544$ mol

$n(CO_2) = 8 \times 1.7544 = 14.035$ mol

$\therefore m(CO_2) = 14.035 \times 44.0 = 618$ g

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

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

$n(C_3H_8) = \frac{6.70}{44.0} = 0.152$ mol

$n(CO_2)$ produced = 3 × 0.152 mol = 0.457 mol

$\therefore m(CO_2)$ produced = 0.457 × 44.0 = 20.1 g

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

$n(C_3H_8) = \frac{6.70}{44.0} = 0.1522$ mol

$n(O_2)$ consumed = 5 × 0.1522 mol = 0.7610 mol

$m(O_2)$ consumed = 0.7610 × 32.0 = 24.4 g

c $\frac{n(H_2O)}{n(C_3H_8)} = \frac{4}{1}$

$n(C_3H_8) = \frac{6.70}{44.0} = 0.1522$ mol

$n(H_2O)$ produced = 4 × 0.1522 mol = 0.6088 mol

$\therefore m(H_2O)$ produced = 0.6088 × 18.0 = 11.0 g

5 The equation for the reaction is:

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

a $\frac{n(O_2)}{n(C_4H_{10})} = \frac{13}{2}$

$n(C_4H_{10}) = \frac{m}{M} = \frac{1.00 \times 10^3}{58.0} = 17.241$ mol

$n(O_2) = \frac{13}{2} \times 17.241 = 112.07$ mol

$m(O_2) = n \times M = 112.07 \times 32.0 = 3586$ g = 3.59 kg

b $\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$

$n(C_4H_{10}) = \frac{m}{M} = \frac{1.00 \times 10^3}{58.0} = 17.24$ mol

$n(CO_2) = \frac{8}{2} \times 17.24 = 68.96$ mol

$m(CO_2) = n \times M = 68.96 \times 44.0 = 3034$ g = 3.03 kg

Section 3.4 Calculations involving combustion of fuels—Part 2

Worked example 3.4.1: Try yourself

MASS–VOLUME STOICHIOMETRIC CALCULATIONS AT STANDARD LABORATORY CONDITIONS

Calculate the volume of carbon dioxide, in L, produced when 300 g of butane is burned completely in oxygen. The gas volume is measured at SLC.	
Thinking	**Working**
Write a balanced equation for the reaction.	$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$
Calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_4H_{10}) = \frac{300}{58.0}$ $= 5.17$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$
Calculate the number of moles of the unknown substance using: n(unknown) = mole ratio × n(known)	$n(CO_2) = \frac{8}{2} \times 5.17$ $= 20.7$ mol
Calculate the volume of the unknown substance using: $V = n \times V_m$	$V(CO_2) = 20.7 \times 24.8$ $= 513$ L

Worked example: Try yourself 3.4.2

MASS–VOLUME STOICHIOMETRIC CALCULATIONS AT NON-STANDARD CONDITIONS

Calculate the volume of carbon dioxide, in L, produced when 5.00 kg of butane is burned completely in oxygen. The gas volume is measured at 40°C and 400 kPa.	
Thinking	**Working**
Write a balanced equation for the reaction.	$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$
Calculate the number of moles of the known substance using: $n = \frac{m}{M}$	$n(C_4H_{10}) = \frac{5000}{58.0}$ $= 86.2$ mol
Find the mole ratio: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$
Calculate the number of moles of the unknown substance using: n(unknown) = mole ratio × n(known)	$n(CO_2) = \frac{8}{2} \times 86.2$ $= 345$ mol
Express the pressure and temperature in required units.	$P = 400$ kPa $T = 40 + 273 = 313$ K
Calculate the volume of the unknown substance using: $V = \frac{nRT}{P}$	$V(CO_2) = \frac{345 \times 8.31 \times 313}{400}$ $= 2242$ L $= 2.24 \times 10^3$ L

Worked example: Try yourself 3.4.3

GAS VOLUME–VOLUME CALCULATIONS

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

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

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

Thinking	**Working**
Use the balanced equation to find the mole ratio of the two gases involved.	1 mol of CH_4 gas produces 1 mol of CO_2 gas.
The temperature and pressure are constant, so volume ratios are the same as mole ratios.	1 volume of CH_4 produces 1 volume of CO_2 gas, so 50 mL of CH_4 produces 50 mL of CO_2.

Worked example: Try yourself 3.4.4

EXCESS REACTANT CALCULATIONS

Calculate the volume of carbon dioxide, in L, produced when 65.0 g of butane is burned completely in 200 L of oxygen. The gas volume is measured at SLC. The equation for the reaction is:

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

a Which reactant is the limiting reactant?

b What is the mass of carbon dioxide formed?

Thinking	**Working**
a Calculate the number of moles of each reactant using $n = \frac{m}{M}$, $n = \frac{V}{V_m}$, or $n = \frac{PV}{RT}$ as appropriate.	$n(C_4H_{10}) = \frac{m}{M}$ $= \frac{65.0}{58.0}$ $= 1.12$ mol $n(O_2) = \frac{V}{V_m}$ $= \frac{200}{24.8}$ $= 8.06$ mol
Use the coefficients of the equation to find the limiting reactant.	The equation shows 2 mol of C_4H_{10} reacts with 13 mol of O_2. So to react all of the O_2 will require $\frac{2}{13} \times n(O_2)$ of C_4H_{10} $= \frac{2}{13} \times 8.06$ $= 1.24$ mol As there is 1.12 mol of C_4H_{10}; therefore, the C_4H_{10} is the limiting reactant (it will be completely consumed).
b Find the mole ratio using: $\frac{\text{coefficient of unknown}}{\text{coefficient of known}}$ The limiting reactant is the known substance.	$\frac{n(CO_2)}{n(C_4H_{10})} = \frac{8}{2}$
Calculate the number of moles of the unknown substance using: n(unknown) = mole ratio × n(known)	$n(CO_2) = \frac{8}{2} \times 1.12$ $= 4.48$ mol
Calculate the volume of the unknown using: $V = n \times V_m$	$V(CO_2) = 4.48 \times 24.8$ $= 111$ L

3.4 Key questions

1 The balanced equation shows that 1 mol of propane reacts with 5 mol of oxygen, and produces 3 mol of carbon dioxide.

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

Remember that $n = \frac{m}{M}$ (The molar mass of propane is 44.0 g mol^{-1})

Remember that under SLC, 1 mol of any gas has a volume of 24.8 L.

Use the formula $n = \frac{V}{V_m}$ rearranged as $V = n \times V_m$.

a i $n(C_3H_8) = \frac{22}{44.0} = 0.50$ mol

$\frac{n(O_2)}{n(C_3H_8)} = \frac{5}{1} \therefore V(O_2) = 5 \times 0.50 \times 24.8 = 62$ L

ii $\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1} \therefore V(CO_2) = 3 \times 0.50 \times 24.8 = 37$ L

b i $n(C_3H_8) = \frac{16.5}{44.0} = 0.375$ mol

$\frac{n(O_2)}{n(C_3H_8)} = \frac{5}{1} \therefore V(O_2) = 5 \times 0.375 \times 24.8 = 46.5$ L

ii $\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1} \therefore V(CO_2) = 3 \times 0.375 \times 24.8 = 27.9$ L

c i $m(C_3H_8) = 3.40$ kg $= 3400$ g

$n(C_3H_8) = \frac{3400}{44.0} = 77.3$ mol

$\frac{n(O_2)}{n(C_3H_8)} = \frac{5}{1} \therefore V(O_2) = 5 \times 77.3 \times 24.8 = 9.58 \times 10^3$ L

ii $\frac{n(CO_2)}{n(C_3H_8)} = \frac{3}{1} \therefore V(CO_2) = 3 \times 77.3 \times 24.8 = 5.75 \times 10^3$ L

2 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31$ J K^{-1} mol^{-1}.

The second step involves using $n = \frac{m}{M}$. The molar mass of octane is 114.0 g mol^{-1}.

The balanced equation shows that 2 mol of octane produces 16 mol of carbon dioxide.

$n(CO_2) = \frac{PV}{RT} = \frac{1.10 \times 101.3 \times 50.0}{8.31 \times (120 + 273)} = 1.71$ mol

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

$n(CO_2) = \frac{2}{16} \times 1.71 = 0.213$ mol

$\therefore m(C_8H_{18}) = n(C_8H_{18}) \times M = 0.213 \times 114.0 = 24.3$ g

3 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31$ J K^{-1} mol^{-1}.

The first step involves using $n = \frac{m}{M}$

The molar mass of hydrogen peroxide is 34.0 g mol^{-1}.
The balanced equation shows that 2 mol of hydrogen peroxide produces 1 mol of oxygen.

$n(H_2O_2) = \frac{m}{M} = \frac{10.0}{34.0} = 0.294$ mol

$(O_2) = \frac{1}{2} \times 0.294 = 0.147$ mol

$V(O_2) = \frac{nRT}{P} = \frac{0.147 \times 8.31 \times 303}{91.0} = 4.07$ L

4 The balanced equation shows that 2 mol of NO_2 is produced from 2 mol of NO.
Therefore, the volumes of gases produced will be equal to the volume of NO reacted (as long as the temperature and pressure are constant).
$\therefore V(NO) = V(NO_2) = 0.5$ L

5 The balanced equation shows that 1 mol of O_2 reacts with 2 mol of CO. Therefore, the volumes of O_2 and CO used also will be in the ratio 1 : 2 (as long as the temperature and pressure are constant).

$\therefore V(CO) = 150$ mL

$\therefore V(O_2) = 75$ mL

Section 3.5 Calculations involving energy changes

Worked example: Try yourself 3.5.1

CALCULATING ENERGY RELEASED BY THE COMBUSTION OF A PARTICULAR AMOUNT OF A FUEL

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

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \quad \Delta H = -3120 \text{ kJ mol}^{-1}$

Thinking	**Working**
Calculate the amount, in moles, of the fuel using: $n = \frac{m}{M}$	$n(C_2H_6) = \frac{10\,000}{30.0}$ $= 333$ mol
Using the thermochemical equation, write a relationship between the number of moles of fuel burned and energy released.	2 moles of C_2H_6 release 3120 kJ. Let 333 moles of C_2H_6 release x kJ.
Calculate the energy released by the fuel in kilojoules.	By proportion: $\frac{333}{2} = \frac{x}{3120}$ $x = \frac{333}{2} \times 3120$ $= 520\,000$ kJ
Convert the energy released to MJ. 1 MJ = 10^3 kJ	520 000 kJ = 520 MJ

Worked example: Try yourself 3.5.2

CALCULATING THE AMOUNT OF FUEL THAT MUST BE BURNED TO PRODUCE A PARTICULAR AMOUNT OF ENERGY

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

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

Thinking	**Working**
Using the thermochemical equation, write a relationship between the number of moles of fuel burned and energy released.	1 mole of CH_4 releases 890 kJ. Let x moles release 5000 kJ.
Calculate the amount of the fuel that must have been burnt to produce the energy.	By proportion: $\frac{1}{x} = \frac{890}{5000}$ $x = \frac{5000}{890}$ $= 5.62$ mol
Calculate the volume of the fuel, at SLC.	$n = \frac{V}{V_m}$ so $V(CH_4) = n \times V_m$ $= 5.62 \times 24.8$ $= 139$ L

3.5 Key questions

1 A. Methane is the simplest hydrocarbon, so it has the formula CH_4. C_2H_6 is the formula for ethane. Incomplete combustion of hydrocarbons produces carbon monoxide, CO, and/or carbon as products.

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

b $2C_8H_{18}(g) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(g)$

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

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

Energy released = 4.68×10^3 kJ = 4.68 MJ

b $n(C_2H_6) = \frac{m}{M} = \frac{100}{30.0} = 3.33$ mol

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

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

Energy released = 5.20×10^3 kJ = 5.20 MJ

c $n(C_2H_6) = \frac{V}{V_m} = \frac{10.0}{24.8} = 0.403$ mol

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

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

$x = \frac{0.403 \times 3120}{2} = 629$ kJ

Energy released = 629 kJ

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

By proportion: $\frac{x}{2} = \frac{100}{3120}$

$x = \frac{2 \times 100}{3120} = 0.0641$ mol

$V(C_2H_6) = n \times V_m = 0.0641 \times 24.8 = 1.59$ L

5 $n(C_8H_{18}) = \frac{250.0}{114.0} = 2.193$ mol

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

By proportion: $\frac{2.193}{2} = \frac{x}{10\,900}$

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

Energy released = 11.95 MJ

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

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

By proportion: $\frac{0.172}{2} = \frac{x}{5772}$

$x = \frac{0.172 \times 5772}{2} = 498$ kJ

Energy released = 498 kJ

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

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

By proportion: $\frac{0.004\,03}{2} = \frac{x}{5772}$

$x = \frac{0.004\,03 \times 5772}{2} = 11.6$ kJ

Energy released = 11.6 kJ

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

By proportion: $\frac{x}{2} = \frac{1.00}{5772}$

$x = \frac{2 \times 1.00}{5772} = 0.000\,347$ mol

$V(C_2H_6) = \frac{nRT}{P} = \frac{0.000347 \times 8.31 \times 288}{108} = 0.007\,68 \text{ L} = 7.68 \text{ mL}$

7 **a** From the thermochemical equations:

1 mol methane releases 890 kJ

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

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

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

By proportion: $\frac{x}{1} = \frac{2000}{890}$

$x = \frac{1 \times 2000}{890} = 2.25$ mol

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

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

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

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

CHAPTER 3 REVIEW

INTRODUCING GASES

1 B

2 A. Temperature is a measure of the average kinetic energy of the particles. As the temperature increases, the average kinetic energy of the particles also increases. Average kinetic energy is proportional to the average speed of the particles. As average kinetic energy increases, the average speed of the particles also increases.

3 smaller, straight-line, weak, elastic, directly, K

4 **a** As volume is reduced, there is an increase in the frequency of molecular collisions per unit wall area. This is measured as an increase in pressure.

b When the temperature of a gas is lowered, the average kinetic energy of the particles decreases. The rate of collisions between particles and the walls of the container decreases and particles collide with less force. As pressure is a measure of the force of molecular collisions per unit wall area of the container, pressure is found to decrease.

c In a mixture of gases, the particles of each gas are moving and colliding with the walls of the container, independently of each other. Each gas therefore exerts a pressure. As the gases behave independently of each other, total pressure is simply the sum of the individual gas (or partial) pressures.

d When more gas is added to a container, the total number of particles in the container increases. Provided that the volume of the container and the temperature have not changed, the collisions of these additional particles means that the total pressure in the container has increased.

5 **a** The pressure inside the container is reduced when some of the gas escapes.

b There are fewer gas molecules to collide with each other and the walls of the container. Pressure is the force exerted by the molecules over a defined area, so this will decrease.

UNIVERSAL GAS EQUATION

6 Under standard laboratory conditions (SLC), one mole of any gas has a volume of 24.8 L. This question involves three steps:

1. Calculate the amount (in mol) of gas at SLC.
2. Find the molar mass (M) of the gas.
3. Use $n = \frac{m}{M}$ to find the mass by rearranging the formula as $m = n \times M$.

$$n = \frac{50.0}{24.8}$$

$$= 2.02 \text{ mol}$$

$M(O_2) = 32.0 \text{ g mol}^{-1}$

$m(O_2) = 2.02 \times 32.0 = 64.5 \text{ g}$

7 This involves using $n = \frac{m}{M}$ and $V = n \times V_m$. You could combine these two formulas to give $V = \frac{m \times V_m}{M}$.

a The molar mass of oxygen is 32.0 g mol^{-1}.

$$\therefore V(O_2) = \frac{8.0}{32.0} \times 24.8 = 6.2 \text{ L}$$

b The molar mass of NO_2 is 46.0 g mol^{-1}.

$$\therefore n(NO_2) = \frac{V}{V_m} = \frac{10}{24.8} = 0.40 \text{ mol}$$

$$\therefore m(NO_2) = 0.40 \times 46.0 = 19 \text{ g}$$

8 B

Calculate $n(O_2)$.

$$n = \frac{m}{M} = \frac{64.0}{32.0}$$

$$= 2.00 \text{ mol}$$

Convert given quantities to correct units.

$n = 2.00$ mol

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

$T = 303$ K

$V = 25.0$ L

Calculate $P(O_2)$.

$$P = \frac{nRT}{V} = \frac{2.00 \times 8.31 \times 303}{25.0}$$

$$= 201 \text{ kPa}$$

9 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

Remember that $n = \frac{m}{M}$.

The molar mass of carbon dioxide is 44.0 g mol^{-1}.

$$V = \frac{nRT}{P} = \frac{10.0 \times 8.31 \times (25 + 273)}{44.0 \times 101.3}$$

$$= 5.56 \text{ L}$$

10 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

Remember that $n = \frac{m}{M}$.

The molar mass of oxygen is 32.0 g mol^{-1}.

$$n(O_2) = \frac{PV}{RT} = \frac{105 \times 10.0}{8.31 \times (20 + 273)} = 0.431 \text{ mol}$$

$$m(O_2) = n \times M = 0.431 \times 32.0 = 13.8 \text{ g}$$

11 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31$ J K^{-1} mol^{-1}.

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

The molar mass of helium is 4.0 g mol^{-1}.

$$n(\text{He}) = \frac{0.20}{4.0} = 0.050 \text{ mol}$$

$$T = \frac{PV}{nR} = \frac{80 \times 4.0}{0.050 \times 8.31} = 770 \text{ K} = 497°\text{C}$$

12 **a** The molar mass of $CO_2 = 44.0$ g mol^{-1} and $m = n \times M$.
$m(CO_2) = 1.00 \times 44.0 = 44.0$ g

b The volume of 1 mole of any gas at SLC = 24.8 L.

c $$\text{Density}(CO_2) = \frac{44.0}{24.8} = 1.77 \text{ g L}^{-1}$$

d Greater. Gas volume decreases as temperature decreases. Since the mass of gas stays the same, density increases.

13 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31$ J K^{-1} mol^{-1}.

a Conversions are: $P = 100 \times 10^3$ Pa = 100 kPa
$T = 27 + 273 = 300$ K

$$n = \frac{PV}{RT} = \frac{100 \times 5.4}{8.31 \times 300} = 0.22 \text{ mol}$$

b The second step involves using $n = \frac{m}{M}$.

$$M = \frac{m}{n} = \frac{10.0}{0.22} = 46 \text{ g mol}^{-1}$$

14 Container A:

$$n(O_2) = \frac{770 \times 101.3 \times 40.0}{760 \times 8.31 \times (25 + 273)} = 1.66 \text{ mol}$$

Container B:

$$n(O_2) = \frac{390 \times 101.3 \times 0.10}{760 \times 8.31 \times (45 + 273)} = 0.0020 \text{ mol}$$

∴ Container A has more oxygen.

15 The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31$ J K^{-1} mol^{-1}.

a Conversions are: 220 m^3 = 220×10^3 L

$$n(\text{air particles}) = \frac{PV}{RT} = \frac{100 \times 220 \times 10^3}{8.31 \times (23 + 273)} = 8944 \text{ mol} = 8.94 \times 10^3 \text{ mol}$$

b The second step involves using $n = \frac{m}{M}$.

The molar mass of oxygen is 32.0 g mol^{-1} and of nitrogen is 28.0 g mol^{-1}.
20% of the room is oxygen.

$$\therefore n(O_2) = \frac{20}{100} \times 8944 = 1789 \text{ mol}$$

$\therefore m(O_2) = 1789 \times 32.0 = 57.2$ kg
80% of the room is nitrogen.

$$\therefore n(N_2) = \frac{80}{100} \times 8944 = 7155 \text{ mol}$$

$\therefore m(N_2) = 7152 \times 28.0 = 200$ kg
∴ Total mass of gas = 57.2 + 200 = 257 kg

CALCULATIONS INVOLVING COMBUSTION OF FUELS

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

$n(C_3H_8) = \frac{6.70}{44.0} = 0.152$ mol

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

$n(CO_2)$ produced = 3 × 0.152 = 0.457 mol

$\therefore$ $m(CO_2)$ produced = 0.457 × 44.0 = 20.1 g

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

$n(O_2)$ consumed = 5 × 0.152 = 0.761 mol

$\therefore$ $m(O_2)$ consumed = 0.761 × 32.0 = 24.4 g

c $\frac{n(H_2O)}{n(C_3H_8)} = \frac{4}{1}$

$n(H_2O)$ produced = 4 × 0.152 = 0.609 mol

$\therefore$ $m(H_2O)$ produced = 0.609 × 18.0 = 11.0 g

17 The balanced equation shows that 1 mol of glucose produces 2 mol of ethanol. The number of moles of each is found using $n = \frac{m}{M}$ where m is the mass in grams and M is the molar mass in g mol^{-1}. Use a periodic table to calculate the molar masses. M(glucose) = 180.0 g mol^{-1} and M(ethanol) = 46.0 g mol^{-1}.

$\frac{n(\text{ethanol})}{n(\text{glucose})} = \frac{2}{1}$

$n(\text{glucose}) = \frac{80.0}{180.0} = 0.444$ mol

$n(\text{ethanol}) = \frac{2}{1} \times n(\text{glucose}) = 0.889$ mol

$\therefore m(\text{ethanol}) = 0.889 \times 46.0 = 40.9$ g

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

$\frac{n(\text{carbon dioxide})}{n(\text{carbon})} = \frac{1}{1}$

$n(\text{carbon}) = \frac{1\,000\,000}{12.0} = 8.3 \times 10^4$ mol

$n(\text{carbon dioxide}) = n(\text{carbon}) = 8.3 \times 10^4$ mol

$\therefore m(\text{carbon dioxide}) = 8.3 \times 10^4 \times 44.0 = 3.7 \times 10^6$ g = 3.7 tonne

19 The balanced equation shows that 1 mol of propane reacts with 5 mol of oxygen and produces 3 mol of carbon dioxide.

Remember that $n = \frac{m}{M}$. The molar mass of propane is 44.0 g mol^{-1}.

Remember that under SLC, 1 mol of any gas has a volume of 24.8 L.

Use the formula $n = \frac{V}{V_m}$ rearranged as $V = n \times V_m$.

a i $n(C_3H_8) = \frac{22}{44.0} = 0.50$ mol

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

$\therefore V(O_2) = 5 \times 0.50 \times 24.8 = 62$ L

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

$\therefore V(CO_2) = 3 \times 0.50 \times 24.8 = 37$ L

b i $n(C_3H_8) = \frac{5.0}{44.0} = 0.11$ mol

$\therefore V(O_2) = 5 \times 0.11 \times 24.8 = 14$ L

ii $\therefore V(CO_2) = 3 \times 0.11 \times 24.8 = 8.5$ L

c i $n(C_3H_8) = \frac{0.145}{44.0} = 0.00330$ mol

$\therefore V(O_2) = 5 \times 0.00330 \times 24.8 = 0.409$ L

ii $\therefore V(CO_2) = 3 \times 0.00330 \times 24.8 = 0.245$ L

d i $n(C_3H_8) = \frac{16.5}{44.0} = 0.375$ mol

$\therefore V(O_2) = 5 \times 0.375 \times 24.8 = 46.5$ L

ii $\therefore V(CO_2) = 3 \times 0.375 \times 24.8 = 27.9$ L

e i $n(C_3H_{8)} = \frac{3400}{44.0} = 77$ mol

$\therefore V(O_2) = 5 \times 77 \times 24.8 = 9.6 \times 10^3$ L

ii $\therefore V(CO_2) = 3 \times 77 \times 24.8 = 5.7 \times 10^3$ L

20 The general gas equation needs to be used: $PV = nRT$. Temperature should be in kelvin, pressure in kPa and volume in L. $R = 8.31$ J K^{-1} mol^{-1}

The second step involves using $n = \frac{m}{M}$. The molar mass of octane is 114.0 g mol^{-1}.

The balanced equation shows that 2 mol of octane produces 16 mol of carbon dioxide.

$$n(CO_2) = \frac{PV}{RT} = \frac{1.10 \times 101.3 \times 50.0}{8.31 \times (120 + 273)} = 1.70 \text{ mol}$$

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

$$n(C_8H_{18}) = \frac{2}{16} \times n(CO_2) = \frac{2}{16} \times 1.70 \text{ mol} = 0.213 \text{ mol}$$

$$\therefore m(C_8H_{18}) = n(C_8H_{18}) \times M = 0.213 \times 114.0 = 24.3 \text{ g}$$

21 The balanced equation for the reaction is:

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$

Since all measurements are made at the same temperature and pressure, the equation gives us not only the mole ratio with which the gases react with each other, but also the volume ratio. For 10.0 L of ethane to react completely $\frac{7}{2} \times 10.0$ of oxygen is required.

$\therefore$35.0 L of oxygen is required for the complete combustion of 10.0 L of ethane.

22 The balanced equation shows that 1 mol of methane reacts with 2 mol of oxygen to give 1 mol of carbon dioxide, and 2 mol of water. At constant temperature and pressure, mole and volume are directly proportional to each other.

a $\therefore V(CH_4)$ used = 5 L

b $\therefore V(O_2)$ used = 10 L

c Use the universal gas equation, $PV = nRT$ and $n = \frac{m}{M}$. The molar mass of water is 18.0 g mol^{-1}.

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

$$n(H_2O) = 2 \times n(CO_2)$$

$$n(H_2O) = 2 \times \frac{PV}{RT} = \frac{2 \times 100 \times 5.0}{8.31 \times (200 + 273)} = 0.25 \text{ mol}$$

$$\therefore m(H_2O) = 0.254 \times 18.0 = 5 \text{ g}$$

23 a The balanced equation shows that the mole ratio of propane to oxygen is 1 : 5. All temperatures and pressures are the same, therefore mole and volume are directly proportional to each other.

$\therefore$ 80 mL of propane would need 400 mL of oxygen to react completely, and 500 mL of oxygen would need 100 mL of propane to react completely.

$\therefore$ There is excess oxygen, which means that all of the propane will react, and that there will be 100 mL of oxygen in excess.

b $V(CO_2) = 3 \times 80$

$= 240$ mL

$V(H_2O) = 4 \times 80$

$= 320$ mL

c The original volume of gases = 80 + 500 = 580 mL

The final volume of gases = 100 + 240 + 320 = 660 mL

$\therefore$ There was an increase in volume of 80 mL.

24 The balanced equation is:

$CaCO_3(s) + 4H_2(g) \rightarrow CH_4(g) + Ca(OH)_2(s) + H_2O(g)$

It shows the mole ratio is 1 : 4 : 1 : 1 : 1.

a When temperature and pressure are constant, mole and volume are directly proportional to each other.

∴ The volume of methane produced will be $\frac{1}{4}$ the volume of hydrogen used.

∴ The volume of methane will be $100 \times \frac{1}{4} = 25$ L.

b The universal gas equation needs to be used: $PV = nRT$. Temperature should be in K, pressure in kPa and volume in L. $R = 8.31$ J K^{-1} mol^{-1}.

$n(H_2) = \frac{PV}{RT} = \frac{100 \times 100}{8.31 \times (400 + 273)} = 1.79$ mol

The mole ratio shows: $\frac{n(CaCO_3)}{n(H_2)} = \frac{1}{4}$

∴ The number of mole $CaCO_3 = \frac{1.79}{4} = 0.447$ mol

The molar mass of $CaCO_3 = 40.1 + 12.0 + 48.0 = 100.1$ g mol^{-1}

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

$m(CaCO_3) = n \times M$

$= 0.447 \times 100.1 = 44.7$ g

25 Write a balanced equation:

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

For each minute of operation:

$n(C_3H_8) = \frac{12.7}{44.0} = 0.289$ mol

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

$n(O_2)$ required $= 0.289 \times 5 = 1.44$ mol

$m(O_2)$ required per minute $= 1.44 \times 32.0 = 46.2$ g

26 Write a balanced equation.

$C(s) + O_2(g) \rightarrow CO_2(g)$

Calculate the mass of carbon in coal.

$m(C) = 13.0 \times 10^6 \times \frac{25}{100}$

$= 3.25 \times 10^6$ tonnes

$= 3.25 \times 10^{12}$ g

Calculate the amount of carbon.

$n(C) = \frac{3.25 \times 10^{12}}{12.0}$

$= 2.71 \times 10^{11}$ mol

From the equation, 1 mol CO_2 is produced from every mole of C. Calculate the amount of carbon dioxide.

$\frac{n(CO_2)}{n(C)} = 1$

$n(CO_2) = 2.71 \times 10^{11}$ mol

Calculate the volume of CO_2 at SLC.

$V(CO_2) = 2.71 \times 10^{11}$ mol $\times 24.8$ L mol^{-1}

$= 6.72 \times 10^{12}$ L

CALCULATIONS INVOLVING ENERGY CHANGES

27 $n(C_4H_9OH) = \frac{m}{M} = \frac{806}{74.0} = 10.9$ mol

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

∴ 10.9 mol of C_4H_9OH yields x kJ

By proportion, $x = 2677 \times 10.9 = 2.92 \times 10^4$

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

28 **a** From the equation:

2 moles of octane release 10 900 kJ.

Let x moles of octane release 100 kJ.

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

$x = \frac{100 \times 2}{10900} = 0.0182$ mol

$m(C_8H_{18}) = n \times M = 0.0182 \times 114.0 = 2.09$ g

b Mass = density × volume ∴ $m(C_8H_{18}) = 0.698 \times 50\,000 = 3.49 \times 10^4$ g

$n(C_8H_{18}) = \frac{m}{M} = \frac{3.49 \times 10^4}{114.0} = 306$ mol

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

∴ 306 mol of C_8H_{18} release x kJ.

By proportion, $x = \frac{10900 \times 306}{2} = 1.67 \times 10^6$ kJ

Energy produced = 1.67×10^3 MJ

29 $n(CO_2) = \frac{m}{M} = \frac{1000000}{44.0} = 2.27 \times 10^4$ mol

From the thermochemical equation, the production of 3 mol CO_2 release 2220 kJ of energy.

By proportion: $\frac{2.27 \times 10^4}{3} = \frac{x}{2220}$

$x = \frac{2.27 \times 10^4 \times 2220}{3} = 1.68 \times 10^7$ kJ = 1.68×10^4 MJ

Energy released = 1.68×10^4 MJ

30 From the thermochemical equation, the production of 4 mol CO_2 releases 3120 kJ of energy.

1 Calculate the volume occupied by the carbon dioxide produced when 3120 kJ is generated:

At SLC, $V(CO_2) = n \times V_m = 4 \times 24.8 = 99.2$ L

2 So production of 99.2 L of CO_2 releases 3120 kJ (3.120 MJ).

Let the production of x L of CO_2 release 1 MJ of energy.

By proportion:

$\frac{x}{99.2} = \frac{1}{3.120}$

$x = \frac{99.2}{3.120}$

= 31.8 L

So $V(CO_2)$ produced at SLC = 31.8 L

31 **a** For CH_4:

1 mol of methane produces 890 kJ.

Let x mol produce 100 000 kJ.

By proportion:

$\frac{x}{1} = \frac{100000}{890}$

$x = \frac{100000}{890} \times 1$

= 112.4 mol

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

$m(CH_4) = n \times M$

$= 112.4 \times 16.0$

$= 1798$ g

$= 1.80$ kg

For C_3H_8:

1 mol of propane produces 2220 kJ.

Let x mol produce 100 000 kJ.

By proportion:

$$\frac{x}{1} = \frac{100\,000}{2220}$$

$$x = \frac{100\,000}{2220} \times 1$$

$= 45.05$ mol

$m(C_3H_8) = n \times M$

$= 45.05 \times 44.0$

$= 1982$ g

$= 1.98$ kg

b For CH_4:

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

$n(CH_4)$ reacted = 112.4 mol (from part **a**)

$$\frac{n(CO_2)}{n(CH_4)} = \frac{1}{1}$$

$n(CO_2) = 112.4$ mol

$m(CO_2) = n \times M$

$= 112.4 \times 44.0$

$= 4949$ g

$= 4.95$ kg

For C_3H_8:

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

$n(C_3H_8)$ reacted = 45.05 mol (from part **a**)

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

$$n(CO_2) = 45.05 \times \frac{3}{1}$$

$= 135$ mol

$m(CO_2) = n \times M$

$= 135 \times 44.0$

$= 5946$ g

$= 5.95$ kg

c For CH_4:

The production of 100 MJ of heat energy releases 4.95 kg of CO_2 (from part **b**)

Let x be the heat energy released by 1 tonne of CO_2

4.95 kg = 4.95×10^{-3} tonne

By proportion:

$$\frac{x}{100} = \frac{1}{4.95 \times 10^{-3}}$$

$$x = \frac{1}{4.95 \times 10^{-3}} \times 100$$

$= 2.02 \times 10^4$ MJ tonne^{-1}

For C_3H_8:

The production of 100 MJ of heat energy releases 5.95 kg of CO_2

Let x be the heat energy released by 1 tonne of CO_2

5.95 kg = 5.95×10^{-3} tonne

By proportion:

$$\frac{x}{100} = \frac{1}{5.95 \times 10^{-3}}$$

$$x = \frac{1}{5.95 \times 10^{-3}} \times 100$$

$$= 1.68 \times 10^4 \text{ MJ tonne}^{-1}$$

d A lower mass of methane is required to produce 100 MJ of energy, so methane has the higher energy content. A lower mass of carbon dioxide is released in generating this amount of energy. This means methane has a higher amount of heat energy produced per tonne of carbon dioxide released.

CONNECTING THE MAIN IDEAS

32 **a** Equal. With pressure, volume and temperature the same, *n* will be the same.

b Carbon dioxide. Each CO_2 molecule contains 3 atoms and each O_2 molecule contains 2 atoms. As there are an equal amount of molecules of each gas, there are more atoms in the CO_2 sample.

c Carbon dioxide. Density = mass ÷ volume. The volume is the same for each gas, but the mass of CO_2 is greater, so it has the greater density.

33 $n(CO_2)$ in 1 tonne $= \frac{10^6}{44.0}$

$$= 2.27 \times 10^4 \text{ mol}$$

The production of 2.27×10^4 mol of CO_2 releases 1.68×10^4 MJ.

Let the production of 3 mol of CO_2 release x MJ.

By proportion:

$$\frac{3}{2.27 \times 10^4} = \frac{x}{16\,800}$$

$$x = \frac{3}{2.27 \times 10^4} \times 16800$$

$$= 2.218 \text{ MJ}$$

$$= 2218 \text{ kJ}$$

The ΔH value is negative because this reaction is exothermic.

$\Delta H = -2.22 \times 10^3 \text{ kJ mol}^{-1}$

34 **a** $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

b **i** $m(C_2H_5OH) = 1.000 \text{ kg} = 1000 \text{ g}$

$n(C_2H_5OH) = \frac{m}{M} = \frac{1000}{46.0} = 21.7 \text{ mol}$

$n(CO_2) = 2 \times n(C_2H_5OH) = 2 \times 21.7 = 43.5 \text{ mol}$

$m(CO_2) = n \times M = 43.5 \times 44.0 = 1913 \text{ g} = 1.91 \text{ kg}$

ii $V(CO_2) = n \times V_m = 43.5 \times 24.8 = 1078 \text{ L} = 1.08 \times 10^3 \text{ L}$

c **i** density $= \frac{m}{V}$ so $m(C_2H_5OH) = d \times V = 0.785 \times 50.0 \times 1000 = 39250 \text{ g} = 39.3 \text{ kg}$

ii $n(C_2H_5OH) = \frac{39250}{46.0} = 853 \text{ mol}$

Reaction of 1 mol C_2H_5OH generates 1367 kJ.

So reaction of 853 mol C_2H_5OH generates x kJ.

By proportion:

$$\frac{853}{1} = \frac{x}{1367}$$

$$x = \frac{853}{1} \times 1367$$

$$= 1\,166\,408 \text{ kJ}$$

$$= 1166 \text{ MJ}$$

Energy released = 1.17×10^3 MJ

d From the equation, 2 mole of CO_2 are released when 1367 kJ of energy is generated.
So x mole of CO_2 is released when 1.00 kJ of energy is generated.

By proportion: $\frac{x}{2} = \frac{1.00}{1367}$

$x = \frac{2 \times 1.00}{1367} = 0.001463$ mol

$n(CO_2) = 0.001463$ mol
$m(CO_2) = n \times M = 0.001463 \times 44.0 = 0.0644$ g

Chapter 4 Redox reactions

Section 4.1 Oxidation and reduction

4.1 Key questions

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

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

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

As the nickel metal goes from solid metal to a positive ion it must be losing electrons, therefore being oxidised.

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

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

5 **a** $Zn(s)$
  b $Ca(s)$
  c Br^- ions in AgBr

6 **a** Oxidant O_2, reductant Zn
  b Oxidant Cl_2, reductant Ca
  c Oxidant Ag^+ in AgBr, reductant Br^- in AgBr

7 **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.

Section 4.2 Oxidation numbers

Worked example: Try yourself 4.2.1

CALCULATING OXIDATION NUMBERS

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

Thinking	Working
Identify an element that has a set value.	Na is a main group metal in group 1. 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.	$\overset{+1}{Na}\overset{+5}{N}\overset{-2}{O_3}$

Worked example: Try yourself 4.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation: $\text{CuO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Cu(s)} + \text{H}_2\text{O(l)}$	
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 a variable oxidation state, let the oxidation number = *x* $x + -2 = 0$ $x = +2$ $\overset{+2}{\text{Cu}}\text{O(s)} + \text{H}_2\text{(g)} \rightarrow \overset{0}{\text{Cu}}\text{(s)} + \text{H}_2\text{O(l)}$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of copper decreased from +2 to 0, so the copper in CuO has been reduced.
Determine the oxidation numbers of a second element on the left-hand and the right-hand side of the equation.	Choose hydrogen as the second element. $\text{CuO(s)} + \overset{0}{\text{H}}_2\text{(g)} \rightarrow \text{Cu(s)} + \overset{+1}{\text{H}}_2\text{O(l)}$
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. $\text{Cu}\overset{-2}{\text{O}}\text{(s)} + \text{H}_2\text{(g)} \rightarrow \text{Cu(s)} + \text{H}_2\overset{-2}{\text{O}}\text{(l)}$ The oxidation number of O has not changed.

4.2 Key questions

1
  - **a** +2
  - **b** +4
  - **c** –4
  - **d** 0
  - **e** +4

2 K_2MnO: 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 4.3 Writing complex redox equations

Worked example 4.3.1: Try yourself

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half-equation for the reduction of an acidified solution of MnO_4^- to solid MnO_2.	
Thinking	**Working**
Balance all elements except hydrogen and oxygen in the half-equation.	There is 1 Mn in MnO_4^- and 1 Mn in MnO_2 so the Mn atoms are balanced. $MnO_4^- \rightarrow MnO_2$
Balance the oxygen atoms by adding water.	There are 4 O atoms in MnO_4^- and only 2 O atoms in MnO_2 so 2 H_2O must be added to the 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 $4H^+$ are 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 are 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 4.3.2: Try yourself

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.	$2SO_3^{2-}(aq) + \overset{4H^+}{\cancel{16H^+(aq)}} + 12e^- \rightarrow 2H_2S(g) + \cancel{6H_2O(l)}$ $3ClO^-(aq) + \cancel{6H_2O(l)} \rightarrow 3ClO_3^-(aq) + \cancel{12H^+(aq)} + 12e^-$ $2SO_3^{2-}(aq) + 4H^+(aq) + 3ClO^-(aq) \rightarrow 2H_2S(g) + 3ClO_3^-(aq)$

4.3 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 $2MnO_2(s) + 4H^+(aq) + S(s) \rightarrow 2Mn^{2+} + 2H_2O(l) + SO_2(g)$

CHAPTER 4 **REVIEW**

OXIDATION AND REDUCTION

1 **a** False
b False
c True
d False

2 loses, positive, loses, gains, negative, gains, 7, gains, bromide

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

4 **a** Oxidation
b Oxidation
c Reduction
d Oxidation

e Reduction

f Reduction

5 **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: $Na^+(aq) + e^- \rightarrow Na(s)$

6 **a** Cu(s)

b Mg(s)

c Zn(s)

d Ni(s)

OXIDATION NUMBERS

7 **a** +4

b –2

c +6

d +6

e +4

f +2

8

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

9 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

10 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

11

	Species	**Oxidation number of the underlined atom**
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

12 **a** **i** 0

ii +2

b **i** +5

ii +4

c oxidant HNO_3; reductant Cu

13

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

WRITING COMPLEX REDOX EQUATIONS

14

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 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.	$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

15 $2IO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow I_2(aq) + 6H_2O(l)$

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

Reduction half-equation: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

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

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^+

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

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

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

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

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

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

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

$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

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

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

18 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:
$Zn(s) + 2MnO_2(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l)$

19 a Half-equations:
$C_6H_8O_6(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2e^-$
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

b The oxidation reaction is: $C_6H_8O_6(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2e^-$
The reduction reaction is: $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

20 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^+.
$6H_3AsO_4(aq) + 2I^-(aq) \rightarrow 3As_2O_3(s) + 2IO_3^-(aq) + 9H_2O(l)$

CONNECTING THE MAIN IDEAS

21 a i +3
ii +2
iii +4

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

22 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 $Cr_2O_7^{2-}(aq)/Cr_2O_3(s)$

23 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 reactant, Fe.

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

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

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

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

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

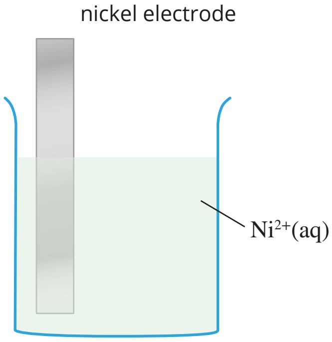
Chapter 5 Galvanic cells as a source of energy

Section 5.1 Galvanic cells

5.1 Key questions

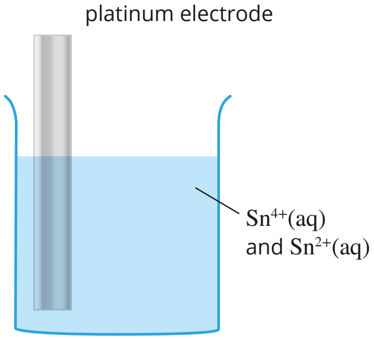
1 D. A is incorrect because in galvanic cells, the electrode in the half-cell in which oxidation occurs is called the anode.
B is incorrect because electrons flow from the anode to the cathode. The cathode is where reduction takes place.
C is incorrect because anions do not flow into the half-cell where 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**



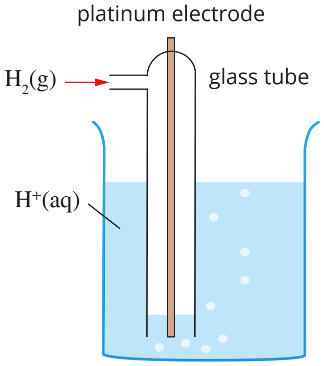
$Ni^{2+}(aq)/Ni(s)$ half-cell

b



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

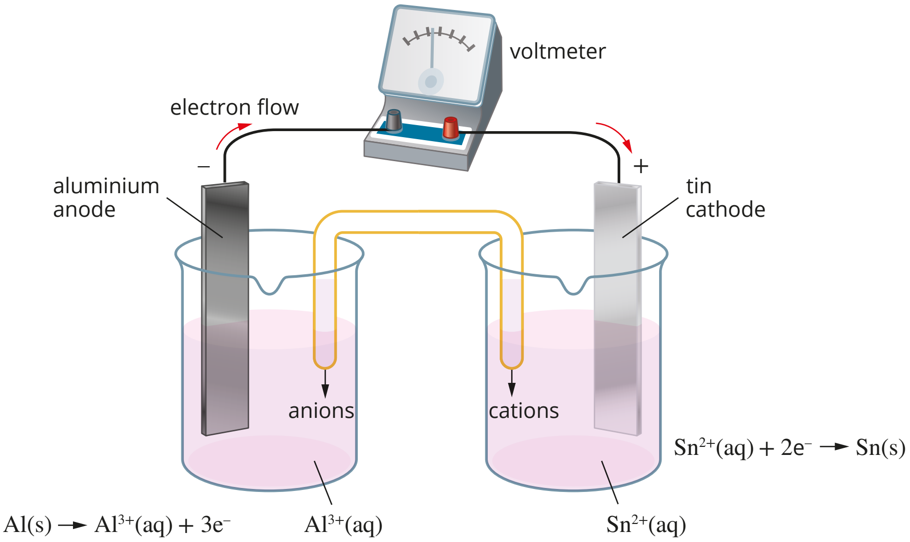
c



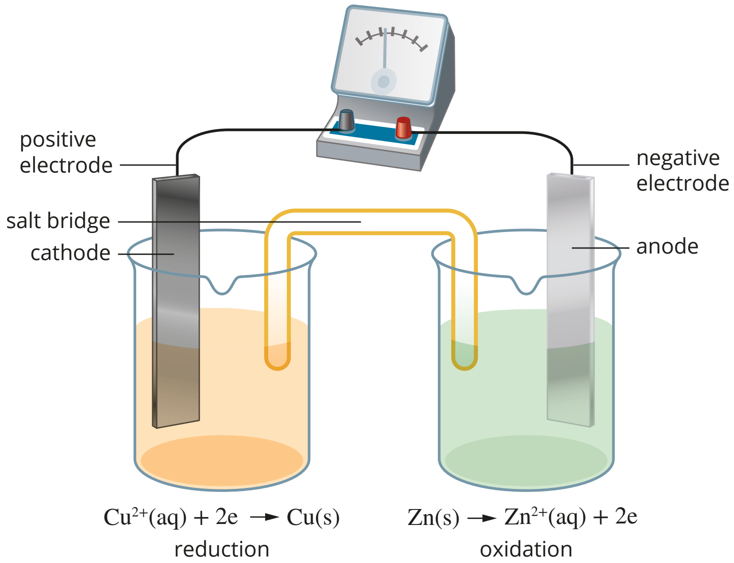
$H^+(aq)/H_2(g)$ half-cell

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



5 $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$



Section 5.2 The electrochemical series

Worked example: Try yourself 5.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $Sn^{2+}(aq)/Sn(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells under standard conditions. 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 $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E° = –0.23$ V
Identify the strongest oxidising agent (the species on the left of the series with the most positive *E*° value) and the strongest reducing agent (bottom right).	Because Sn^{2+} is higher on the left side of the table than Ni^{2+}, it is the stronger oxidising agent. Ni, being lower on the right side of the table than Sn, is the stronger reducing agent.
Write the two half-equations that will occur. The strongest oxidising agent will react with the strongest reducing agent. (Hint: The reduction equation has the most positive *E*° value and the oxidation equation has the most negative *E*° value.)	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).

5.2 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:

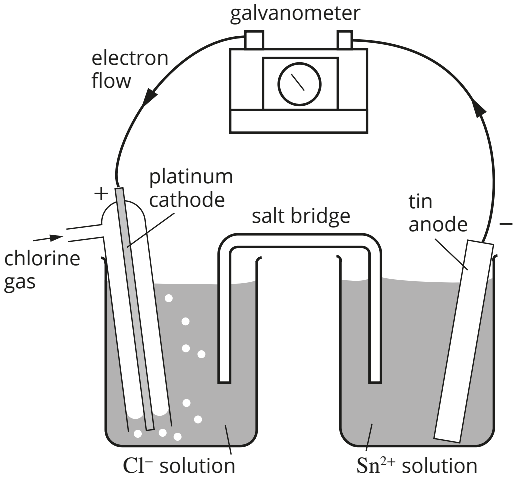
$[Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)] \times 3$

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

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

c The lead electrode will be the cathode and the aluminium electrode will be the anode.

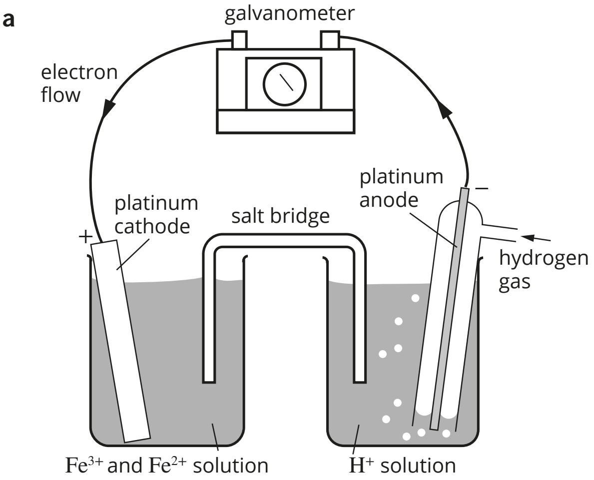
2



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

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

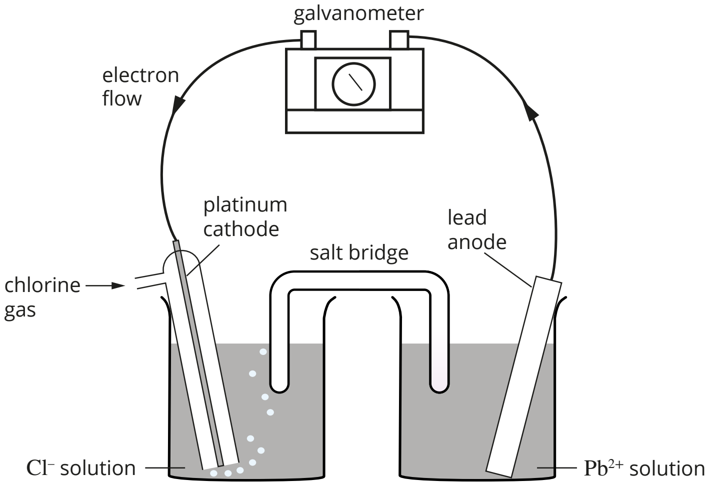
3 **a**



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

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

b



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

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

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 – (–1.67)
= 1.54 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 5.3 Predicting direct redox reactions

Worked example: Try yourself 5.3.1

PREDICTING DIRECT REDOX REACTIONS

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

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

5.3 Key questions

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

2 C. Ag^+ 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 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 between Fe and Cl^- because they are both reducing agents.

Section 5.4 Everyday sources of power

5.4 Key questions

1 Secondary cells can be recharged whereas primary cells cannot.

2 D. On recharging a secondary cell, the cell reactions are reversed. Oxidation now occurs at the positive terminal (the anode) and reduction occurs at the negative terminal (the cathode).

3 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.

4 **a** True
b True
c False
d True
e False
f False

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

CHAPTER 5 REVIEW

GALVANIC CELLS

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.

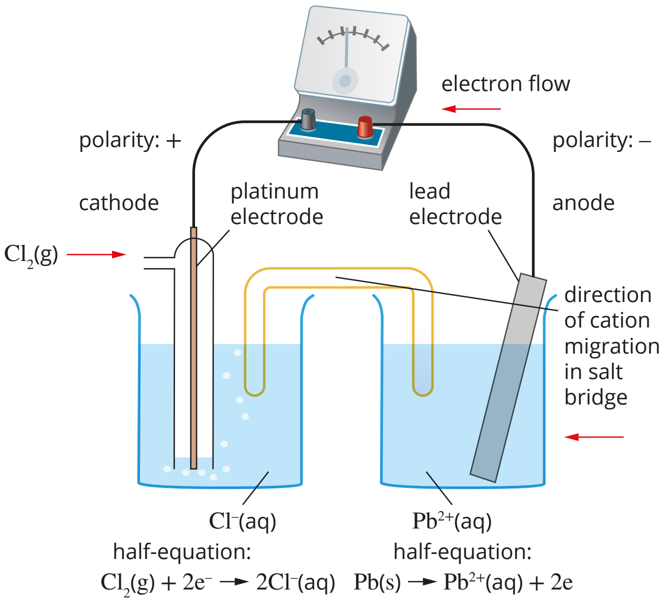
3 **a** Oxidant: a substance that causes another substance to be oxidised and is reduced in the process. Reductant: a substance that causes another substance to be reduced and is oxidised in the process.

b Anode: electrode at which oxidation occurs. Cathode: electrode at which reduction occurs.

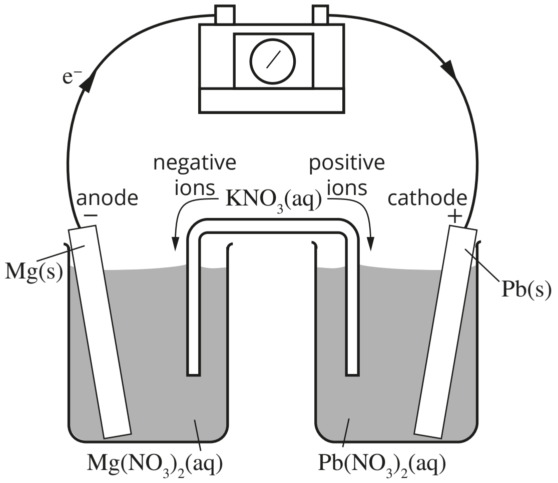
c Conjugate redox pair: an oxidant and its corresponding reduced form, e.g. Cu^{2+}/Cu. The reduced form has gained electrons. Conjugate acid–base pair: A conjugate acid contains one more hydrogen ion or proton than the base.

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



5 **a**



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

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

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

c 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.

THE ELECTROCHEMICAL SERIES

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.

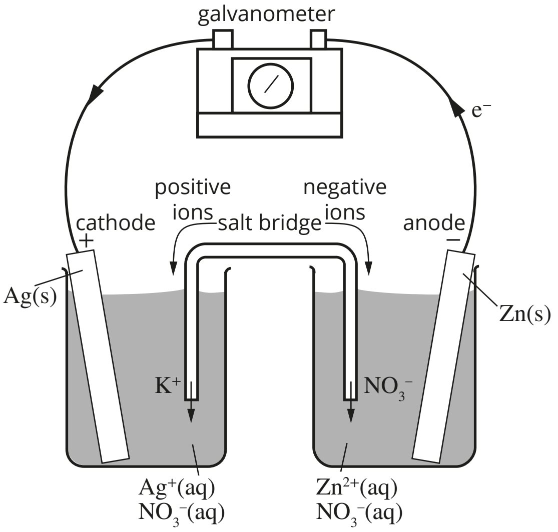
In the second cell, the reducing agents are Fe^{2+} and Br^{-}. Because Fe^{2+} is contained in the half-cell with the anode, Fe^{2+} is the stronger reducing agent.

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 $E° = E° (Br_2(l)/Br^-(aq)) – E° (Ni^{2+}(aq)/Ni(s)) = 1.09 – (–0.23) = 1.32$ 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 $E° = E° (Fe^{3+}(aq)/Fe^{2+}(aq)) – E° (Ni^{2+}(aq)/Ni(s)) = 0.77 – (–0.23) = 1.00$ V
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{2+}(aq)/Fe(s)$
  cell $E° = E° (Ni^{2+}(aq)/Ni(s)) – E° (Fe^{2+}(aq)/Fe(s)) = –0.23 – (–0.44) = 0.21$ V

9 **i**

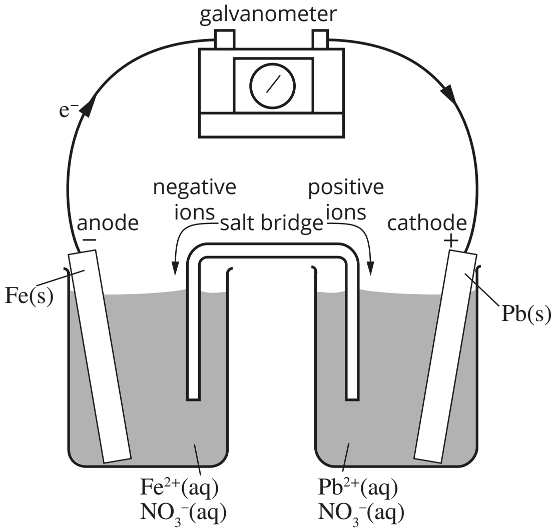


Cathode (+): $Ag^+(aq) + e^- \longrightarrow Ag(s)$

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

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

ii

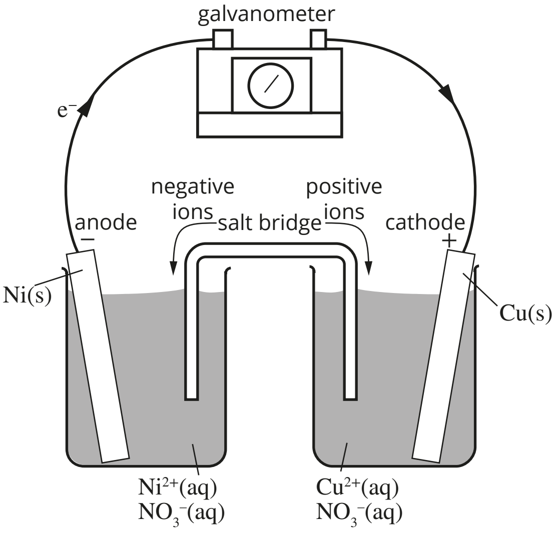


Cathode (+): $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$

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

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

iii



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

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

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

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 $B^{2+} > A^{2+} > C^{2+} > D^{2+}$.

PREDICTING DIRECT REDOX REACTIONS

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.

EVERYDAY SOURCES OF POWER

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

Primary cell: A non-rechargeable galvanic cell

Secondary cell: A rechargeable galvanic cell

17 **a** Electrons flow away from the negative electrode (anode), through the external circuit, to the positive electrode (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 In secondary or rechargeable cells such as lithium ion cells or a lead–acid battery, the products of cell reaction remain in contact with the electrodes and are in forms that can be converted back to reactants.

19 When a cell discharges, oxidation occurs at the anode which has a negative polarity. Reduction occurs at the cathode, which has positive polarity. The oxidation and reduction reactions in the cell generate electricity. When the cell is recharged, the direction of the electron flow is reversed. An external supply of electricity is required to reverse these reactions. Oxidation now occurs at the positive electrode while reduction occurs at the negative electrode.

20 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.

CONNECTING THE MAIN IDEAS

21 half-cells, anode, cathode, negative, positive

cannot, can

increases, side reactions

22 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 oxidant 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 oxidant 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.

23 **a** Bromine is a stronger oxidant than iodine, so it reacts with iodide ions. Because bromine is a weaker oxidant than chlorine, bromine does not react with chloride ions.

b Hydrogen peroxide acts as both a strong oxidant and as a weak reductant. (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 oxidant. Tin metal can reduce Sn^{4+} ions so that they re-form Sn^{2+} ions.

d Zinc is a stronger reductant 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.

24 The brown stain contains iodine (I_2). A reductant 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.

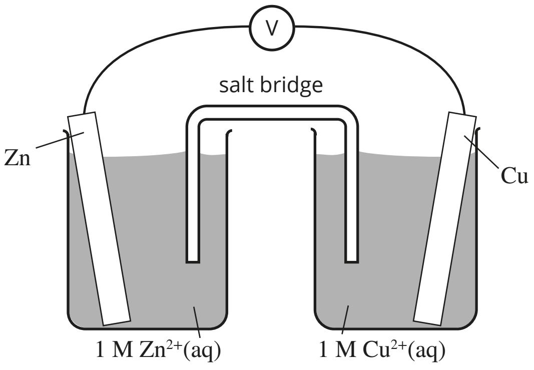
25 The electrochemical series is based on reactions occurring under standard conditions of 25°C (298 K), 1 bar (100 kPa) pressure and 1 M concentration and can only be used to predict the possibility of reaction occurring under these conditions. The series gives no information about the rate of reactions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

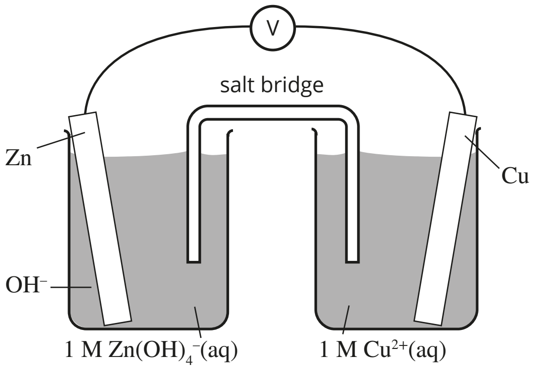
26 **a** $Zn(s) + 4OH^-(aq) + Cu^{2+}(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2Cu(s)$

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).





Chapter 6 Fuel cells as a source of energy

Section 6.1 Continuous sources of electrical energy

6.1 Key questions

1 A

2 B, C, G

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

4 **a** $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$
   b Reduction of $O_2(g)$
   c NaOH(aq) or KOH(aq)
   d Oxygen is reduced, forming OH^- ions at the cathode of the fuel cell, so an increase in pH occurs at this electrode initially. The OH^- ions migrate to the anode where they are consumed. Once the rate of production of OH^- ions at the cathode becomes equal to the rate at which they depart, the pH near the electrode will be constant.
   e A fuel cell converts chemical energy into electrical energy directly, with relatively little energy being converted into thermal energy. If electrical energy were obtained by burning methanol (in a process similar to that used to obtain electrical energy from coal in coal-fired power stations), the energy 'losses' of the various energy transformations involved would be greater. In particular, large losses occur when thermal energy is converted into mechanical energy.

5 Fuel cells are about twice as efficient as coal-fired power stations. Consequently, fuel cells produce the same quantity of energy from about half as much fuel. Less fuel means less carbon dioxide gas is produced. As carbon dioxide is a major greenhouse gas, the use of fuel cells has the potential to reduce the greenhouse effect.

CHAPTER 6 REVIEW

CONTINUOUS SOURCES OF ELECTRICAL ENERGY

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

2 C

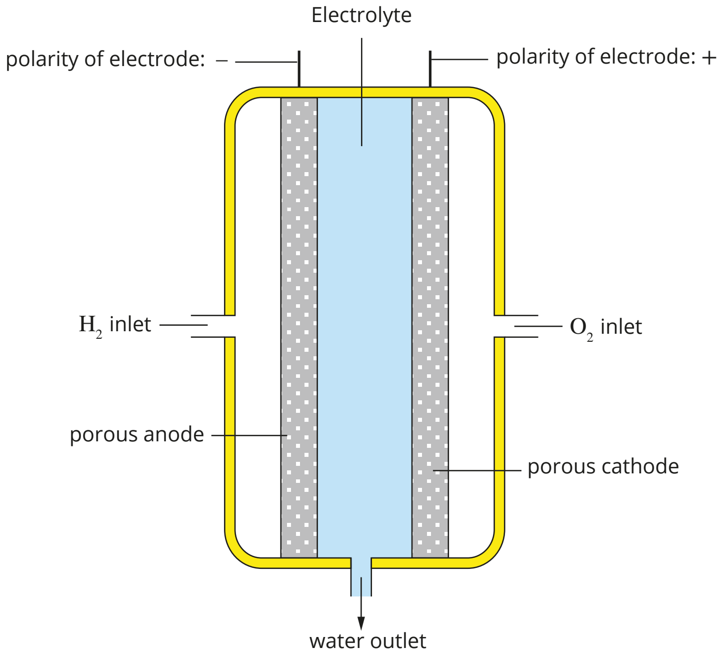
3 B. B is the only option that is not a fuel. In a fuel cell, the fuel is oxidised at the anode.

4 B

5 **a** True
   b False
   c True
   d False
   e False

6 Chemical, electrical, fuel, oxidation, oxidising agent, reduced, reactants, electrolyte, electrolyte, no direct contact, more, much less, energy and water, hydrogen

7



8 **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

9 **a** $CH_3CH_2OH(g) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
b $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
c Cations will move towards the cathode. Because H^+ ions are involved in the reduction reaction, positive charge is decreasing at the cathode. To maintain charge neutrality, cations from the electrolyte will move towards the cathode.
d Yes. The net cell reaction in the fuel cell is the oxidation of ethanol to form carbon dioxide and water. Like ethanol, methane in natural gas can be oxidised to carbon dioxide and water. Provided the electrode materials used in the cell act as effective catalysts for both reactions, it is likely that the use of natural gas would produce a voltage.

10 **a** $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$. Oxidation occurs at the anode, which is the negative electrode in a fuel cell. CH_4 is the fuel that is oxidised.
b Cell potential difference = high half-cell $E°$ – lower half-cell $E°$
= +1.23 – (+0.17)
= 1.06 V

11 **a** $HCHO(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
b $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$. Reduction occurs at the cathode. Oxygen is the oxidising agent; therefore, it undergoes reduction. Since an alkaline electrolyte is used in the fuel cell, oxygen has to be reduced to form OH^- ions.

CONNECTING THE MAIN IDEAS

12 **a** $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
b X is the anode and Y is the cathode.
c Because fuel cells are more efficient at converting chemical energy to electrical energy, there will be less CO_2 emitted to the atmosphere per joule of energy generated.

13 **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.

14 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 7 Rate of chemical reactions

Section 7.1 Investigating the rate of chemical reactions

7.1 Key questions

1 C

2 **a** Increasing
b Increasing
c Increasing
d Increasing
e Adding

3 **a** $CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$
b The reaction rate is decreasing because the gradient of the graph is decreasing.

4 **a** Using smaller pieces of wood with a larger surface area
b Using a brick cleaner with a higher concentration
c Increasing the temperature of the oven

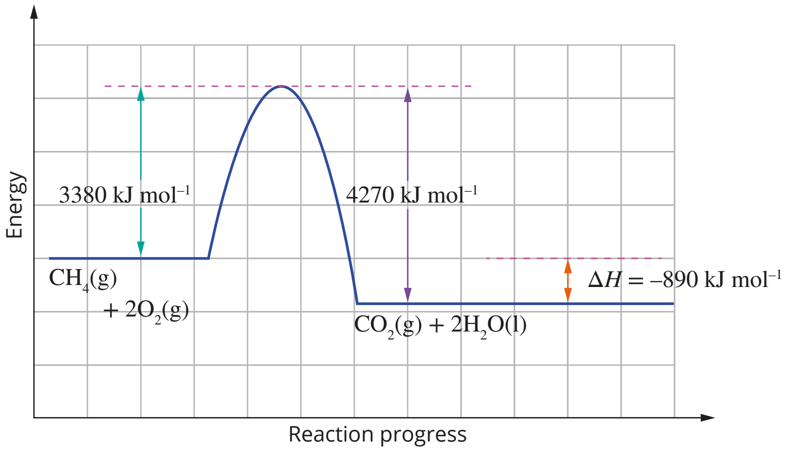
Section 7.2 Collision theory

7.2 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 **a** $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
b –890 kJ mol^{-1}
c



4 139 kJ mol^{-1}

Section 7.3 Effect of temperature on rate of reaction

Worked example: Try yourself 7.3.1

USING COLLISION THEORY TO EXPLAIN CHANGES IN RATES OF REACTIONS

Iron anchors recovered from shipwrecks at considerable depths can show little corrosion after years in the sea. Explain this observation in terms of collision theory.	
Thinking	**Working**
Consider the state of the reactants.	The iron anchor is a solid. The oxygen is a gas dissolved in the sea water.
Relate the state of the reactant to the factor that affects the reaction rate and explain in terms of collision theory.	The surface area of the iron anchor is relatively small. The concentration of oxygen at greater depths in the ocean is much lower. The frequency of collisions with reacting particles that could cause corrosion would be low so the rate of corrosion would also be low.
Return to the question to complete your answer.	The surface area of the iron anchor is relatively small so the frequency of collisions with reacting particles would be low. The concentration of oxygen at greater depths is also low so the frequency of collisions is further reduced. Therefore, the rate of corrosion is reduced.

7.3 Key questions

1 D. An increase in concentration increases collision frequency between reactant particles.

2 A, B and C. A is true because a reaction with a large activation energy would have a low proportion of reactant particles colliding with energy equal to or greater than the activation energy for the reaction.

B is true because a low temperature means a low proportion of reactant particles collide with energy equal to or greater than the activation energy for the reaction.

C is true because for a reaction to occur, reactant particles need to collide with the correct orientation.

3 D, F, B, E, C and A. D is slowest because it has the lowest surface area, lowest concentration and lowest temperature.

F is faster (than D) because it has a larger surface area.

B is faster (than F) because it has a higher temperature.

E is faster (than B) because it has a larger surface area.

C is faster (than E) because it has a higher temperature.

A is the fastest because it has the largest surface area, highest concentration and highest temperature.

4 **a** At higher temperatures the molecules that react to form fibreglass plastics have greater energy. They collide more frequently and are more likely to have a total energy exceeding the activation energy of the reaction involved, increasing the rate of reaction.

b Fine particles have a large surface area, resulting in a high frequency of collisions of aluminium particles with gas molecules (such as oxygen) in the air and hence rapid reaction rate. The aluminium can burn vigorously and release a large quantity of heat.

c At high altitude, such as in Nepal, air pressure is considerably lower than at any location in the Australian bush and so the water boils at a lower temperature in Nepal (up to 30°C lower). Thus, the average kinetic energy of the molecules in the potato is lower, so they are less likely to have a total energy exceeding the activation energy of the reactions involved in cooking a potato, so the potato cooks slower.

Section 7.4 Catalysts

1 D. A and C are decreased because a catalyst decreases the activation energy required for a reaction.

2 **a** A substance that increases the rate of a chemical reaction without itself undergoing permanent change.

b The minimum amount of energy required by the reactants in order to form products in a reaction.

3 When salt is mixed with sugar, the salt acts as a catalyst and lowers the activation energy of the combustion reaction between sugar and oxygen.

4 **a** Reactions involving a heterogeneous catalyst take place at the surface of the catalyst. Reactants form bonds with the catalyst, lowering the activation energy of reactions and allowing them to proceed more rapidly.

b A porous pellet has a much larger surface area than a solid lump. More reactants may be in contact with the surface of a porous pellet at any instant, producing a faster rate of reaction.

CHAPTER 7 REVIEW

INVESTIGATING THE RATE OF CHEMICAL REACTIONS

1 D

2 C. Powder has a higher surface area than chips, and 2 M is a higher concentration than 1 M.

3 B

4 B. The rate of reaction is a measure of the change in concentration of a substance over time. Only B has units that correspond to concentration (mol L^{-1}) per unit time (s^{-1}).

5 **a** A gas is produced so mass is lost from the mixture.

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

$= \frac{5.00}{63.5}$

$= 0.0787$ mol

$n(\text{HNO}_3) = cV$

$= 2.00 \times 0.500 = 1.00$ mol

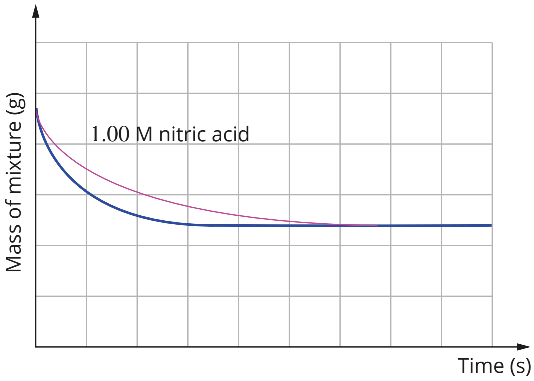
$n(\text{HNO}_3)$ react with Cu $= \frac{8}{3} \times n(\text{Cu})$

$= \frac{8}{3} \times 0.0787$

$= 0.210$ mol

$0.210 < 1.00$; therefore HNO_3 is in excess. So Cu is limiting.

c

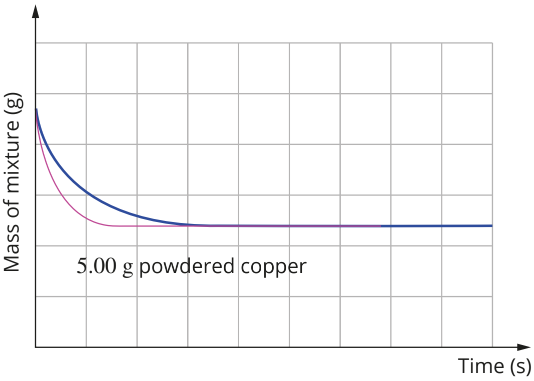


Decreased rate of mass loss due to lower nitric acid concentration.

($n(\text{HNO}_3) = cV = 1.00 \times 0.500 = 0.500$ mol)

Copper is still limiting, so final mass remains the same.

d



Increased rate of mass loss due to increased copper surface area.

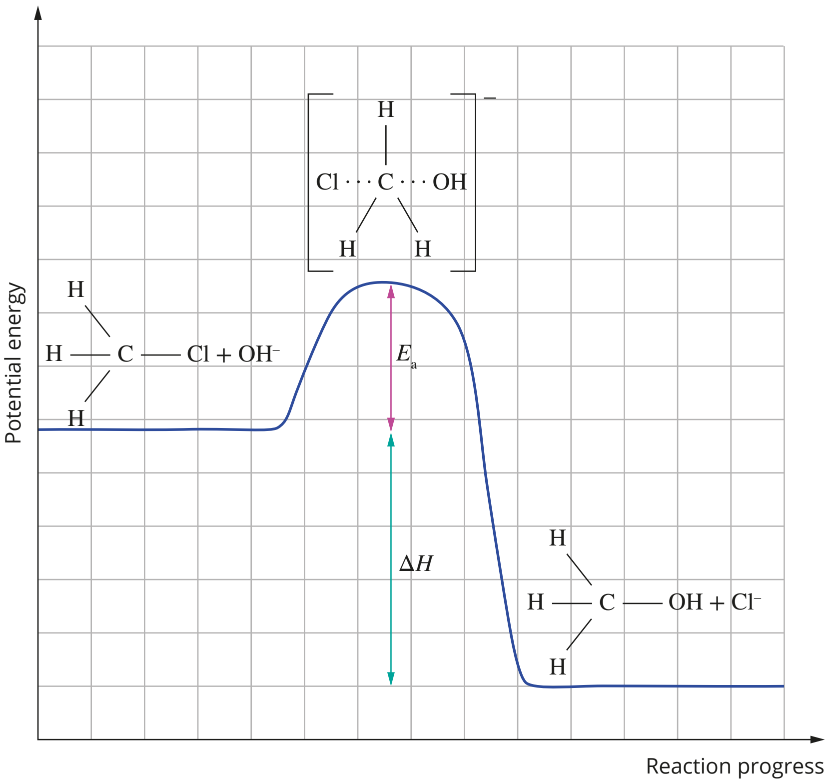
Copper is still limiting, so final mass remains the same.

COLLISION THEORY

6 Reactant particles must: collide with each other, collide with sufficient energy to break the bonds within the reactants, collide with the correct orientation to break the bonds within the reactants and so allow the formation of new products.

7 Collision 1 has the correct collision orientation, allowing bonds to break within the reactants and bonds to form within the products.

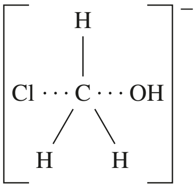
8 **a**



b Activation energy is the minimum amount of energy required by the reactants in order to form products in a reaction. It is related to the energy required to break bonds in the reactants.

c The reaction is exothermic.

d



e C–Cl bond is being broken in chloromethane. C–O bond is beginning to form between chloromethane and hydroxide ion.

9 **a** The single H–H bond in each hydrogen molecule and the double O=O bond in each oxygen molecule are broken in the course of this reaction.

b Two H–O bonds are formed in each new water molecule during the reaction.

c The energy change for the reaction is the difference between the energy absorbed to break the bonds in the H_2 and O_2 reactants, and the energy released when the bonds in the H_2O product are made.

d No reaction occurs until sufficient energy is supplied to overcome the activation energy.

EFFECT OF TEMPERATURE ON RATE OF REACTION

10 B. B is correct because an increase in surface area increases the frequency of collisions between reactant particles.

11 D

12 **a** At lower temperatures the molecules that react to cause the apple to brown have less energy. They collide less frequently and are less likely to have a total energy exceeding the activation energy of the reaction involved, decreasing the rate of reaction.

b Using pure oxygen gas instead of air increases the concentration of oxygen. This results in a higher frequency of collisions between hydrogen and oxygen molecules and hence an increased reaction rate.

CATALYSTS

13 A. Reactant is not gaseous so increasing pressure of oxygen gas would have no effect on the rate of reaction.

14 C

15 **a** Surface area of a solid reactant, concentration of reactants in a solution, pressure of any gaseous reactants, temperature of the reaction, presence of a catalyst

b **i** Surface area of a solid reactant, concentration of reactants in a solution, pressure of any gaseous reactants

ii Temperature of the reaction (also increases collision frequency), presence of a catalyst

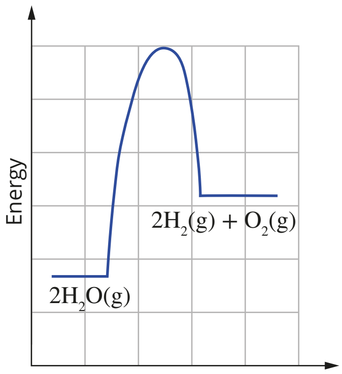
16 1. Increasing the pressure of the gases would cause an increase in the number of collisions between the reactant molecules in a given time, so more collisions would occur with the correct orientation to react and with energy that is greater than or equal to the activation energy. As a result, the rate of reaction would increase.

2. Adding a catalyst would allow the reaction to occur by a different pathway with a lower activation energy. The proportion of collisions with energy greater than the activation energy would thus be increased. As a result, the rate of reaction would increase.

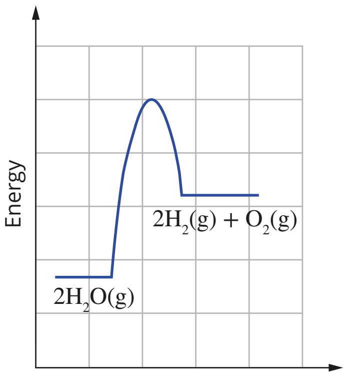
17 **a** 1370 kJ mol^{-1}

b –572 kJ mol^{-1}

c Without catalyst



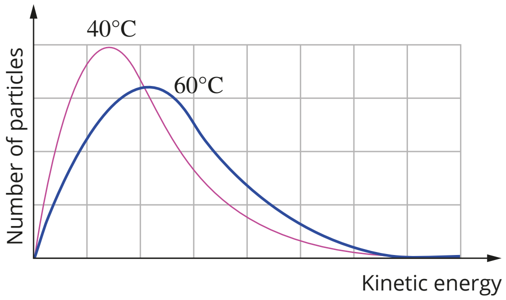
With catalyst



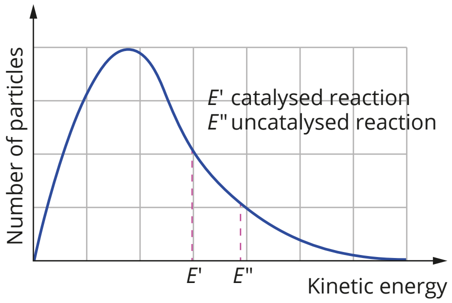
d +572 kJ mol^{-1}

CONNECTING THE MAIN IDEAS

18 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.

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

b n(CaCO) = 10.0 g/100.1 g mol^{-1} = 0.0999 mol

n(HCl) = 0.1 M × 0.1 L = 0.01 mol

∴ $CaCO_3$ is in excess

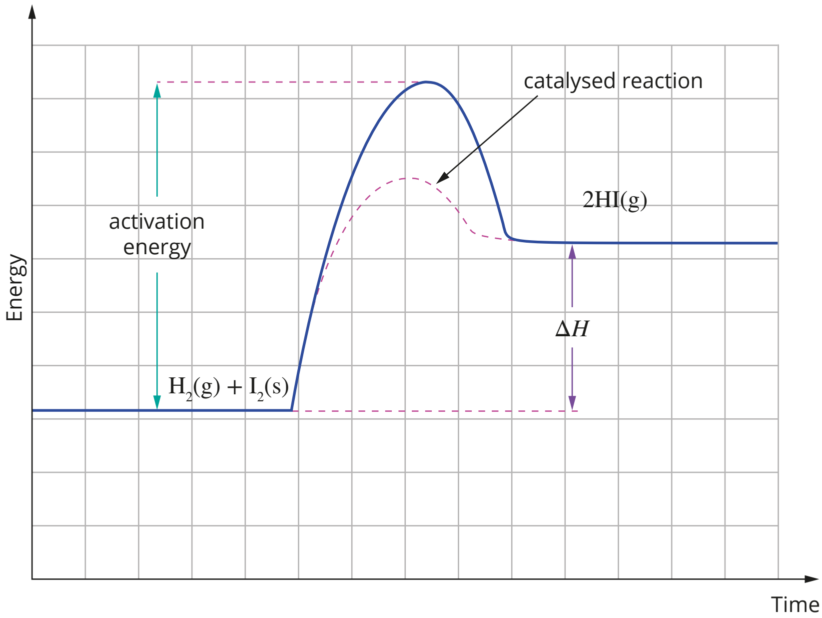
c The rate of reaction can be measured by:

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

e Increase temperature; increase concentration of hydrochloric acid.

20 a, c



b The reaction is endothermic.

21 **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 to 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.

22 **a** Higher body temperature increases the rate of reactions. Increased pulse and breathing rate increases the concentration of reactants.

b Lower body temperature decreases rate of metabolic reactions in the body.

23 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.

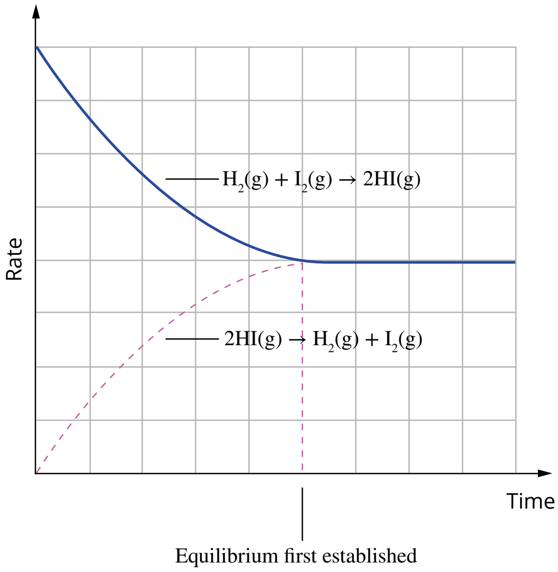
Chapter 8 Extent of chemical reactions

Section 8.1 Dynamic equilibrium

8.1 Key questions

1 C. A and D are false because the extent of reaction gives no indication of the rate of reaction. 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



3 closed, decreases, less, backward, increases, equal

4 **a** 0.07 M
- **b** 0 M
- **c** 0.03 M
- **d** 0.08 M
- **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 8.2 The equilibrium law

Worked example 8.2.1: Try yourself

DETERMINING THE UNITS FOR AN EQUILIBRIUM EXPRESSION

Write the equilibrium expression and determine the units for K_c for the reversible reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	
Thinking	**Working**
Write the expression for K_c. $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$
Substitute the units of concentration into the expression for K_c. Solve to find the units of K_c.	$\frac{M^2}{M^2 \times M} = \frac{1}{M} = \text{L mol}^{-1}$

8.2 Key questions

1 $Q_c = \frac{[HCl]^2}{[H_2][Cl_2]}$

2 The reaction quotient $Q_c < K_c$. The reaction will shift to the right to establish equilibrium. This causes the concentration of the products to increase.

3 **a** A system in which all the species are in the same state

b $Q_c = \frac{[\text{products}]^{\text{coefficient}}}{[\text{reactants}]^{\text{coefficient}}}$ and is equal to K_c at equilibrium

c The equilibrium constant is the ratio of the equilibrium concentrations of the products over the equilibrium concentrations of the reactants raised to the power of their coefficients. It is given the symbol K_c and the value for the equilibrium constant changes with temperature.

4 $\frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

As $Q_c > K_c$, in order to reach equilibrium $[[Cu(NH_3)_4]^{2+}]$ must decrease and the concentration of the reactants increase. This will occur if the reaction moves backwards in the direction of producing more reactants.

Section 8.3 Working with equilibrium constants

8.3 Key questions

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

b Since $\frac{[N_2][H_2]^3}{[NH_3]^2} = 100\ M^2$

$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{1}{100} = 0.01\ M^{-2}$

c $K_c = \frac{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}{[NH_3]}$

d The expression in part **c** is equal to the square root of $\frac{[N_2][H_2]^3}{[NH_3]^2} = 10\ M$.

e **i** When an equation is reversed, the value of the equilibrium constant is the reciprocal of the original constant.

ii When the coefficients are halved, the new equilibrium constant has a value equal to the square root of the original constant.

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

$= \sqrt{4.0 \times 10^{-4}}$

$= 0.020\ M^{\frac{1}{2}}$

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

$= \frac{1}{0.020}$

$= 50\ M^{\frac{1}{2}}$

3 **a** $K_c = 8.35\ M^4$

b $K_c = 0.767\ M^{-\frac{1}{2}}$

c $K_c = 1.30\ M^{\frac{1}{2}}$

d $K_c = 0.346\ M^{-2}$

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 8.4 Calculations involving equilibrium

Worked example: Try yourself 8.4.1

CALCULATING THE EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Calculate the value of the equilibrium constant, K_c, for the reaction at that temperature.

Thinking	**Working**
Find the molar concentrations for all species at equilibrium. Convert mol to mol L^{-1} using $c = \frac{n}{V}$.	$N_2O_4 = \frac{n}{V}$ $= \frac{0.120}{3.00}$ $= 0.0400\ M$ $[NO_2] = \frac{n}{V}$ $= \frac{0.500}{3.00}$ $= 0.167\ M$
Write the expression for K_c.	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
Substitute into the expression for K_c to determine the value of K_c.	$K_c = \frac{0.167^2}{0.0400}$ $= 0.694$
Determine the units of K_c.	$\frac{M^2}{M} = M$ $K_c = 0.694\ M$

Worked example: Try yourself 8.4.2

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium with an equilibrium constant of 0.72 M at 250°C.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

An equilibrium mixture contains 0.040 M N_2O_4 at 250°C. What is the equilibrium concentration of NO_2 in this mixture?

Thinking	**Working**
Write the expression for K_c.	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
Substitute the known values into the expression for K_c.	$0.72 = \frac{[NO_2]^2}{0.040}$
Reorganise the expression to make the unknown the subject and calculate the concentration of this species.	$[NO_2] = \sqrt{0.72 \times 0.040}$ $= 0.17$ M

Worked example: Try yourself 8.4.3

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetroxide (N_2O_4) at 60°C:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

0.350 mol of N_2O_4 was placed in a 2.0 L vessel. When equilibrium was achieved, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at this temperature.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled ‘I’ (Initial), ‘C’ (Change) and ‘E’ (Equilibrium):
<table>
<tr><th></th><th colspan="2">Reactants ⇌ Products</th></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
Enter the data provided in the table.
When a species is consumed, the change is negative; when a species is produced, the change is positive.</td>
<td>Initially, there is:
0.350 mol of $N_2O(g)$
0 mol of the product $NO_2(g)$.
Let x mol of N_2O_4 react; 2x mol of NO_2 is produced.
At equilibrium, there is 0.120 mol of $NO_2(g)$.
<table>
<tr><th></th><th colspan="2">$N_2O_4(g) \rightleftharpoons 2NO_2(g)$</th></tr>
<tr><td>I</td><td>0.350 mol</td><td>0 mol</td></tr>
<tr><td>C</td><td>$-x$</td><td>$+2x$</td></tr>
<tr><td>E</td><td>$0.350 - x$</td><td>$2x = 0.120$ mol</td></tr>
</table></td></tr>
<tr><td>Using the coefficients from the equation, calculate the moles of all species at equilibrium.</td>
<td>Initially no NO_2 was present, so because 0.120 mol NO_2 has been produced at equilibrium:
$2x = 0.120$ mol
$x = 0.0600$ mol
We can enter these values in the table:
<table>
<tr><th></th><th colspan="2">$N_2O_4(g) \rightleftharpoons 2NO_2(g)$</th></tr>
<tr><td>I</td><td>0.350</td><td>0</td></tr>
<tr><td>C</td><td>$-x = -0.0600$</td><td>$+2x = 0.120$</td></tr>
<tr><td>E</td><td>$0.350 - 0.0600$
$= 0.290$</td><td>$2x = 0.120$</td></tr>
</table></td></tr>
</table>

Using the volume of the vessel, calculate the equilibrium concentrations for all species at equilibrium. Use the formula $c = \frac{n}{V}$.	The volume of the vessel is 2.00 L. $[N_2O_4] = \frac{n}{V}$ $= \frac{0.290}{2.00}$ $= 0.145$ M $[NO_2] = \frac{n}{V}$ $= \frac{0.120}{2.00}$ $= 0.0600$ M
Write the expression for K_c and substitute the equilibrium concentrations. Calculate the equilibrium constant, K_c, and include the units for the equilibrium constant.	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$ $= \frac{0.0600^2}{0.145}$ $= 0.0248$ M

8.4 Key questions

1 From the equation, write the expression for the equilibrium constant:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Calculate equilibrium concentrations of reactants and products.

$[NO_2]$ = 0.40 mol/2.0 L
= 0.20 M

$[N_2O_4]$ = 0.80 mol/2.0 L
= 0.40 M

Substitute equilibrium concentrations in the equilibrium expression and calculate the value of the equilibrium constant.

$$K = \frac{0.20^2}{0.40}$$

= 0.10 M

2 $K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.28}{2.4 \times 10^{-2} \times 0.108} = 1.1 \times 10^2\ M^{-1}$

3 $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{15.5^2}{0.0542^2 \times [O_2]} = 6.44 \times 10^5\ M^{-1}$

$$[O_2] = \frac{15.5^2}{0.0542^2 \times (6.44 \times 10^5)}$$

= 0.127 M

4

	$PCl_3(g)$ +	$Cl_2(g) \rightleftharpoons$	$PCl_5(g)$
I	4.45	5.50	0
C	$-x = -0.35$	$-x = -0.35$	$+x = 0.35$
E	$4.45 - x$ $= 4.45 - 0.35$ $= 4.10$	$5.50 - x$ $= 5.50 - 0.35$ $= 5.15$	$x = 0.35$

Vessel volume = 2.00 L

$[PCl_3] = \frac{4.10}{2.00} = 2.05$ M, $[Cl_2] = \frac{5.15}{2.00} = 2.58$ M, $[PCl_5] = \frac{0.35}{2.00} = 0.18$ M

$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.18}{2.05 \times 2.58} = 0.033\ M^{-1}$

5

	N_2(g) +	$3H_2$(g) ⇌	$2NH_3$(g)
I	5.89	8.23	0
C	$-x = -0.24$	$-3x = -0.72$	$+2x = 0.48$
E	$5.89 - x$ $= 5.89 - 0.24$ $= 5.65$	$8.23 - 3x$ $= 8.23 - 0.72$ $= 7.51$	$2x = 0.48$

Volume of vessel = 5.00 L

$[N_2] = \frac{5.65}{5.00} = 1.13$ M, $[H_2] = \frac{7.51}{5.00} = 1.50$ M, $[NH_3] = \frac{0.48}{5.00} = 0.0960$ M

$$K_c = \frac{[NH_5]^2}{[N_2][H_2]^3} = \frac{0.0960^2}{1.13 \times 1.50^3} = 2.41 \times 10^{-3}\ M^{-2}$$

6 **a** From the equation, write the expression for the equilibrium constant.

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

Calculate equilibrium concentrations of reactants.

$[H_2]$ = 0.220 mol/2.0 L = 0.110 M

$[I_2]$ = 0.110 mol/2.0 L = 0.055 M

Substitute equilibrium concentrations in the equilibrium expression and calculate the concentration of HI.

$$48.8 = \frac{0.110 \times 0.055}{[HI]^2}$$

$$[HI]^2 = \frac{0.110 \times 0.055}{48.8}$$

$$[HI] = \sqrt{\frac{0.110 \times 0.055}{48.8}}$$

$= 0.01113$ M

$= 0.011$ M

b

	2HI(g) ⇌	H_2(g) +	I_2(g)
I	4.00	0	0
C	$-2x = -0.88$	$+x = 0.44$	$+x = 0.44$
E	$4.00 - 2x$ $= 4.00 - 0.88$ $= 3.12$ 3.12 mol/2.0 L = 1.56 M	$x = 0.44$ 0.44 mol/2.0 L = 0.22 M	$x = 0.44$ 0.44 mol/2.0 L = 0.22 M

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$= \frac{0.22 \times 0.22}{1.56^2}$$

$= 0.01989$

$= 0.020$

c The reaction quotient for this reaction is $\frac{[H_2][I_2]}{[HI]^2}$

Calculate equilibrium concentrations of reactants.

$[H_2]$ = 0.240 mol/2.0 L = 0.12 M

$[I_2]$ = 0.320 mol/2.0 L = 0.16 M

[HI] = 1.00 mol/2.0 L = 0.50 M

The value of the reaction quotient is $\frac{0.12 \times 0.16}{0.50^2} = 0.077$

The value of the reaction quotient is greater than the value of the equilibrium constant at the same temperature as calculated in part **b**. Thus the system is not at equilibrium. A net backwards reaction will occur. As the reaction moves towards equilibrium, the concentrations of H_2 and I_2 will decrease and the concentration of HI will increase until the value of the reaction quotient is equal to the equilibrium constant.

7

	$2NO(g)$	**$2H_2(g) \rightleftharpoons$**	**$N_2(g)$ +**	**$2H_2O(g)$**
I	0.100	0.051	0	0.100
C	$-x = -(0.100 - 0.062)$ $= -0.038$	$-x = -0.038$	$+x/2$ $= +0.038/2$ $= +0.019$	$+x/2$ $= +0.038/2$ $= +0.019$
E	0.062	$0.051 - x$ $= 0.051 - 0.038$ $= 0.013$	$0 + x/2$ $= 0 + 0.019$ $= 0.019$	$0.100 + x/2$ $= 0.100 + 0.019$ $= 0.119$

Volume of vessel = 1.0 L so mol = concentration

$$K_c = \frac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$$

$$= \frac{0.119^2 \times 0.019}{0.113^2 \times 0.062^2}$$

$$= 5.5\ M^{-1}$$

Section 8.5 Le Châtelier's principle

8.5 Key questions

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

2 **a** Net back reaction
  b Net forward reaction

3 For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ the equilibrium law is:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

When SO_3 is added to the system, it increases the concentration of the products. The concentration fraction, Q_c, will increase. Because $Q_c > K_c$, the system will favour the back reaction in order to decrease the value of Q_c until equilibrium is re-established ($Q_c = K_c$).

For the reaction $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ the equilibrium law is:

$$K_c = \frac{[CH_3COO^-][H_3O]^+}{[CH_3COOH^-]^2[H_2O]}$$

When CH_3COO^- is removed from the system, it decreases the concentration of the products. The concentration fraction, Q_c, will decrease. As $Q_c < K_c$, the system will favour the forward reaction in order to increase the value of Q_c until equilibrium is re-established ($Q_c = K_c$).

4 C

5 incomplete, haemoglobin, oxygen, CO–haemoglobin, O_2–haemoglobin, oxygen, O_2, O_2–haemoglobin

Section 8.6 Further applications of Le Châtelier's principle

Worked example: Try yourself 8.6.1

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 in 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 increases the amount of the reactants, including Cl_2. (Note that the PCl_3 and Cl_2 concentrations will still be lower than they were at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.)

8.6 Key questions

1 B. This gaseous equilibrium contains two particles on both sides of the equation so it is not affected by changes in volume or pressure at constant temperature.

2 a Net forward reaction
  b No effect
  c Net forward reaction

3 a i Increase
    ii Increase
    iii Decrease
  b i Cannot cause forward reaction
    ii Increase
    iii Cannot cause forward reaction

4 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 reestablish equilibrium.
  a As the volume is increased the concentration of NO_2 will decrease, although the reaction will favour the formation of NO_2 according to Le Châtelier's principle the adjustment can only partially oppose the change so the corresponding increase in concentration will not reach the initial NO_2 concentration level.
  b The mass of NO_2 will be higher. By favouring the forward reaction the shift in equilibrium will result in a higher yield of NO_2

5 a Decreasing the temperature would favour the forward exothermic process, resulting in 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.

Section 8.7 Optimising the yield of industrial processes

8.7 Key questions

1 high, temperature, catalyst, reaction rate

2 High temperature and low pressure increase the equilibrium yield of SO_2.

3 58.1%

Theoretical yield: $n(Cl_2O) = \frac{2.85}{87.0} = 0.0328$ mol

$n(HOCl) = 2 \times n(Cl_2O) = 0.0655$ mol

$m(HOCl)$ at 100% yield = $0.0655 \times 52.5 = 3.44$ g

% yield = $\frac{2.00}{3.44} \times 100 = 58.1\%$

4 **a** The reaction is exothermic, so equilibrium yield will be increased at low temperatures. As 3 moles of gaseous reactants become 2 moles of gaseous products, high pressure would favour a higher equilibrium yield. An excess of a reactant can be used to increase equilibrium yield.

b Reaction rate would be increased by increased pressure, high temperatures and the use of a catalyst.

c The use of high pressure is expensive and can be dangerous so the reaction is run at 1 atm to reduce costs. The moderate temperature is used to ensure a reasonable rate of reaction without impacting too highly on the equilibrium yield. The decrease in reaction rate due to the lower temperature is offset by the addition of a catalyst. This compromise ensures the most efficient yield and rate for the plant.

5 Temperatures higher than 200°C are required to obtain an acceptably fast rate of reaction.

6 **a** The reaction is exothermic.

b As the reaction is an exothermic process, the gases are cooled before being pumped back into the reaction system to maximise equilibrium yield. Pumping hot gases into the reaction mixture would cause the temperature to rise and favour the back reaction, reducing the yield of ammonia.

CHAPTER 8 REVIEW

DYNAMIC EQUILIBRIUM

1 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.

2 **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.

THE EQUILIBRIUM LAW

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

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

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

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

5 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.

6 As Q_c for the reaction is larger than K_c, the reaction must move to decrease Q_c. This will happen with a decrease in the concentration of the products. There will be a net backwards reaction, decreasing the concentration of ethyl ethanoate as the mixture reaches equilibrium.

WORKING WITH EQUILIBRIUM CONSTANTS

7 **a** less than

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

c moves to the right

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

b 10^{10}

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

9 **a** $K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

b **i** The coefficients of each species has been halved. $K_c = \sqrt{32} = 5.7$

ii The reaction is the reverse of that in part **a**. $K_c = \frac{1}{32} = 0.031$

iii Each of the coefficients has been doubled. $K_c = 32^2 = 1.0 \times 10^3$

iv The reaction is reversed and the coefficients halved. $K_c = \frac{1}{\sqrt{32}} = 0.18$

CALCULATIONS INVOLVING EQUILIBRIUM

10 The reaction is not at equilibrium and will shift towards the left to reach equilibrium.

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.25^2}{1.0 \times 1.0^3} = 0.063\ M^{-2}$$

The reaction quotient is greater than K_c so the reaction will move to decrease Q_c, so the equilibrium will shift to the left, to produce more reactants.

11 Container is 2 L

$$[H_2O] = \frac{0.020}{2} = 0.010\ M$$

$$[H_2] = \frac{0.030}{2} = 0.015\ M$$

$$[CO] = \frac{0.040}{2} = 0.020\ M$$

$$[CO_2] = \frac{0.050}{2} = 0.025\ M$$

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{0.010 \times 0.020}{0.015 \times 0.025} = 0.53$$

12 $K_c = \frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}][Sn^{2+}]} = \frac{0.40^2 \times 0.20}{0.30^2 \times 0.10} = 3.6$ (no units)

13 Write the expression for the equilibrium constant.

$$K_c = \frac{[C_3H_6O][H_2]}{[C_3H_8O]}$$

Calculate equilibrium concentrations of reactants and products.

$[C_3H_6O]$ = 0.082 mol/20 L
= 0.0041 M

$[H_2]$ = 0.082 mol/20 L
= 0.0041 M

$[C_3H_8O]$ = 0.018 mol/20 L
= 0.0009 M

Substitute equilibrium concentrations in the equilibrium expression and find the value of the equilibrium constant.

$$K_c = \frac{0.0041 \times 0.0041}{0.0009}$$

= 0.0187 M

= 0.019 M

14 a $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b Calculate equilibrium concentrations of reactants and products.

$[PCl_5] = 4.50 \text{ mol}/3.00 \text{ L}$
$= 1.50 \text{ M}$
$[Cl_2] = 0.900 \text{ mol}/3.00 \text{ L}$
$= 0.300 \text{ M}$
$[PCl_3] = 6.00 \text{ mol}/3.00 \text{ L}$
$= 2.00 \text{ M}$

Use the expression for the equilibrium constant from part **a**.

Substitute equilibrium concentrations in the equilibrium expression.

$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.400 \text{ M}$

c Rearrange the expression to find $[Cl_2]$.

$[Cl_2] = K_c \times \frac{[PCl_5]}{[PCl_3]}$

Substitute equilibrium concentrations in the equilibrium constant expression and find the value of $[Cl_2]$.

$[Cl_2] = 0.400 \times \frac{0.0020}{0.0010}$

$= 0.80 \text{ M}$

d Note that the equation is reversed and the temperature is constant. For the reverse reaction the equilibrium constant is the reciprocal of the forward reaction.

$K_c = \frac{1}{0.400} \text{ M}^{-1}$

$= 2.5 \text{ M}^{-1}$

15

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
I	0.540	0
C	$-x = -0.140$	$+2x = 0.280$
E	$0.540 - x$ $= 0.540 - 0.140$ $= 0.400$ 0.400 mol/2.0 L = 0.20 M	$2x = 0.280$ 0.280 mol/2.0 L = 0.140 M

Substitute equilibrium concentrations in the equilibrium expression and find the value of the equilibrium constant.

$K_c = \frac{[NO_2]^2}{[N_2O_4]}$

$= \frac{0.140^2}{0.200}$

$= 0.0980 \text{ M}$

16 a Write the expression for the equilibrium constant.

$K_c = \frac{[C]^2[D]}{[A][B]^3}$

Calculate equilibrium concentrations of reactants and products.

$[A] = 2.0 \text{ mol}/2.0 \text{ L}$
$= 1.0 \text{ M}$
$[B] = 0.50 \text{ mol}/2.0 \text{ L}$
$= 0.25 \text{ M}$
$[D] = 3.0 \text{ mol}/2.0 \text{ L}$
$= 1.5 \text{ M}$

b Substitute equilibrium concentrations in the equilibrium expression and calculate the equilibrium concentration of C.

$$K_c = 0.024 = \frac{[C]^2 \times 1.5}{1.0 \times 0.25^3}$$

$$[C]^2 = \frac{0.024 \times 1.0 \times 0.25^3}{1.5}$$

$$[C] = \sqrt{\frac{0.024 \times 1.0 \times 0.25^3}{1.5}}$$

$$= 0.0158$$

$$= 0.016 \text{ M}$$

c Convert the equilibrium concentration of C into a mole value.

$[C] = 0.016$ M

$n(C) = 0.016 \text{ M} \times 2.0 \text{ L}$

$= 0.032$ mol

LE CHÂTELIER'S PRINCIPLE

17 **a** Increase
b Increase

18 **a** Net back reaction
b Net forward reaction
c No effect

19 If Ca^{2+} ions were inefficiently absorbed from food, decreased concentrations of these ions could 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.

20 **a** **i** Net forward reaction
ii No change
iii Net forward reaction
b **i** Increase
ii No change
iii No change
c Likely to be large

21

	Colour change (lighter or darker)	**Explanation**
a The temperature is increased to 450°C at constant volume.	Yes (lighter)	Exothermic reaction, so K_c will decrease as temperature increases, so a net back reaction occurs.
b The volume of the container is increased at constant temperature.	Yes (lighter)	As volume increases the colour of the gas mixture will decrease. (A net back reaction will also occur, further lightening the colour.)
c A catalyst is added at constant volume and temperature.		Addition of a catalyst would have not changed the colour because the rate of the forward and back reactions are increased equally.
d More oxygen is added at constant volume and temperature.	Yes (darker)	Addition of oxygen will cause a net forward reaction to occur.

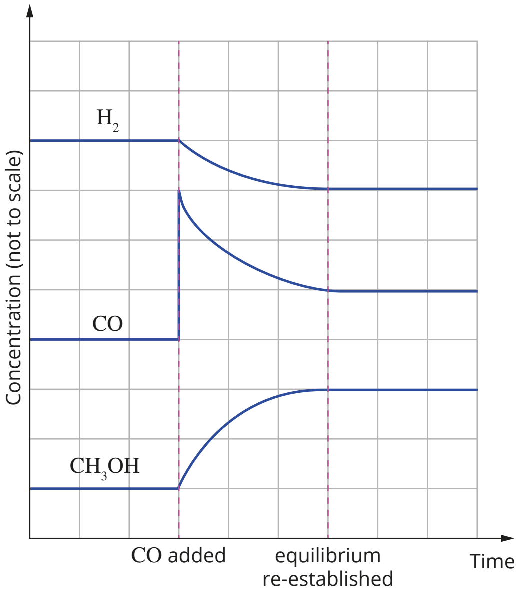
22 The patient is treated with excess oxygen. This is done to drive the equilibrium towards the formation of oxyhaemoglobin.

23 B. CO displaces O_2 and the production of carboxyhaemoglobin is increased.

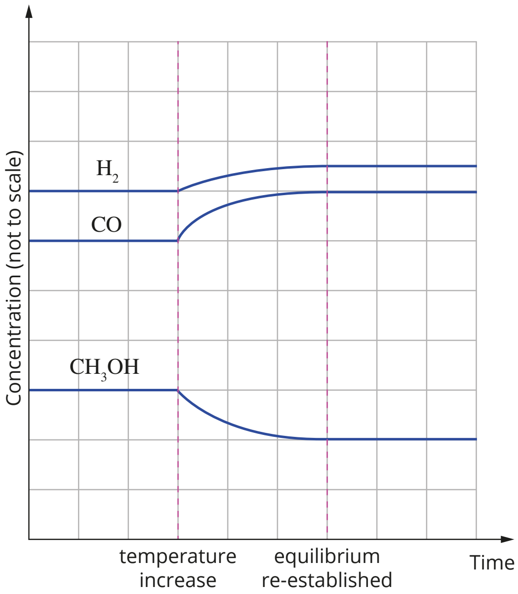
OPTIMISING THE YIELD OF INDUSTRIAL PROCESSES

24 **a** **i** Decrease
   ii Decrease
   iii increase
   iv No change
   v No change
  b **i** Increase
   ii Increase
   iii Increase
   iv Increase
   v No change

25 **a** **i** High temperature; high pressure
   ii Low temperature; high pressure
  b Temperature
  c Use a catalyst.
  d **i**



   ii



26 **a** **i** Increase

ii Increase

b In practice, satisfactorily high equilibrium yields of sulfur trioxide can be obtained without needing to use high pressures, which would involve more expensive equipment.

c The purpose of recycling the gases from the absorption tower is to increase the yield of sulfur trioxide and to minimise emissions of sulfur oxides, which act as pollutants.

d The rate of reaction and the magnitude of K_c.

CONNECTING THE MAIN IDEAS

27 **a** Write the expression for the equilibrium constant.

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

$$= 0.052\ M^{-2}$$

Because a 1 L vessel is used, the concentrations are the same as the amount in moles. Substitute the concentration values into the reaction quotient.

$$Q_c = \frac{0.20^2}{0.20 \times 0.20^3}$$

$$= 25$$

$Q_c > K_c$; therefore the system is not at equilibrium. The system will shift in the direction that makes $Q_c = K_c$. Since $Q_c > K_c$, the reaction must shift to left, resulting in a net back reaction.

b Because a 1 L vessel is used, the concentrations are the same as the amount in moles. Substitute the given concentration values into reaction quotient.

$$Q_c = \frac{0.0^2}{0.050 \times 0.050^3}$$

$$= 0.0\ M^{-2}$$

$Q_c < K_c$; therefore, the system is not at equilibrium. The system will shift in the direction which makes $Q_c = K_c$. Because $Q_c < K_c$, the reaction must shift to right, resulting in a net forward reaction.

28 **a** For the initial mixture, the ratio $\frac{[CH_2][H_2O]}{[CO][H_2]^3} = \frac{0.300 \times 0.400}{0.100 \times 0.200^3} = 150\ M^{-2}$

A net back reaction will occur so this ratio becomes equal to K_c.

i Increase

ii Increase

iii Decrease

iv Decrease

b Endothermic

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

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

c **i** $n(O_2) = 4 \times n(CS_2) = 4 \times 0.028 = 0.112$ mol

ii $[CS_2] = \frac{0.028}{20} = 0.0014$ M

$[O_2] = \frac{0.112}{20} = 0.0056$ M

$[SO_3] = \frac{0.022}{20} = 0.0011$ M

$[CO_2] = \frac{0.014}{20} = 0.00070$ M

$$K_c = \frac{[CS_2][O_2]^4}{[SO_3][CO_2]}$$

$$= \frac{0.0014 \times 0.0056^4}{0.0011^2 \times 0.00070}$$

$$= 1.6 \times 10^{-3}\ M^{-2}$$

d **i** Increase
  ii Increase
  iii No effect
  iv Decrease
  v No effect

30 **a** $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

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

c 1.56 M^{-1}

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

e 3.50 M^{-1}

f Increased pressure by reducing volume. Also, because the value of K_c at 25–30 minutes is larger than at 15–20 minutes and this is an exothermic reaction, a decrease in temperature must have occurred.

Chapter 9 Production of chemicals by electrolysis

Section 9.1 Electrolytic cells

Worked example 9.1.1: Try yourself

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the electrochemical series to predict the products of the electrolysis of 1 M zinc sulfate solution with copper electrodes at 25°C.	
Thinking	**Working**
Identify which species are present in the solution.	$Zn^{2+}(aq)$, $SO_4^{2-}(aq)$ and $H_2O(l)$
Identify what the electrodes are made of.	Copper
Refer to the electrochemical series and identify the possible reactions. Write these half-equations in the order they appear in the series.	By referring to the electrochemical series, you can see that a number of reactions need to be considered as the cell contains two oxidising agents, Zn^{2+}, and H_2O, and two reducing agents, Cu and H_2O. $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ 1.23 V $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ 0.34 V $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ –0.76 V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ –0.83 V The SO_4^{2-} ions are not involved in the reaction.
Determine the reactions that could occur at the anode.	At the anode (+), oxidation reactions that could occur are: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Determine the most likely reaction at the anode.	The strongest reducing agent, Cu(s), will be oxidised: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Determine the reactions that could occur at the cathode.	At the cathode (–), reduction reactions that could occur are: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
Determine the most likely reaction at the cathode.	The strongest oxidising agent, $Zn^{2+}(aq)$, will be reduced. $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
Combine the two half-reactions to obtain the overall reaction in the electrolysis cell.	The overall equation is: $Zn^{2+}(aq) + Cu(s) \rightarrow Zn(s) + Cu^{2+}(aq)$

9.1 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 **a** Nickel rod. The nickel rod is the negative electrode, which attracts positive Ni^{2+} ions in the solution towards it. Electrons from the power supply are ‘pushed’ towards the negative electrode. The Ni^{2+} ions are reduced to solid Ni.

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

Nickel rod (negative): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

c $2H_2O(l) + 2Ni^{2+}(aq) \rightarrow O_2(g) + 4H^+(aq) + 2Ni(s)$

5 **a**

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23 V
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	–0.13 V
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44 V
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83 V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.34 V

Although NO_3^- ions are attracted to the anode, they cannot be ionised because nitrogen is already in its highest oxidation state (+5).

b Anode: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$. Pb(s) is oxidised instead of Fe(s), even though Fe(s) is the stronger reducing agent, because Fe(s) is at the cathode where there is a continuous supply of electrons.

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$. As water is a stronger oxidising agent than Mg^{2+}, water will be reduced in preference to the Mg^{2+}.

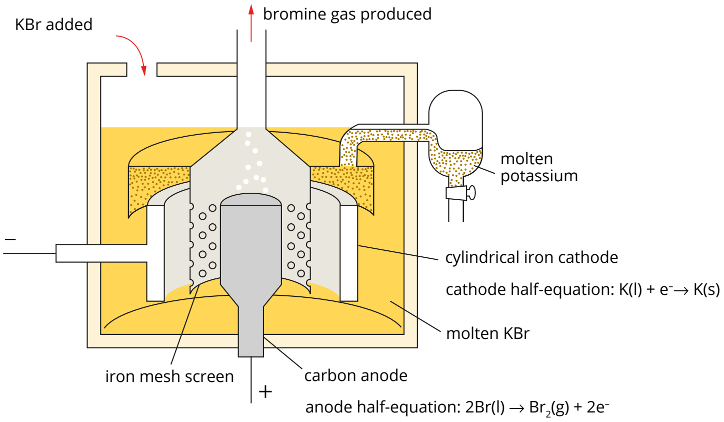
c $Pb(s) + 2H_2O(l) \rightarrow Pb(OH)_2(s) + H_2(g)$

Section 9.2 Commercial electrolytic cells

9.2 Key questions

1 D. The electrolytic production of aluminium could not occur with an aqueous electrolyte because water is a stronger oxidising agent than aluminium ions so water would be preferentially reduced.

2



3 **a** An inert electrode would be suitable. A reactive electrode would be oxidised at the anode, releasing cations into the solution, thus contaminating the electrolyte. The only reactive electrode that would be suitable is a zinc electrode.

b Zinc ions are a stronger oxidising agent than water, so the zinc ions are preferentially reduced at the cathode. It is also cheaper than the molten electrolyte.

c The strongest reducing agent present is water, so it is oxidised at the anode to produce oxygen gas:

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

4 **a** It is cheaper to obtain chlorine by electrolysis of concentrated sodium chloride solution than from molten sodium chloride because electrical energy is required in order to melt sodium chloride.

b Fluorine is the strongest oxidising agent known. Since a stronger oxidising agent than fluorine would be required to convert F^- ions into fluorine, the element cannot be made by direct reaction. However, it is generated at the anode during electrolysis of molten metal fluorides.

c Na^+ ions are stronger oxidising agents than Ca^{2+} ions, so sodium metal is formed at the cathode in preference to calcium.

Section 9.3 Faraday's laws

Worked example: Try yourself 9.3.1

CALCULATING MASS OF A PRODUCT AT AN ELECTRODE

A copper-plating cell operates with a steady current of 20.0 A for 15.0 minutes. What mass of copper is plated on the object at the cathode? The equation for the reaction is:

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

Thinking	**Working**
Calculate the quantity of charge passing through a cell using the formula: $Q = I \times t$. Remember that time must be expressed in seconds.	$Q = 20.0 \times (15.00 \times 60)$ $= 1.80 \times 10^4$ C
Calculate the number of moles of electrons that passed through the cell using the equation: $Q = n(e^-) \times F$	$n(e^-) = \frac{Q}{F}$ $= \frac{1.8 \times 10^4}{96500}$ = 0.187 mol
Use the mole ratio from the equation to determine the amount, in moles, of metal plated at the cathode.	The cathode reaction is: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ 2 moles of electrons will deposit 1 mole of silver metal. Mole ratio: $\frac{n(Cu)}{n(e^-)} = \frac{1}{2}$ $n(Cu) = \frac{n(e\ )}{2}$ = 0.0933 mol
Calculate the mass of metal plated at the cathode.	The molar mass of Cu is 63.5 g mol^{-1}. $m(Cu) = n \times M$ $= 0.0933 \times 63.5$ = 5.92 g

Worked example: Try yourself 9.3.2

CALCULATING TIME TO PRODUCE A PRODUCT AT AN ELECTRODE

How long would it take, in hours, to deposit 20.0 g of silver at the cathode of a silver-plating cell operating at a current of 6.50 A? The half-equation for the reaction is:

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

Thinking	**Working**
Calculate the amount of substance that was deposited or consumed at the electrode using the formula: $n = \frac{m}{M}$	$n(Ag) = \frac{m}{M}$ $= \frac{20.0}{107.9}$ $= 0.185$ mol
Calculate the number of moles of electrons that passed through the cell using the mole ratio from the equation.	The cathode reaction is: $Ag^+(aq) + e^- \rightarrow Ag(s)$ 1 mol of electrons will deposit 1 mol of silver metal. $\frac{n(e^-)}{n(Ag)} = \frac{1}{1}$ so: $n(e^-) = 1 \times n(Ag)$ $= 0.185$ mol
Calculate the quantity of charge which passed through the cell using the formula: $Q = n(e^-) \times F$	$Q = 0.185 \times 96\,500$ $= 1.79 \times 10^4$ C
Calculate the time required using the formula: $t = \frac{Q}{I}$	$t = \frac{Q}{I}$ $= \frac{1.79 \times 10^4}{6.50}$ $= 2.75 \times 10^3$ s
Convert seconds to hours by dividing by (60 × 60).	$t = \frac{2.75 \times 10^3}{60 \times 60} = 0.764$ h

9.3 Key questions

1 **a** 1 F = 1 mol of electrons = 1 mol of silver. $Ag^+(aq) + e^- \rightarrow Ag(s)$

b 2 F = 2 mol of electrons = 1 mol of zinc. $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

c 2 F = 2 mol of electrons = 1 mol of chlorine. $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

d 2 F = 2 mol of electrons = 1 mol of hydrogen. $H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

2 $Q = I \times t$

$= 10.0 \times 55.0 \times 60$

$= 3.30 \times 10^4$ C

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

$n(e^-) = \frac{Q}{F}$

$= \frac{3.3 \times 10^4}{96\,500}$

$= 0.342$ mol

$n(Ni) = \frac{1}{2}\, n(e^-)$

$= \frac{1}{2} \times 0.342$

$= 0.171$ mol

$m(\text{Ni}) = nM$
$= 0.171 \times 58.7$
$= 10.0 \text{ g}$

3 $n(\text{Pb}) = \frac{m}{M}$
$= \frac{15.6}{207.2}$
$= 0.0753 \text{ mol}$
$n(\text{e}^-) = 2n \times (\text{Pb})$
$= 2 \times 0.0753$
$= 0.151 \text{ mol}$
$Q = n(\text{e}^-) \times F$
$= 0.151 \times 96\,500$
$= 1.45 \times 10^4 \text{ C}$
$t = \frac{Q}{I}$
$= \frac{1.45 \times 10^4}{1.2}$
$= 1.21 \times 10^4 \text{ s}$
$= \frac{1.21 \times 10^4}{(60 \times 60)}$
$= 3.36 \text{ h}$

4 **a** $Ag^+(aq) + e^- \rightarrow Ag(s)$. In an electroplating cell, the negative terminal is the cathode where reduction occurs. $Ag^+(aq)$ ions are reduced to Ag(s).

b $n(\text{Ag}) = \frac{m}{M}$
$= \frac{0.055}{107.9}$
$= 5.1 \times 10^{-4} \text{ mol}$
$Ag^+(aq) + e^- \rightarrow Ag(s)$
$n(\text{e}^-) = n(\text{Ag}) = 5.1 \times 10^{-4} \text{ mol}$
$Q = n(\text{e}^-)F = It$
$I = \frac{n(\text{e}^-)F}{t}$
$= \frac{5.1 \times 10^{-4} \times 96\,500}{7.0 \times 60}$
$= 0.12 \text{ A}$

5 $Q = It$
$= 0.50 \times 30.0 \times 60$
$= 9.0 \times 10^2 \text{ C}$
$n(\text{e}^-) = \frac{Q}{F}$
$= \frac{9.0 \times 10^2}{96\,500}$
$= 9.3 \times 10^{-3} \text{ mol}$
$n(\text{metal}) = \frac{m}{M}$
$= \frac{0.700}{150.0}$
$= 4.67 \times 10^{-3} \text{ mol}$
$\frac{n(\text{e}^-)}{n(\text{metal})} = \frac{9.3 \times 10^{-3}}{4.67 \times 10^{-3}}$
$= 2.0$

2 mol of electrons are required to produce 1 mol of metal. ∴ The metal ions have a charge of +2.

CHAPTER 9 REVIEW

ELECTROLYTIC CELLS

1 **a** In galvanic cells the anode is negative and the cathode is positive; in electrolytic cells the anode is positive and the cathode is negative.

b In galvanic cells the direction of electron flow is determined by the cell reaction; in electrolytic cells the direction of electron flow is determined by the external power supply. Direction of electron flow is always from anode to cathode through the external circuit.

c In galvanic cells chemical energy is converted into electrical energy; in electrolytic cells electrical energy is converted into chemical energy.

d Galvanic cell reactions occur spontaneously; electrolytic cell reactions are non-spontaneous.

2 Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Cathode: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$

Overall: $Zn^{2+}(l) + 2Cl^-(l) \rightarrow Zn(l) + Cl_2(g)$

3 In the cell with copper electrodes, $Cu^{2+}(aq)$ is the strongest oxidant and $Cu(s)$ is the strongest reductant.

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

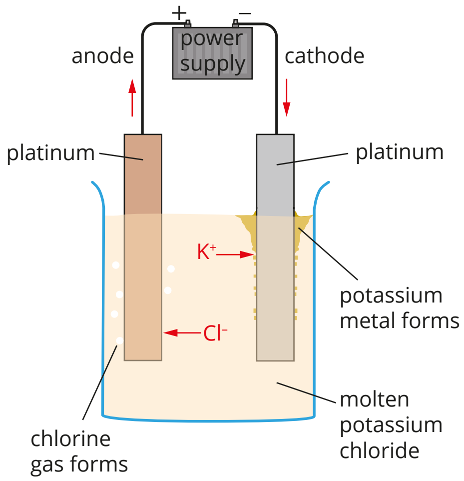
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

In the cell with the platinum electrodes, $Cu^{2+}(aq)$ is the strongest oxidant and $H_2O(l)$ is the strongest reductant.

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

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

4



5 The electrolyte solution contains water. As water is a stronger oxidising agent than Mg^{2+}, water will be reduced in preference to the Mg^{2+}. The reaction that did occur was:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

6 **a**

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow H_2O(l)$	+1.23 V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34 V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76 V
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83 V

The SO_4^{2-} ions are not involved in the reaction.

b Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$. Because $Cu(s)$ is a stronger reducing agent than water, $Cu(s)$ will be oxidised in preference to water.

Cathode: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$. Because $Zn^{2+}(aq)$ is a stronger oxidant than water, $Zn^{2+}(aq)$ will be reduced in preference to water.

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

7

Experiment	Cathode reaction	Anode reaction
a	$K^+(l) + e^- \rightarrow K(l)$	$2I^-(l) \rightarrow I_2(l) + 2e^-$
b	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
c	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
d	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
e	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

COMMERCIAL ELECTROLYTIC CELLS

8 If an aqueous solution of sodium chloride was used instead of molten sodium chloride, water would be present. Water is a stronger oxidising agent and reducing reducing agent than $Na^+(aq)$ and $Cl^-(aq)$ respectively. This means water is preferentially oxidised and reduced instead of $Cl^-(aq)$ and $Na^+(aq)$ respectively. Therefore, neither sodium nor chlorine would be produced.

However, at higher sodium chloride concentrations, $Cl^-(aq)$ is reduced instead of water so chlorine is produced.

9 **a** Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

b The semipermeable membrane only allows Na^+ ions to move through from the anode compartment to the cathode compartment. This allows for a very pure sodium hydroxide product to be produced. The semi-permeable membrane also prevents mixing between the reactive products.

10 The electrochemical series shows that the oxidising strength of H_2O is greater than that of Al^{3+}. If water is present in an electrolysis cell, it reacts preferentially at the cathode and electrolysis of aqueous aluminium salts does not yield aluminium metal.

FARADAY'S LAWS

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

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

$= \frac{1.5}{65.4}$

$= 0.0229$ mol

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

$n(e^-) = 2n(Zn)$

$= 2 \times 0.0299$

$= 0.0459$ mol

$Q = n(e^-)F = It$

$t = \frac{n(e^-)F}{I}$

$= \frac{0.0459 \times 96\,500}{3.5 \times 10^{-5}}$

$= 1.26 \times 10^8$ s

$1.26 \times 10^8 \text{ s} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ year}}{365 \text{ days}} = 4.0$ years

12 $Q = It$

$= 5.0 \times 75.0 \times 60$

$= 2.25 \times 10^4$ C

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

$$n(e^-) = \frac{Q}{F} = \frac{2.25 \times 10^4}{96\,500} = 0.233 \text{ mol}$$

$$n(Cu) = \frac{1}{2} n(e^-) = \frac{1}{2} \times 0.233 = 0.117 \text{ mol}$$

$$m(Cu) = nM = 0.117 \times 63.5 = 7.4 \text{ g}$$

13 **a** Write a balanced equation. Remember that $K_2Sn(OH)_6$ contains Sn^{4+} ions.

$Sn^{4+}(aq) + 4e^- \rightarrow Sn(s)$

b A faraday is the charge on 1 mol electrons. So the number of faradays is the same as the mole of electrons. Use stoichiometry to calculate the amount of electrons.

$$\frac{n(e^-)}{n(Sn)} = \frac{4}{1}$$

$n(e^-) = 4 \times 1.00$ mol

$= 4.00$ mol

So number of faradays = 4.00 F

c Calculate the number of coulombs, using $Q = It$.

$Q = 25.0$ A $(5.00 \times 60 \times 60)$ s $= 450\,000$ C

Calculate the amount in mol of electrons, using $n = \frac{Q}{F}$.

$$n(e^-) = \frac{450\,000 \text{ C}}{96\,500 \text{ C mol}^{-1}} = 4.663 \text{ mol}$$

Use stoichiometry to calculate the amount of Sn.

$$\frac{n(Sn)}{n(e^-)} = \frac{1}{4}$$

$$n(Sn) = \frac{4.663}{4} = 1.166 \text{ mol}$$

Calculate the mass of tin, using $n = \frac{m}{M}$

$m(Sn) = 1.166 \text{ mol} \times 118.7 \text{ g mol}^{-1} = 138$ g

14 **a** Anode: $2H_2O(l) + 4H^+(aq) \rightarrow O_2(g) + 4e^-$

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

b Calculate the amount of electrons, remembers that 1 F is the charge on to 1 mol electrons.

$n(e^-) = 0.400$ mol

Use stoichiometry to calculate the amount of Cu^{2+} deposited as Cu.

$$\frac{n(Cu^{2+})}{n(e^-)} = \frac{1}{2}$$

$$n(Cu^{2+}) = \frac{0.400}{2} = 0.200 \text{ mol}$$

Calculate the amount of Cu^{2+} remaining.

$n(Cu^{2+})$ remaining = $n(Cu^{2+})$ initial – $n(Cu^{2+})$ discharged = (1.00 L × 1.00 M) mol – 0.200 mol = 0.800 mol

Calculate the concentration of Cu^{2+} remaining.

$$c(Cu^{2+}) = \frac{0.800 \text{ mol}}{1.00 \text{ L}} = 0.800 \text{ M}$$

15 a $Ag^+(aq) + e^- \rightarrow Ag(s)$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$

b Calculate the amount of Ag deposited, using $n = \frac{m}{M}$.

$$n(Ag) = \frac{10.0\text{ g}}{107.9\text{ g mol}^{-1}} = 0.09268\text{ mol}$$

Use stoichiometry to calculate the amount in mol of electrons that passed through all cells.

$$\frac{n(e^-)}{n(Ag)} = \frac{1}{1}$$

$n(e^-) = 0.09268$ mol

Use stoichiometry to calculate the amount of Cu and Cr deposited.

$$\frac{n(Cu)}{n(e^-)} = \frac{1}{2}$$

$$n(Cu) = \frac{0.09268}{2} = 0.04634\text{ mol}$$

$$\frac{n(Cr)}{n(e^-)} = \frac{1}{3}$$

$$n(Cr) = \frac{0.09268}{3} = 0.03089\text{ mol}$$

Calculate the masses of Cu and Cr deposited.

$m(Cu) = 0.04634\text{ mol} \times 63.5\text{ g mol}^{-1}$
$= 2.94$ g

$m(Cr) = 0.03089\text{ mol} \times 52.0\text{ g mol}^{-1}$
$= 1.61$ g

16 a Cathode

b Negative

c Calculate the volume of Ag required, using volume = area × thickness.

$V(Ag) = 900\text{ cm}^3 \times 0.00500\text{ cm} = 4.5\text{ cm}^3$

Calculate the mass of Ag required, using density = $\frac{m}{V}$

$m(Ag) = 10.5\text{ g cm}^{-3} \times 4.5\text{ cm}^3 = 47.25$ g

Calculate the amount of Ag.

$$n(Ag) = \frac{47.25\text{ g}}{107.9\text{ g mol}^{-1}} = 0.4379\text{ mol}$$

Use stoichiometry to calculate the amount in mol of electrons required.

$$\frac{n(e^-)}{n(Ag)} = \frac{1}{1} = 0.4379\text{ mol}$$

Calculate the amount of charge required, using $n(e^-) = \frac{Q}{F}$

$Q = 0.4379\text{ mol} \times 96\,500\text{ C mol}^{-1}$
$= 42\,258$ C

Calculate the time required, using $Q = It$.

$$t = \frac{42\,258\text{ C}}{0.500\text{ A}} = 84\,516\text{ s} = 23.5\text{ h}$$

17 **a** Write balanced half-equations.

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

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

Calculate the quantity of charge, using $Q = It$.

$Q = 10.0\text{ A }(20 \times 60)\text{ s} = 12\,000\text{ C}$

Calculate the amount in mol of electrons, using $n(e^-) = \frac{Q}{F}$

$$n(e^-) = \frac{12\,000\text{ C}}{96\,500\text{ C mol}^{-1}}$$

$$= 0.1244\text{ mol}$$

Use stoichiometry to calculate the amount of Cu^{2+} deposited as Cu.

$$\frac{n(Cu^{2+})}{n(e^-)} = \frac{1}{2}$$

$$n(Cu^{2+}) = \frac{0.1244}{2}$$

$$= 0.0622\text{ mol}$$

Calculate the mass of Cu deposited.

$m(Cu) = 0.0622\text{ mol} \times 63.5\text{ g mol}^{-1} = 3.95\text{ g}$

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

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

Because the reverse reaction is occurring at each electrode [Cu] will remain constant, 1.00 M.

c Write balanced half-equations after the change of electrode.

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

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

$\therefore O_2(g)$ is produced

d Calculate the quantity of charge, using $Q = It$.

$Q = 10.0\text{ A }(20 \times 60)\text{ s} = 12\,000\text{ C}$

Calculate the amount in mol of electrons, using $n(e^-) = \frac{Q}{F}$

$$n(e^-) = \frac{12\,000\text{ C}}{96\,500\text{ C mol}^{-1}}$$

$$= 0.1244\text{ mol}$$

Use stoichiometry to calculate the amount of Cu^{2+} deposited as Cu.

$$\frac{n(Cu^{2+})}{n(e^-)} = \frac{1}{2}$$

$$n(Cu^{2+}) = \frac{0.1244}{2}$$

$$= 0.0622\text{ mol}$$

Calculate the amount of Cu^{2+} ions remaining in solution.

$$[Cu^{2+}\text{ remaining}] = \frac{0.1878\text{ mol}}{0.250\text{ L}}$$

$$= 0.7512\text{ M}$$

$$= 0.75\text{ M}$$

18 Calculate the quantity of charge.

$Q = It$

$= 125\,000 \times 24 \times 60 \times 60 = 2.16 \times 10^9\text{ C}$

Calculate the amount in mol of electrons.

$$n(e^-) = \frac{Q}{F}$$

$$= \frac{2.16 \times 10^9}{96\,500}$$

$$= 2.24 \times 10^4$$

Write a balanced equation.

$M^{2+} + 2e^- \rightarrow M$

i.e. mole ratio $M^{2+} : e^- = 1 : 2$

Calculate the number of moles of M.

$n(\text{M}) = \frac{1}{2} n(\text{e}^-)$

$= \frac{1}{2} \times 2.24 \times 10^4$

$= 1.12 \times 10^4$ mol

Mass M produced = 2.72×10^5 g

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

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

$= \frac{2.72 \times 10^5}{1.12 \times 10^4}$

$= 24.3$ g mol^{-1}

Inspection of a periodic table shows that this divalent metal must be magnesium.

19 **a** $Q = It$

$Q = 5.00 \times (16 \times 60) = 4500$ C

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

B: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

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

D: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

c Write the half-equation.

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

Calculate the amount in mol of electrons, using $n(\text{e}^-) = \frac{Q}{F}$

$n(\text{e}^-) = \frac{4500 \text{ C}}{96\,500 \text{ C mol}^{-1}}$

$= 0.0466$ mol

Use stoichiometry to calculate the amount of Cu consumed.

$\frac{n(\text{Cu})}{n(\text{e}^-)} = \frac{1}{2}$

$n(\text{Cu}) = \frac{0.0466}{2}$

$= 0.0233$ mol

Calculate the mass of Cu consumed.

$m(\text{Cu}) = 0.0233 \text{ mol} \times 63.5 \text{ g mol}^{-1} = 1.48$ g

d Write the half-equation.

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Calculate the amount in mol of electrons, using $n(\text{e}^-) = \frac{Q}{F}$

$n(\text{e}^-) = \frac{4500 \text{ C}}{96\,500 \text{ C mol}^{-1}}$

$= 0.0466$ mol

Use stoichiometry to calculate the amount of H_2 produced.

$\frac{n(H_2)}{n(\text{e}^-)} = \frac{1}{2}$

$n(H_2) = \frac{0.0466}{2}$

$= 0.0233$ mol

Calculate the volume of H_2 gas produced at STP.

$V(H_2) = 0.0233 \text{ mol} \times 22.4 \text{ L mol}^{-1} = 0.522$ L

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

As the concentration of copper ions increases in the solution due to the anode reaction, the copper will be deposited on the cathode because Cu^{2+} is a stronger oxidant than H^+.

CONNECTING THE MAIN IDEAS

20 **a** Write half-equations.

Cathode: $Na^+(l) + e^- \rightarrow Na(l)$

Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Calculate the quantity of charge, using $Q = It$.

$Q = (30 \times 10^3)\ A\ (24 \times 60 \times 60)\ s = 2.592 \times 10^9\ C$

Calculate the amount in mol of electrons, using $n(e^-) = \frac{Q}{F}$

$n(e^-) = \frac{2.592 \times 10^9\ C}{96\ 500\ C\ mol^{-1}} = 26\ 860.1\ mol$

Use stoichiometry to calculate the amount of Na.

$\frac{n(Na)}{n(e^-)} = \frac{1}{1}\ n(Na) = 26\ 860.1\ mol$

Calculate the mass of Na.

$m(Na) = 26860.1\ mol \times 23.0\ g\ mol^{-1} = 618\ kg = 6.2 \times 10^2\ g$

b $n(e^-) = \frac{1}{2} n(Cl_2)$

$= \frac{1}{2} \times 26860.1$

$= 13430.05\ mol$

$V(Cl_2) = nV_m$

$= 13430.05 \times 22.7$

$= 304862$

$= 3.0 \times 10^5\ L$

21 **a** Write balanced half-equations.

Cathode: $Al^{3+}(\text{in cryolite}) + 3e^- \rightarrow Al(l)$

Anode: $C(s) + 2O^{2-}(\text{in cryolite}) \rightarrow CO_2(g) + 4e^-$

Calculate the amount of Al, using $n = \frac{m}{M}$.

$n(Al) = \frac{1.00 \times 10^6\ g}{27.0\ g\ mol^{-1}} = 3.704 \times 10^4\ mol$

Use stoichiometry to calculate the amount in mol of electrons.

$\frac{n(e^-)}{n(Al)} = \frac{3}{1}\ n(e^-) = 3 \times 3.704 \times 10^4\ mol = 1.111 \times 10^5\ mol$

Calculate the number of coulombs, using $n = \frac{Q}{F}$.

$Q = 1.111 \times 10^5\ mol \times 96\ 500\ C\ mol^{-1}$

$= 1.072 \times 10^{10}\ C$

Calculate the time for which current flowed, using $Q = It$.

$t = \frac{1973 \times 10^{10}\ C}{150\ 000\ A} = 71481\ s = 19.9\ h$

b Use stoichiometry to calculate the amount in mol of electrons.

$\frac{n(e^-)}{n(Al)} = \frac{3}{1}\ n(e^-) = 3 \times 3.704 \times 10^4\ mol = 1.111 \times 10^5\ mol$

Use stoichiometry to calculate the amount of C.

$\frac{n(C)}{n(e^-)} = \frac{1}{4}\ n(C) = \frac{1.111 \times 10^5}{4} = 2.78 \times 10^4\ mol$

Calculate the mass of C, using $n = \frac{m}{M}$.

$m(C) = 2.78 \times 10^4\ mol \times 12.0\ g\ mol^{-1} = 3.333 \times 10^5\ g = 333\ kg$

c $n(CO_2) = n(C) = 2.78 \times 10^4\ mol$

$V(CO_2) = nV_m$

$= 2.78 \times 10^4 \times 22.4$

$= 622720$

$= 6.23 \times 10^5\ L$

22 **a** Write a balanced equation.

$Al^{3+}(\text{in cryolite}) + 3e^- \rightarrow Al(l)$

Calculate the amount of Al, using $n = \frac{m}{M}$.

$n(Al) = \frac{1.00 \times 10^6 g}{27.0\ g\ mol^{-1}} = 37037$ mol

Use stoichiometry to calculate the amount in mol of electrons.

$\frac{n(e^-)}{n(Al)} = \frac{3}{1}$

$n(e^-) = 3 \times 37064$ mol $= 111111$ mol

Calculate the electric charge required, using $n(e^-) = \frac{Q}{F}$.

$Q = 111111$ mol × 96500 C mol^{-1} = 1.072×10^{10} C = 1.07×10^{10} C

b Energy (J) = VC

$= 5.00\ V \times 1.07 \times 10^{10}\ C = 5.36 \times 10^{10}$ J

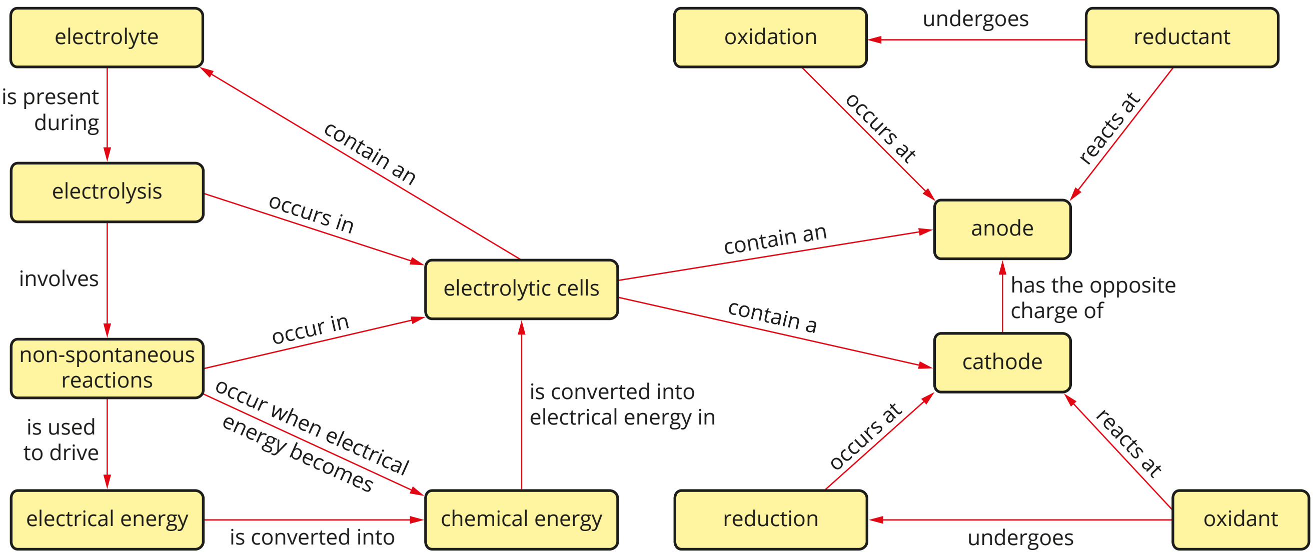
c Calculate the number of kilowatt hours required.

Number of kWh = $\frac{5.36 \times 10^{10} J}{3\,600\,000\ J} = 1.49 \times 10^4$ kWh

Calculate the cost of electricity.

Cost = $1.49 \times 10^4 \times \$0.12 = \$1787 = \$1790$

23



24 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.

25 **a** $n(Ti) = \frac{m}{M}$

$= \frac{14.37\ g}{47.9\ g\ mol^{1}}$

= 0.300 mol

b $4.0\ V = 4.0\ J\ C^{-1} = 0.0040\ kJ\ C^{-1}$

$Q = \frac{463.2}{0.0040}$

$= 115800$

$= 1.2 \times 10^5$ C

c $Q = n(\text{e}^-)F$

$$n(\text{e}^-) = \frac{Q}{F}$$

$$= \frac{115\,800}{96\,500}$$

$$= 1.2 \text{ mol}$$

d $\text{Ti}^{x+}(\text{aq}) + x\text{e}^- \rightarrow \text{Ti(s)}$

$$\frac{n(\text{e}^-)}{n(\text{Ti})} = \frac{x}{1}$$

$$= \frac{1.2}{0.300}$$

$$= 4.0$$

$x = 4$

The charge of the titanium ion is +4.

e $\therefore \text{EF} = \text{TiO}_2$

Chapter 10 Structure and nomenclature of organic compounds

Section 10.1 Diversity of carbon compounds

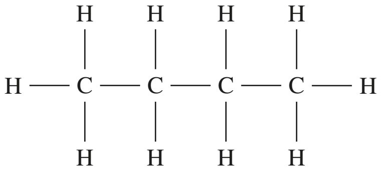
10.1 Key questions

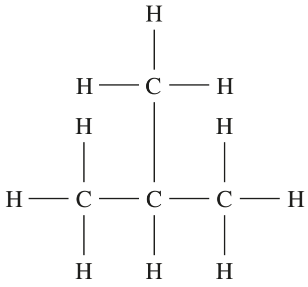
1 B, because the C–F bond requires the most energy to break.

2 **a** A formula that represents the three-dimensional arrangement of atoms in a molecule.
  b A formula that summarises the structural formula of a compound without showing the arrangement of atoms in space. The carbon atoms and the attached hydrogen atoms, as well as any functional groups, are listed on one line in the order in which they appear in the structural formula.
  c An organic compound in which all the carbon atoms are joined by single bonds.
  d An organic compound that contains one or more multiple bonds, such as carbon–carbon double or triple bonds.
  e Isomers that arise from a functional group being in different locations on the carbon chain.

3 A and C are alkanes. Each carbon has four bonds to other atoms and the molecular formulas follow the rule C_nH_{2n+2}.

4 **a** Butane (C_4H_{10})
  b





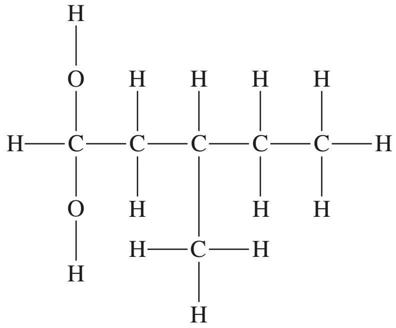
5 The carbon atoms in hydrocarbons have four bonds to other atoms. According to the valence shell electron repulsion theory, the angle around between each bond is 109.5° and the geometry around each carbon is tetrahedral. This means that carbon–carbon bonds are much less than 180° and so the chain is zig-zag shaped.

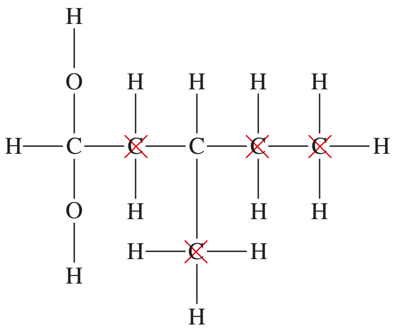
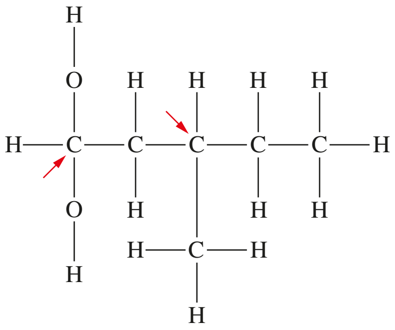
Section 10.2 Stereoisomers

Worked example: Try yourself 10.2.1

IDENTIFYING CHIRAL CENTRES IN ORGANIC MOLECULES

Identify any chiral centres in the following molecule.



<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Eliminate the carbon atoms that cannot be chiral centres. This includes all $-CH_3$ and $-CH_2-$ groups and any atom that is part of a double or triple bond, because these carbon atoms cannot be bonded to four different groups.</td><td>
This leaves two carbon atoms that may or may not be chiral centres.</td></tr>
<tr><td>For each remaining carbon atom, examine the groups attached to the atom. If there are four different groups, the atom is a chiral centre.</td><td>
The first carbon atom from the left has the following groups attached:
–H
–OH
–OH
$-CH_2-$
The four groups are not all different so this carbon atom is not a chiral centre.
The third carbon atom from the left has the following groups attached:
–H
$-CH_2CH_3$
$-CH_2CH(OH)_2$
$-CH_3$
The two $-CH_2-$ groups are different as one is attached to $-CH_3$ and the other is attached to $-C(OH)_2H$. This means the four groups are all different so this carbon atom is a chiral centre.</td></tr>
</table>

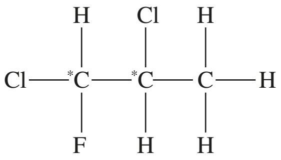
10.2 Key questions

1 The screw does not have a plane of symmetry because of the spiralling thread. The thread in the mirror image is spiralling in the wrong direction to superimpose on the original. The screw is chiral. The nail has a vertical plane of symmetry and so it is superimposable on its mirror image. The nail is achiral.

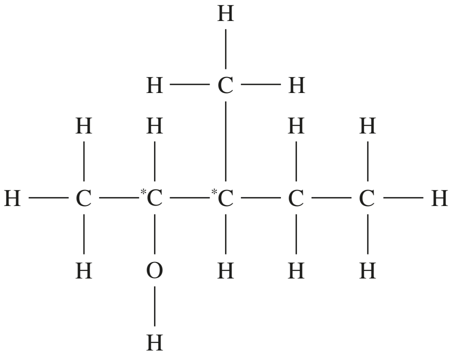
2 Carbon number 3 is a chiral centre as it is attached to four different groups. Carbon 1 is not a chiral centre as it is attached to three hydrogens. Carbons 2 and 4 are not chiral centres as they only have bonds to three other atoms.

3 **a** 0

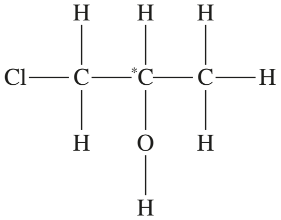
b 2



c 2



d 1

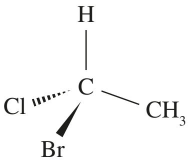


4 **a** Alkenes i, ii, iv and v have *cis–trans* isomers because each carbon in the double bond has two different groups attached.

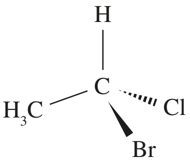
b Alkenes i and iii are *cis* isomers because the two alkyl chains are on the same side of the double bond.

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.

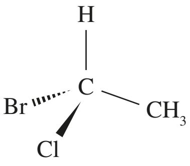
5 The enantiomer is shown as a mirror image of the original molecule. The enantiomer is rotated to put the hydrogen and methyl groups in the same arrangement and the bromine and chlorine atoms are inverted showing it is not superimposable.



original



enantiomer as mirror image

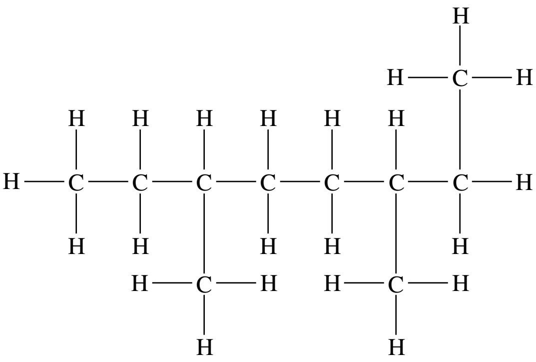
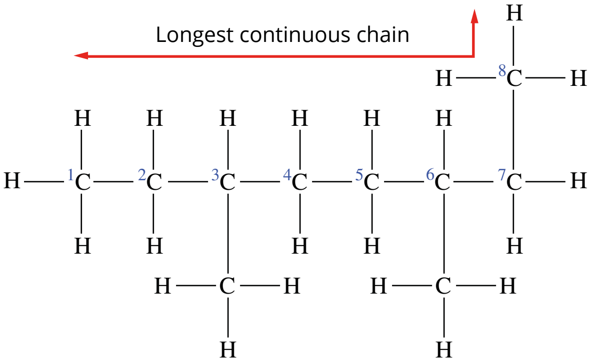
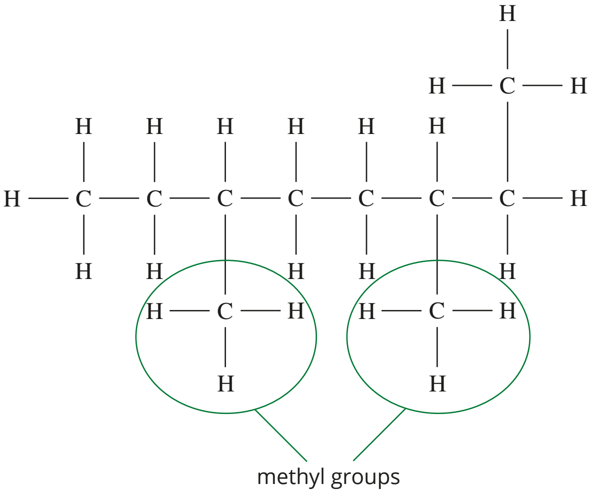


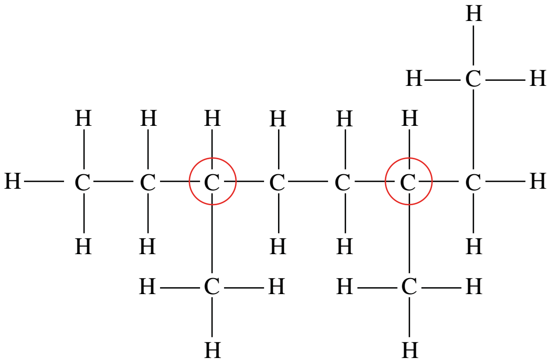
rotated enantiomer

Section 10.3 **Hydrocarbons**

Worked example: Try yourself 10.3.1

NAMING AN ISOMER OF AN ALKANE WITH MORE THAN ONE ALKYL BRANCH

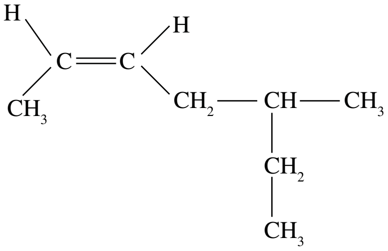
<table>
<tr><td colspan="2">Write the systematic name of the molecule with the following structure.
</td></tr>
<tr><td>Thinking</td><td>Working</td></tr>
<tr><td>Identify the parent name by counting the longest continuous chain of carbon atoms.</td><td>
There are eight carbon atoms in the longest continuous chain, so the parent name is octane.</td></tr>
<tr><td>Identify any alkyl side chains by counting the number of carbon atoms in any branches.</td><td>
There is one carbon atom in each of the alkyl groups, so they are methyl groups.</td></tr>
</table>

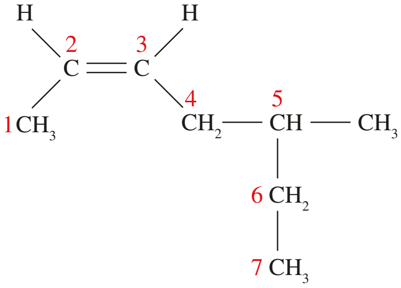
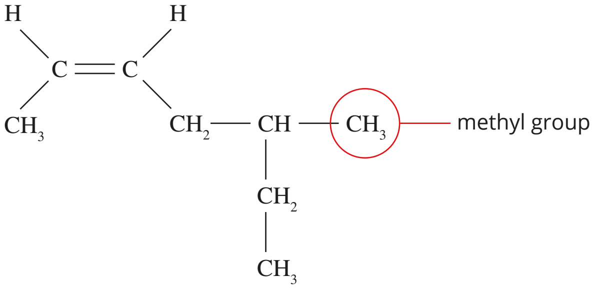
Identify the number(s) of the carbon atom(s) to which any alkyl group is attached. Count from the end that will give the lowest possible number to the carbons the groups are attached to.	 Each methyl group is attached to the third carbon from an end so it does not matter which end to count from. This will give numbers 3 and 6 to the methyl groups.
Assemble the name of the isomer, listing alkyl groups in alphabetic order with the number of the carbon atom before each group.	The name of the isomer is 3,6-dimethyloctane.

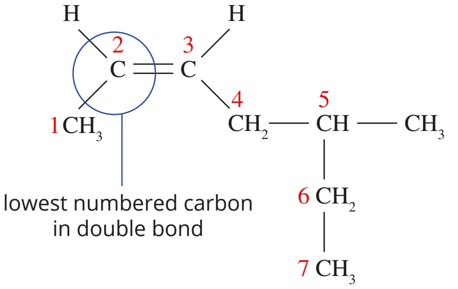
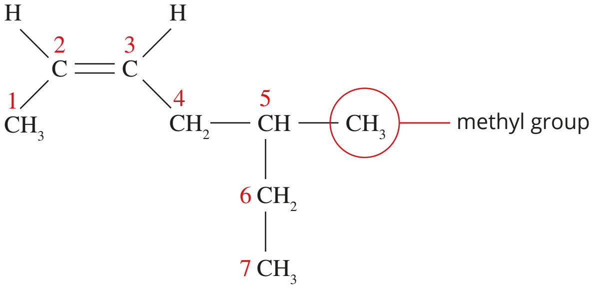
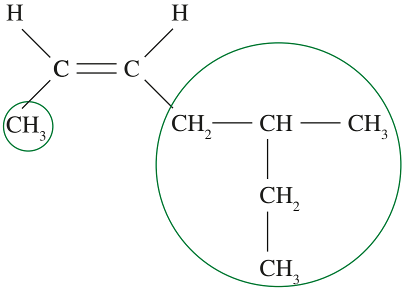
Worked example: Try yourself 10.3.2

NAMING A *CIS-TRANS* ISOMER OF AN ALKENE

Write the systematic name of the following alkene.



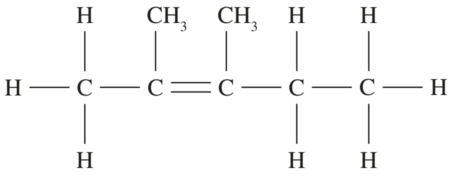
Thinking	**Working**
Identify the parent name by counting the longest continuous chain of carbon atoms.	 There are seven carbon atoms in the longest continuous chain, so the parent name is heptene.
Identify any alkyl side chains by counting the number of carbon atoms in any branches.	 There is one carbon 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.	*cis*-5-Methylhept-2-ene

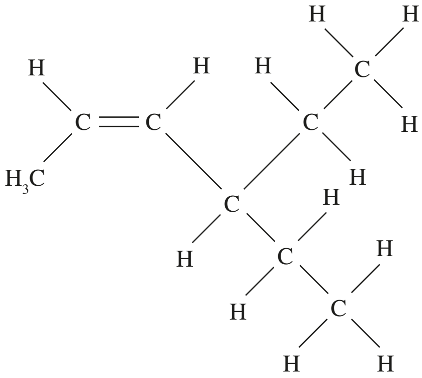
10.3 Key questions

1 **a** 3,3-Dimethylhex-1-yne
  b Methylbut-2-ene
  c *cis*-4-Ethylhex-2-ene

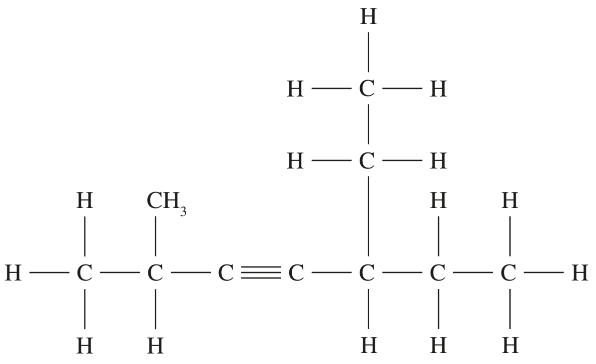
2 **a**



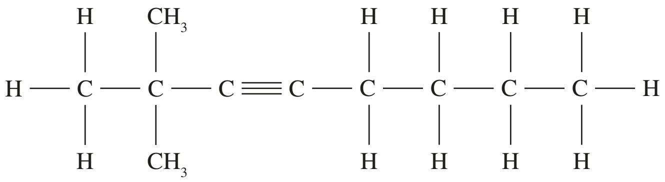
b



c

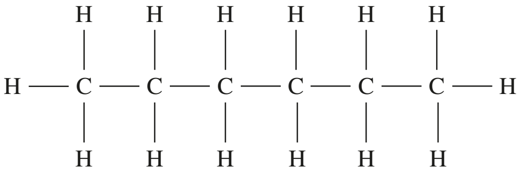


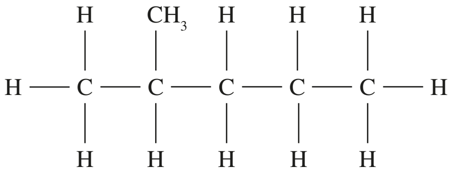
d

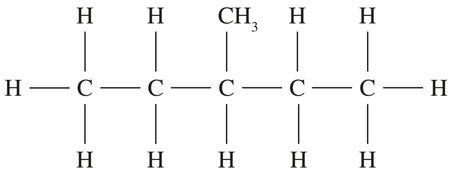


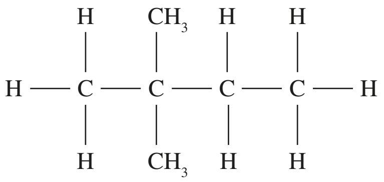
3 5-Ethyl-2-methylhept-3-yne and 2,2-dimethyloct-3-yne are structural isomers of the formula $C_{10}H_{18}$.

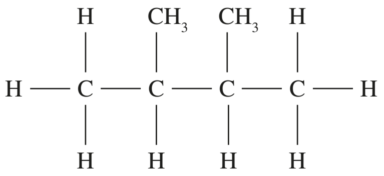
4 There are five possible isomers.











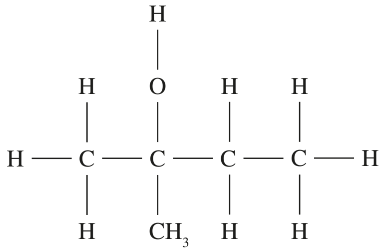
Section 10.4 Functional groups—Part 1

10.4 Key questions

1 2-Fluoro-3-bromopentane

2 $CH_3CFICHClCH_2CH_2CH_3$

3 2-Methylbutan-2-ol



4 **a** 1-Bromopropane
   b 2-Chloro-4-methylpentane
   c Pentan-1-ol
   d Octan-4-amine

5 Chloroethane has no isomers and so numbers are not needed. In propan-3-amine, the carbons should be numbered from the carbon atom closest to the amino functional group. Thus the amino group is located on the first carbon instead of the third carbon. Hence, the correct name is propan-1-amine.

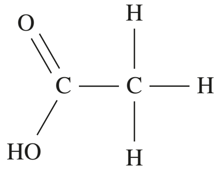
Section 10.5 Functional groups—Part 2

10.5 Key questions

1 **a** Ketones
   b Aldehydes
   c Amides
   d Esters

2 **a** Methyl methanoate
   b Methanoic acid
   c Propyl butanoate
   d Methyl ethanoate
   e Ethyl hexanoate

3 Ethanoic acid

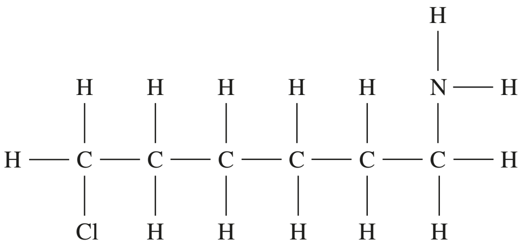


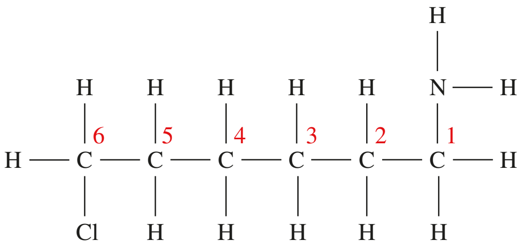
Section 10.6 An overview of IUPAC nomenclature

Worked example: Try yourself 10.6.1

NAMING AN ORGANIC MOLECULE WITH TWO FUNCTIONAL GROUPS

Name this molecule according to IUPAC rules.

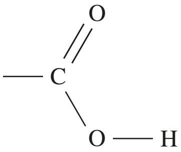


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	There are six carbons in the longest chain, so the parent name is hexane.
Identify the functional groups present.	The two functional groups present are chloro and amino.
Determine which functional group 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.

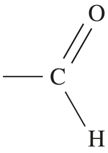
10.6 Key questions

1 **a** $-C\equiv C-$

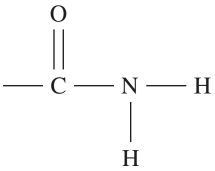
b



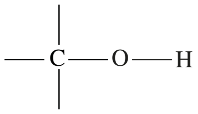
c



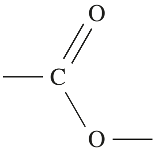
d



e

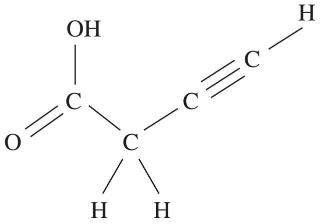


f

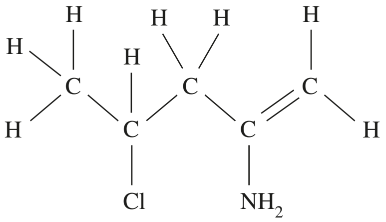


2 **a** 3-Hydroxybutanoic acid
b 3-Methylpentan-2-amine
c 4-Chloro-3-ethylpenan-2-ol
d 5-Fluoropent-2-yne

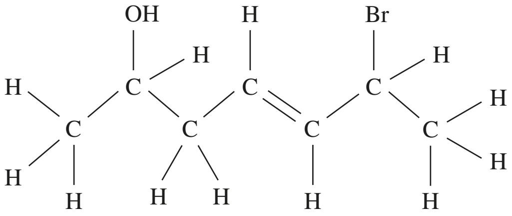
3 **a**



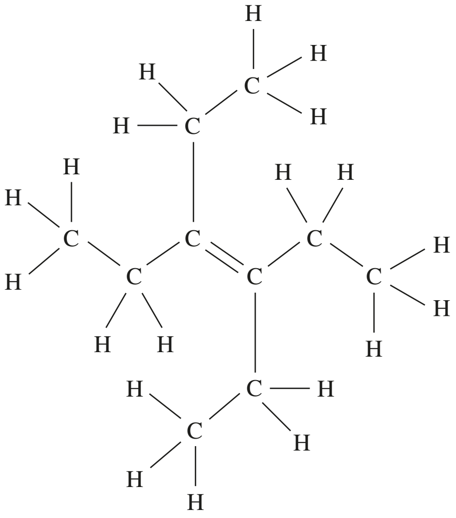
b



c



d



4 **a** **i** $CH_2{=}CHCH_2NH_2$
ii $CH_3CHClCH_2CH_2COOH$
iii $CH_2{=}CHCHOHCH_2CH_3$

b **i** Amino groups have priority over alkenes and so -amine should go at the end and have the lowest number. The correct name is prop-2-en-1-amine.

ii Carboxylic acid groups always go at the end of the chain and contain carbon 1. The correct name is 4-chloropentanoic acid.

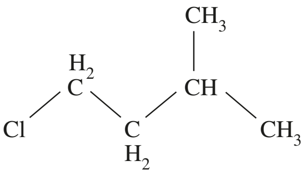
iii The ethyl chain is a part of the longest carbon chain. Hydroxyl groups have priority over alkenes and so –ol should go at the end. Numbering of the longest carbon chain should aim to minimise the number of the hydroxyl and alkene functional groups. Therefore the carbon-carbon double bond is at carbon number 1 and the hydroxyl group is at carbon number 3. The correct name is pent-1-en-3-ol.

CHAPTER 10 REVIEW

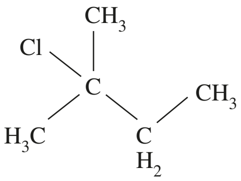
DIVERSITY OF CARBON COMPOUNDS

1 **a** 8

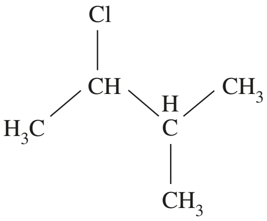
b



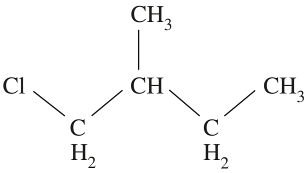
1-chloro-3-methylbutane



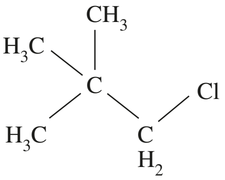
2-chloro-2-methylbutane



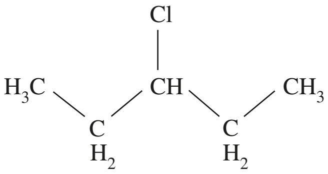
2-chloro-3-methylbutane



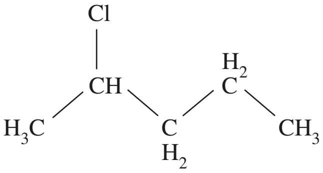
1-chloro-2-methylbutane



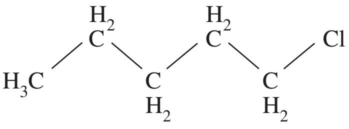
1-chloro-2,2-dimethylpropane



3-chloropentane



2-chloropentane



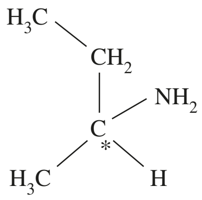
1-chloropentane

2 A positional isomer occurs when a functional group may be attached to more than one position in an organic molecule. A chain isomer occurs when the carbon chain of an organic molecule can be rearranged to form a new structure.

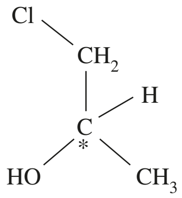
3 $CH_2{=}CHCH_2CH_3$ (but-1-ene) represents a straight chain positional isomer. The other straight chain positional isomer is $CH_3CH{=}CHCH_3$ (but-2-ene). A chain isomer of this structure is $(CH_3)_2C{=}CH_2$ (methylpropene) which has a different carbon backbone with a methyl branch at carbon 2.

STEREOISOMERS

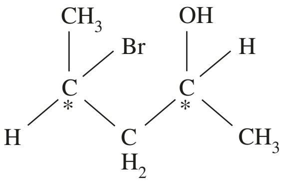
4 **a**



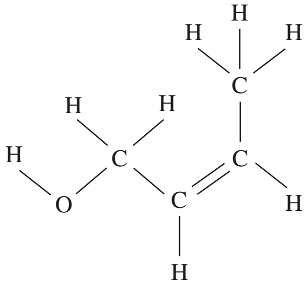
b



c



5



6 This structure contains enough carbons and functional groups to have both positional and chain isomers. In addition, there may be *cis–trans* isomerism about the double bond as there are two different groups attached to each carbon. The second carbon has two different alkyl chains, a hydroxyl and a hydrogen atom, meaning that this is a chiral centre, and the molecule has an enantiomer.

HYDROCARBONS

7 **a** C_5H_{12}
b C_6H_{12}
c C_4H_6
d C_7H_{14}

8 3 (pentane, methylbutane, dimethylpropane)

9 If an ethyl group is on the second carbon, then the longest chain is 6 carbons long and the name would be 3 methylhexane.

FUNCTIONAL GROUPS—PART 1

10 **a** N and H
b Cl
c H and O

11 Propan-1-ol is a primary alcohol; the carbon to which the hydroxyl group is attached has only one alkyl group attached to it. Propan-2-ol is a secondary alcohol; the carbon to which the hydroxyl group is attached has two alkyl groups attached to it.

12 **a** 2-Aminopropan-1-ol
b 8-Chlorooctan-2-ol
c 2-Iodoheptan-3-amine

FUNCTIONAL GROUPS—PART 2

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.

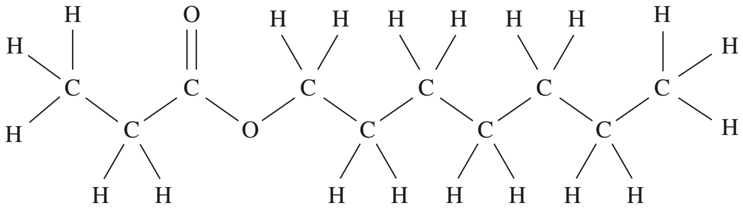
14 Carboxyl and amide carbons have three bonds within the functional group. They can only make one bond to connect to a carbon chain and so can never be within a chain.

AN OVERVIEW OF IUPAC NOMENCLATURE

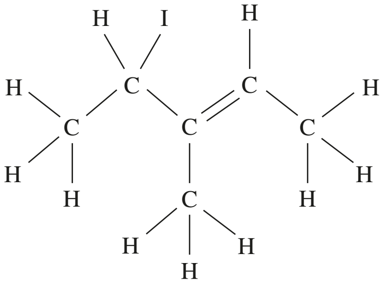
15 **a** But-3-enoic acid
- **b** 4-Aminobutan-2-ol
- **c** Butyl ethanoate
- **d** *trans*-2-Methylhex-3-ene
- **e** 4-Fluorobut-1-yne
- **f** *cis*-1-Bromobut-2-ene

CONNECTING THE MAIN IDEAS

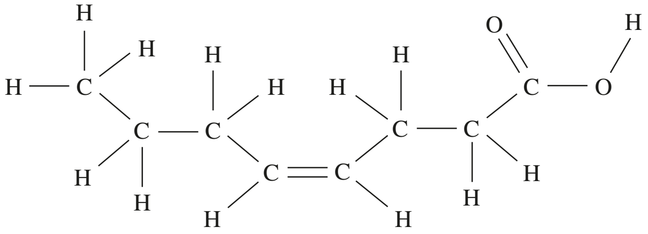
16 **a**



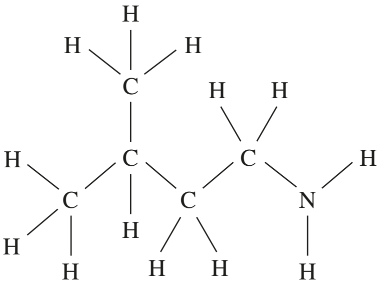
b



c



d



17 **a** $CH_3CH_2CH_2CH_2CH{=}CHCH_2COOH$
- **b** $CH_3CH_2CH_2CH_2CH_2COOCH_3$
- **c** $CH_2FCH_2CH_2OH$
- **d** $CH_2OHCH_2CH_2COOH$
- **e** $CH_3CH_2CH(CH_3)CH(CH_3)CH_2NH_2$

18 **a** $CH_3CH_2CH_2COCH_3$
- **b** $CH_3CH(CH_3)CH_2CH_2OH$
- **c** $CH_3CH_2CONH_2$
- **d** $CH{\equiv}CCH_2CHClCH_3$
- **e** $CH_3CH_2COOCH_2CH_3$

19 **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** Hydroxyl group has higher priority than amino group so the name should be 2-aminoethanol. No number is need for the hydroxyl as isomers are not possible with this group in this chain.
- **c** The triple bond has higher priority than the chloro group so the name should be 3-chlorohex-1-yne.
- **d** 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.
- **e** The double bond has higher priority than the methyl groups so the name should be 4,4-dimethylpent-2-ene.
- **f** 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.

20 **i** **a** Primary alcohol
- **b** Chloroalkane
- **c** Secondary alcohol
- **d** Carboxylic acid
- **e** Amine
- **f** Alkane
- **g** Alkene

ii **a** Heptan-1-ol
- **b** 4-Chloroheptane
- **c** Hexan-2-ol
- **d** Pentanoic acid
- **e** Butan-2-amine
- **f** 2-Methyloctane
- **g** 2-Methylpropene

21 Various answers possible.

Chapter 11 Properties and reactions of organic compounds

Section 11.1 Boiling points and solubilities of organic compounds

11.1 Key questions

1 alkane, 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, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2Cl$, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COOH$

4 **a** Miscible
  b Miscible
  c Immiscible
  d Miscible

Section 11.2 Viscosities and flashpoints of organic compounds

11.2 Key questions

1 ii, iv, i, iii

2 Propan-1-ol, propan-1,2-diol, glycerol

3 A. As chain length of the hydrocarbon increases, the strength of dispersion forces increases. The molecules therefore cling to each other more and are therefore more viscous. Because two-stroke fuel is made up of both petrol and lubricating oil, A is the only correct answer. It will be more viscous than petrol, but less viscous than lubricating oil as it still contains short chain hydrocarbons found in the petrol.

4 A

5 **a** –39°C
  b Ethanal is an aldehyde, which contains a polar carbonyl group. The presence of the permanent dipole will result in dipole–dipole interactions between ethanal molecules. The greater intermolecular force will mean the flashpoint will be higher for ethanal than for the non-polar ethane. Both ethanol and ethanoic acid can form hydrogen bonds, which are stronger than the dipole–dipole interactions for ethanol. Therefore, the flashpoint of ethanal must be below 16.6°C.

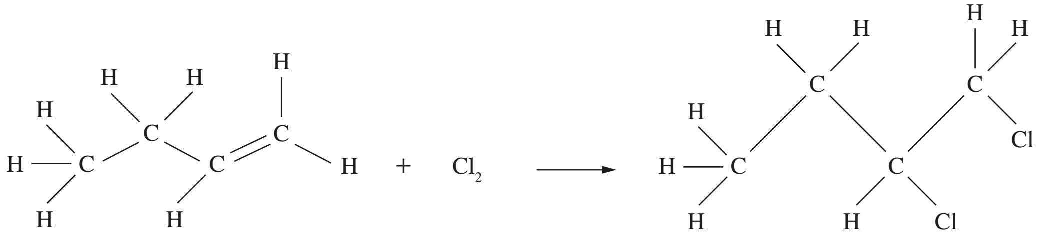
Section 11.3 Chemical properties of alkanes, haloalkanes and alkenes

11.3 Key questions

1 $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$
$CH_3Cl(g) + Cl_2(g) \rightarrow CH_2Cl_2(g) + HCl(g)$
$CH_2Cl_2(g) + Cl_2(g) \rightarrow CHCl_3(g) + HCl(g)$
$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$

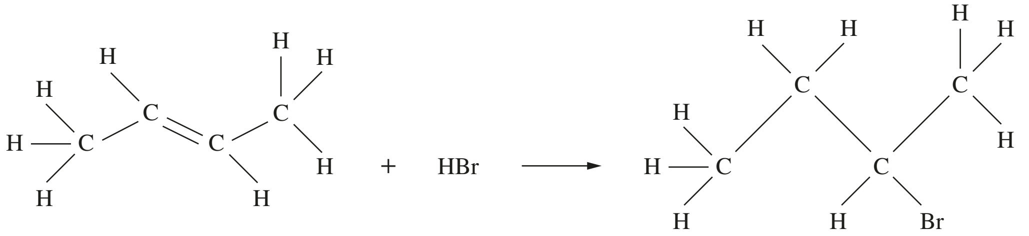
2 **a** Chloroethane
  b 1,2-Dichloroethane
  c Ethanol
  d Ethane

3 **a**



but-1-ene 1,2-dichlorobutane

b



but-2-ene 2-bromobutane

4 **a** Ethanamine
- **b** Butan-2-ol
- **c** Pentan-2-ol
- **d** Butan-2,3-diol

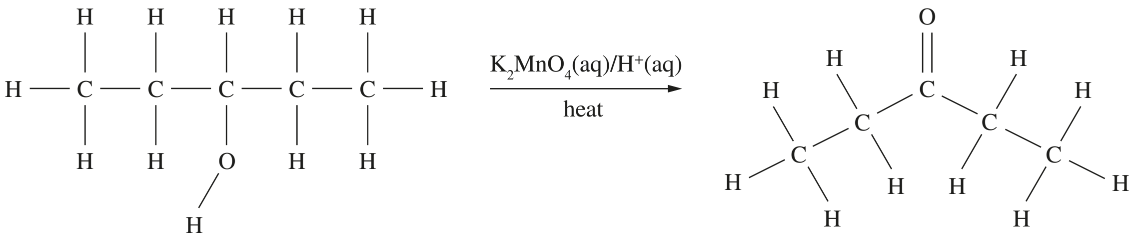
5 **a** $CH_3Cl(g) \xrightarrow{OH^-} CH_3OH(aq)$
- **b** $CH_3CH_2BrCH_3(l) \xrightarrow{NH_3} CH_3CH_2NH_2CH_3(l)$
- **c** $CH_3CH_2CH_2Cl(l) \xrightarrow{OH^-} CH_3CH_2CH_2OH(l)$

Section 11.4 Reactions of alcohols, carboxylic acids and esters

11.4 Key questions

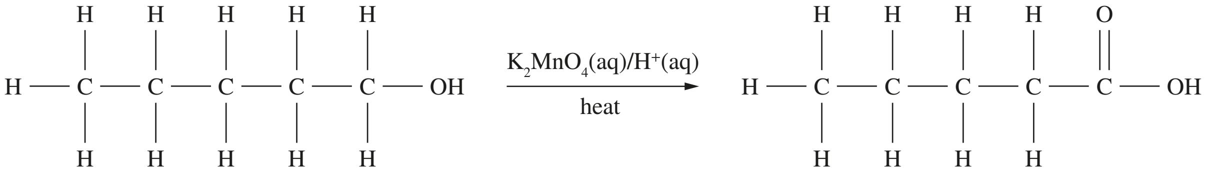
1 **a** Tertiary
- **b** Secondary
- **c** Secondary

2 **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 clear 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 orange to green as the reaction proceeds.



Reasoning: The aldehyde will be produced first but because there is no mention of how harsh the reaction conditions are it is assumed they oxidise completely to the carboxylic acid

3 **a** Water must be present as a reagent and the reaction requires an alkali or dilute acid catalyst.

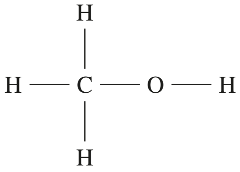
b **i** Methanol and butanoic acid

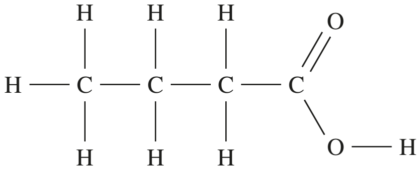
ii Propan-1-ol and ethanoic acid

iii Hexanol and propanoic acid

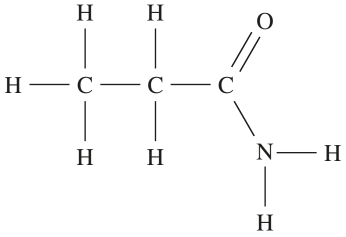
4 pentanamide, water, condensation

5 **a** Methanol and sodium butanoate; however, the addition of acid to the sodium butanoate will form butanoic acid

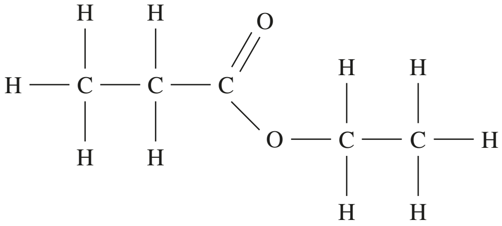

methanol


butanoic acid

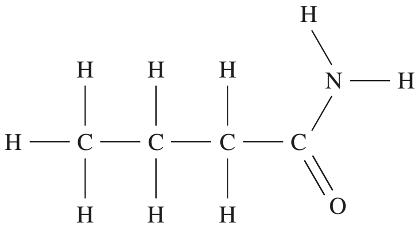
b


propanamide

c


ethyl propanoate

d


butanamide

Section 11.5 Reaction pathways

11.5 Key questions

1 **a** Ethene $\xrightarrow{H_2O}$ ethanol $\xrightarrow{NH_3}$ ethylamine

b Butane $\xrightarrow{Cl_2}$ 1-chlorobutane $\xrightarrow{OH^-}$ butan-1-ol

c 1-Chloropentane $\xrightarrow{OH}$ 1-pentanol $\xrightarrow{K_2Cr_2O_7/H^+}$ pentanoic acid

2 **a** Methane $\xrightarrow{Cl_2\text{, UV light}}$ chloromethane $\xrightarrow{OH^-}$ methanol $\xrightarrow{K_2Cr_2O_7/H^+}$ methanoic acid

b Ethene $\xrightarrow{H_2O}$ ethanol

c This synthesis can be carried out in three stages: (1) synthesis of propan-1-ol, (2) synthesis of methanoic acid and (3) synthesis of 1-propyl methanoate

1 Propane $\xrightarrow{Cl_2}$ 1-chloropropane $\xrightarrow{OH^-}$ propan-1-ol

2 Methane $\xrightarrow{Cl_2}$ chloromethane $\xrightarrow{OH^-}$ methanol $\xrightarrow{K_2Cr_2O_7/H^+}$ methanoic acid

3 Propan-1-ol + methanoic acid $\xrightarrow{H^+}$ 1-propyl methanoate + water

3 **a** Pentan-1-ol

b Sodium hydroxide

c Pentanoic acid

d Acidified potassium dichromate or potassium permanganate and heat

e Ammonia

4 This synthesis is carried out in three parts: (1) synthesis of 1-butanol, (2) synthesis of ethanoic acid and (3) synthesis of butyl ethanoate.

1 Butane $\xrightarrow{Cl_2}$ 1-chlorobutane $\xrightarrow{OH}$ butan-1-ol

2 Ethene $\xrightarrow{H_2O}$ ethanol $\xrightarrow{K_2Cr_2O_7/H^+}$ ethanoic acid

3 Ethanoic acid + butan-1-ol $\xrightarrow{H^+}$ butyl ethanoate + water

Section 11.6 Yield and the chemical industry

Worked example: Try yourself 11.6.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

80.0 g of propan-1-ol was oxidised to propanoic acid using an acidified solution of $K_2Cr_2O_7$. The propanoic acid obtained at the end of the reaction had a mass of 55.0 g. Calculate the percentage yield of this oxidation reaction.

Thinking	**Working**
Write an equation for the reaction.	$C_3H_7OH(l) \xrightarrow{K_2Cr_2O_7/H^+} C_2H_5COOH$
Use the formula $n = \frac{m}{M}$ to determine the amount of reactant. Give your answer to three significant figures,	$n(C_3H_7OH) = \frac{m(C_3H_7OH)}{M(C_3H_7OH)}$ $= \frac{80.0}{60.0}$ $= 1.33$ mol
Use the mole ratio for the reaction to determine the amount, in moles, of the product that would be made if all of the reactant reacted.	Mole ratio $= \frac{n(C_3H_7OH)}{n(C_2H_5COOH)} = \frac{1}{1}$ $m(C_2H_5COOH) = \frac{1}{1} \times n(C_3H_7OH)$ $= 1.33$ mol
Use the formula $m = n \times M$ to determine the mass of the product if all of the reactant reacts. This is the theoretical yield of the product.	$m(C_2H_5COOH) = n \times M$ $= 1.33 \times 74$ $= 98.42$ g
Calculate the percentage yield for this reaction from the formula: percentage yield $= \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$	percentage yield $= \frac{55.0}{98.42} \times \frac{100}{1}$ $= 55.9\%$

Worked example: Try yourself 11.6.2

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: $\frac{90}{100} \times \frac{80}{100} \times \frac{60}{100} \times \frac{100}{1}$ $= 43\%$

Worked example: Try yourself 11.6.3

CALCULATING ATOM ECONOMY

Calculate the percentage atom economy in the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol.
The equation for the reaction is:

$$CH_3CH_2CH_2OH(aq) + NaI(aq) + H_2SO_4(aq) \rightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$$

Thinking	**Working**
Calculate the total molar mass of the reactants.	$M(CH_3CH_2CH_2OH) + M(NaI) + M(H_2SO_4)$ $= [(3 \times 12.0) + (8 \times 1.00) + 16.0] + (23.0 + 127) + [(2 \times 1.00) + 32.0 + (4 \times 16.0)]$ $= 308\text{ g mol}^{-1}$
Calculate the molar mass of the required product.	$M(\text{iodopropane})$ $= (3 \times 12.0) + (7 \times 1.00) + 127$ $= 170\text{ g mol}^{-1}$
Calculate the atom economy for the reaction using the formula: $\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$	$\text{Atom economy} = \frac{170}{308} \times 100$ $= 55.2\%$

11.6 Key questions

1 $n(\text{ethanol})\ 20.0\text{ g}/46\text{ g mol}^{-1} = 0.435\text{ mol}$

Theoretical yield: $n(\text{ethanoic acid}) = n(\text{ethanol}) = 0.435\text{ mol}$

Mass (ethanoic acid) $= 0.435 \times 60.0 = 26.1\text{ g}$

$$\%\text{ yield} = \frac{21.5}{26.1} \times 100$$
$$= 82.4\%$$

2 **a** yield $= 0.7 \times 0.5 \times 0.9$

$= 0.32 = 32\%$

b yield $= 0.7 \times 0.1 \times 0.9$

$= 0.063 = 6.3\%$

3 $n(C_2H_4) = \frac{150}{28} = 5.36\text{ mol}$

$n(C_2H_5OH) = n(C_2H_4) = 5.36\text{ mol}$

$m(C_2H_5OH) = 5.36 \times 46 = 247\text{ g}$

4 Reaction 1:

Mass of reactants $= 2 \times M(CH_2CH_2) + 2 \times M(Cl_2) + M(Ca(OH)_2)$

$= 2[(2 \times 12.0) + (4 \times 1.00)] + [2(2 \times 35.5)] + [40.1 + 2(16.0 + 1.00)]$

$= 272.1\text{ g mol}^{-1}$

Mass of product $= 2 \times M(H_2COCH_2)$

$= 2 \times [(2 \times 1.00) + (2 \times 12.0) + 16.0 + (2 \times 1.00)]$

$= 88.0\text{ g mol}^{-1}$

$$\text{Atom economy} = \frac{88.0}{272.1} \times 100 = 32.3\%$$

Reaction 2:

Mass of reactants $= M(\mathrm{CH_2CH_2}) + M\,\frac{1}{2}(\mathrm{O_2})$

$= [(2 \times 12.0) + (4 \times 1.00)] + [16.0]$

$= 44\ \mathrm{g\ mol^{-1}}$

Mass of product $= M(\mathrm{H_2COCH_2}) = [(2 \times 1.00) + (2 \times 12.0) + 16.0 + (2 \times 1.00)]$

$= 44\ \mathrm{g\ mol^{-1}}$

Atom economy $= \frac{44}{44} \times 100 = 100\%$

5 Total molar mass of reactants $= M(\mathrm{C_6H_6}) + M(\mathrm{H_2SO_4}) + M(\mathrm{NaOH})$

$= [(6 \times 12.0) + 6 \times 1.00]] + [(2 \times 1.00) + (1 \times 32.1) + (4 \times 16.0)] + [23.0 + 16.0 + 1.00]$

$= 256\ \mathrm{g\ mol^{-1}}$

Total molar mass of products $= M(\mathrm{C_6H_5OH})$

$= [(6 \times 12.0) + (5 \times 1.00) + 16.0 + 1.00]$

$= 94.0\ \mathrm{g\ mol^{-1}}$

Atom economy $= \frac{94.0}{256} \times 100 = 36.7\%$

6 Working: atom economy $= \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}}$

$\frac{76.6}{100} = \frac{2.00}{x}$

$x = \frac{2.00}{0.766}$

$= 2.61$ kg

CHAPTER 11 REVIEW

BOILING POINTS AND SOLUBILITIES OF ORGANIC COMPOUNDS

1 Methylpropane and butane have the lowest boiling points because alkanes are non-polar, so dispersion forces are the only intermolecular forces. Dispersion forces are not as strong as other intermolecular forces so the boiling points of alkanes are low. Molecules of butane have a greater surface area and can fit more closely together than molecules of methylpropane, forming stronger intermolecular bonds. Dipole–dipole interactions exist between the polar regions of the molecules. Hydrogen bonds exist between the propan-1-ol molecules because of the electronegative nature of the oxygen atom. These bonds are stronger than the dispersion forces between methylpropane and butane molecules and dipole–dipole forces in methyl methanoate molecules.

2 Boiling points of compounds are determined by the strength of the intermolecular forces. Weak dispersion forces are present in all molecules, polar or non-polar, so must be kept as close to constant as possible when making comparisons on the effect of changing functional groups. Because dispersion forces increase with molecular size, it is important to select compounds of a similar molar mass.

3 **a** $\mathrm{CH_3CH(CH_3)CH(CH_3)CH_2CH_2OH}$, $\mathrm{CH_3CH(CH_3)CH_2CH_2CH_2CH_2OH}$, $\mathrm{CH_3(CH_2)_5CH_2OH}$

b They would have greater solubility in hexane because hexane is a non-polar solvent. The presence of the single polar hydroxyl group would not be sufficient to overcome the non-polar characteristic of the large hydrocarbon chains.

VISCOSITIES AND FLASHPOINTS OF ORGANIC COMPOUNDS

4 **a** Viscosity is a measure of how well a liquid flows.

b The flashpoint of a fuel is defined as the lowest temperature at which the fuel will ignite with an ignition source.

5 Octane will have the higher viscosity and higher flashpoint.

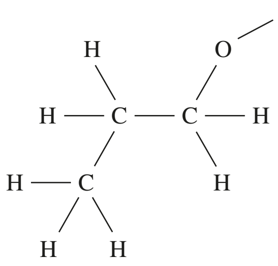
Intermolecular forces determine both the viscosity and flashpoint of organic compounds. This is because octane has the higher molar mass. Both octane and pentane are non-polar hydrocarbons so the only intermolecular forces between molecules are dispersion forces. As the size of the molecules increases so does the strength and number of dispersion forces between molecules.

CHEMICAL PROPERTIES OF ALKANES, HALOALKANES AND ALKENES

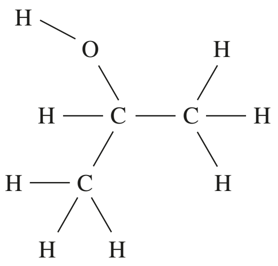
6

Reactants	**Type of reaction**	**Product**
Alkene and hydrogen	Addition (hydrogenation)	Alkane
Alkene and hydrogen bromide	Addition	Bromoalkane
Alkene and water (with a catalyst)	Addition (hydrolysis)	Alcohol
Alkene and bromine	Addition	Dibromoalkane
Alkene in the presence of a catalyst	Addition polymerisation	Saturated hydrocarbon polymer

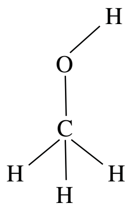
7 **a**



or



b



8 **a** $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2\text{, UV light}} CH_2CH_2Cl(l)$

b $CH_3CH_2CH_2CH_2Cl(l) \xrightarrow{OH} CH_3CH_2CH_2CH_2OH(aq)$

c $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

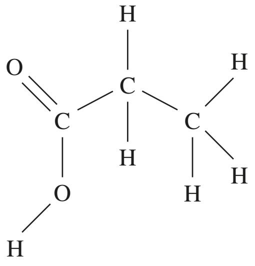
REACTIONS OF ALCOHOLS, CARBOXYLIC ACIDS AND ESTERS

9 **a** Aldehyde, carboxylic acid

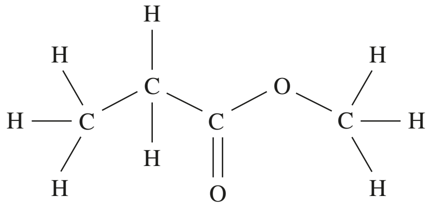
b Ketone

c No reaction will occur.

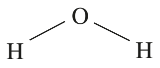
10 **a**



b



and



11 **a** $CH_3CH_2COOCH_3(l) + H_2O(l)$

b $CH_3COO(CH_2)_4CH_3(l) + H_2O(l)$

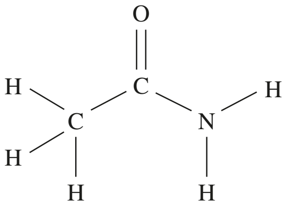
c $HCOOCH(CH_3)_2(l) + H_2O(l)$

12 a CH_3COOH

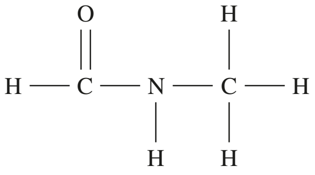
b $CH_3CH_2CH_2OH$, CH_3COOH

c CH_3CH_2OH, $HCOOH$

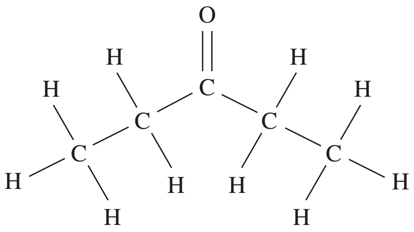
13 a



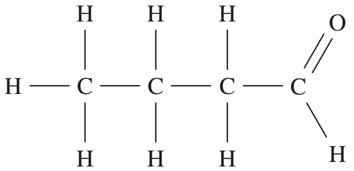
b



c



d



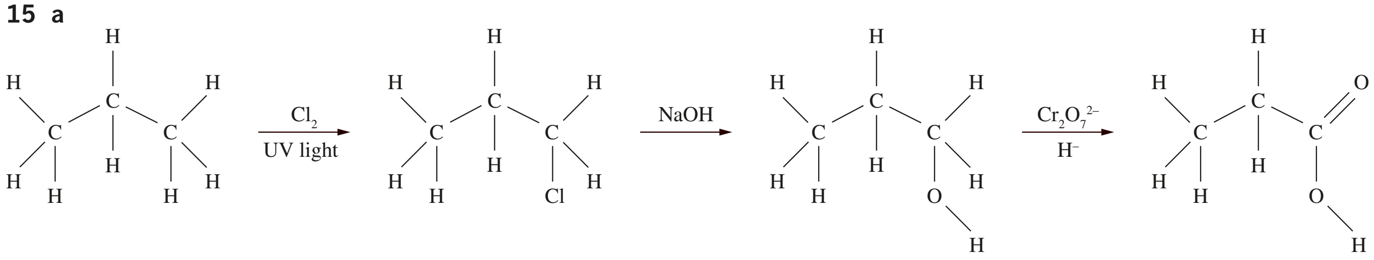
REACTION PATHWAYS

14 a Cl_2 and sunlight

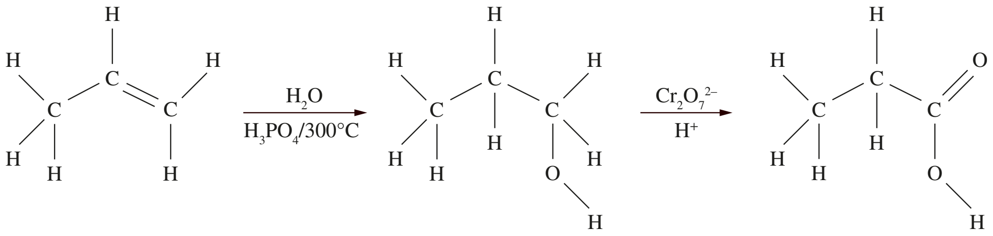
b Propan-2-ol

c Propan-2-amine

15 a



b



16 a 1 Ethene $\xrightarrow{HCl}$ chloroethane $\xrightarrow{OH}$ ethanol

2 1-Chloropropane $\xrightarrow{OH}$ propan-1-ol $\xrightarrow{Cr_2O_7^{2-}/H^+}$ propanoic acid

Overall: ethanol + propanoic acid $\xrightarrow{H_2SO_4}$ ethyl propanoate

b Ethene $\xrightarrow{Cl_2}$ chloroethane $\xrightarrow{NaOH}$ ethanol $\xrightarrow{Cr_2O_7^{2-}/H^+}$ ethanoic acid $\xrightarrow{ROH/H_2SO_4}$ ethyl ethanoate

YIELD AND THE CHEMICAL INDUSTRY

17 63.9%

18 a 3.26 g

Working: molar ratio of salicylic acid to aspirin is 1 : 1

$M(C_7H_6O_3) = 138 \text{ g mol}^{-1}$

$$
\begin{aligned}
n(C_7H_6O_3) &= \frac{2.5}{138} \\
&= 0.0181 \text{ mol} \\
n(\text{aspirin}) &= 0.0181 \text{ mol} \\
M(\text{aspirin}) &= M(C_9H_8O_4) \\
&= 180 \text{ g mol}^{-1} \\
m(\text{aspirin}) &= 0.0181 \times 180 \\
&= 3.26 \text{ g}
\end{aligned}
$$

b $$\% \text{ yield} = \frac{2.35}{3.36} \times 100 = 69.9\%$$

CONNECTING THE MAIN IDEAS

19 a i $CH_3CH_3(g) \xrightarrow{Cl_2\text{, UV light}} CH_3CH_2Cl(g)$

ii $CH_2CH_2(g) \xrightarrow[H_3PO_4/300° \text{ C}]{H_2O} CH_3CH_2OH(g)$

iii $CH_3CH_2Cl(g) \xrightarrow{OH} CH_3CH_2OH(aq)$

iv $CH_3CH_2OH(aq) \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH(aq)$

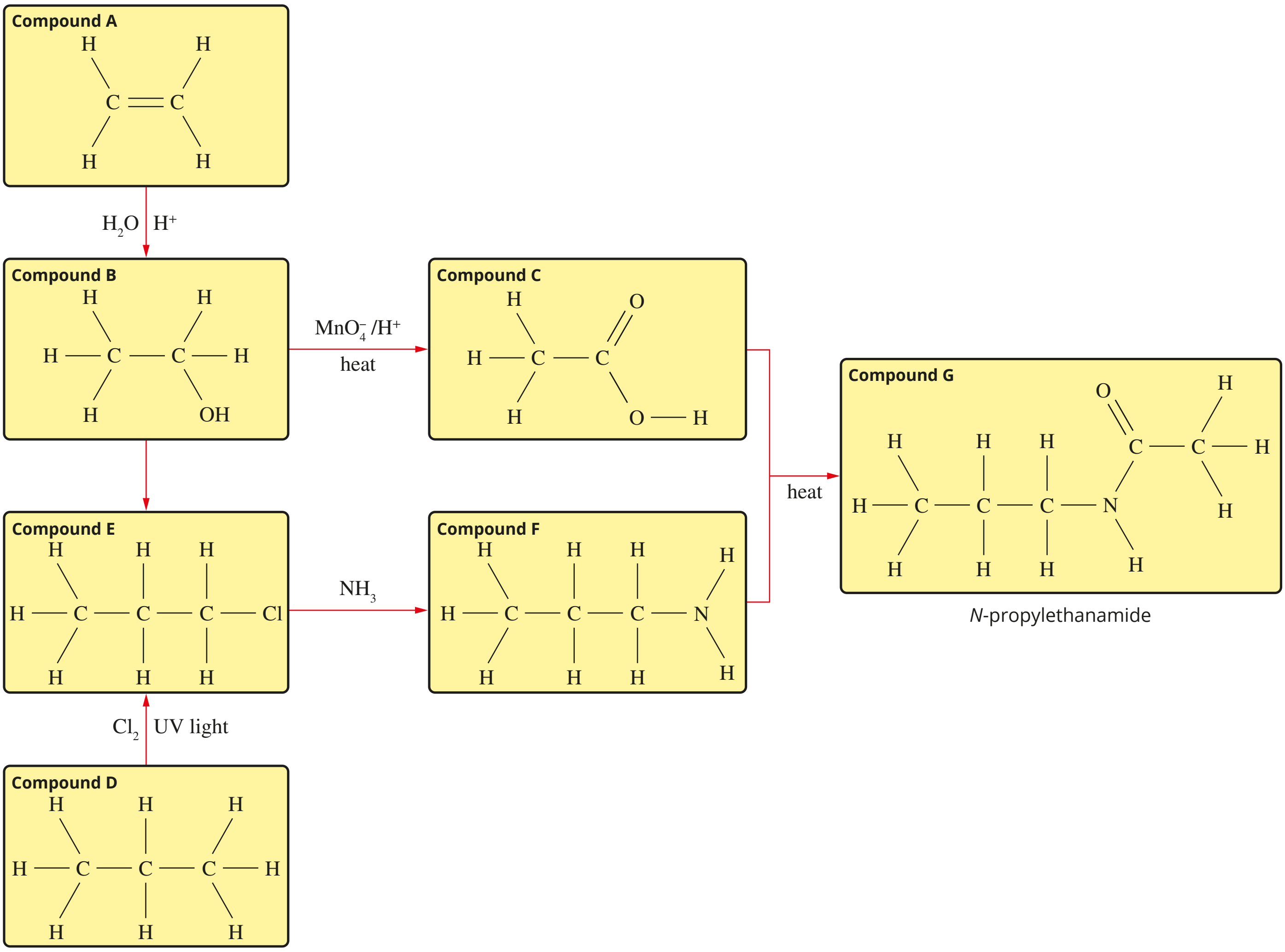
b i Substitution

ii Addition

iii Substitution

iv Oxidation

20 a



N-propylethanamide

b The bromine test for unsaturated hydrocarbons. When aqueous Br_2 is added to A, an addition reaction will occur and the solution will turn from orange to colourless. If Br_2(aq) is added to D, no reaction will occur and the solution will remain orange.

c B. Although both compounds can form hydrogen bonds with water, the larger size (greater number of carbon atoms) of propanamine (F) will give it lower solubility.

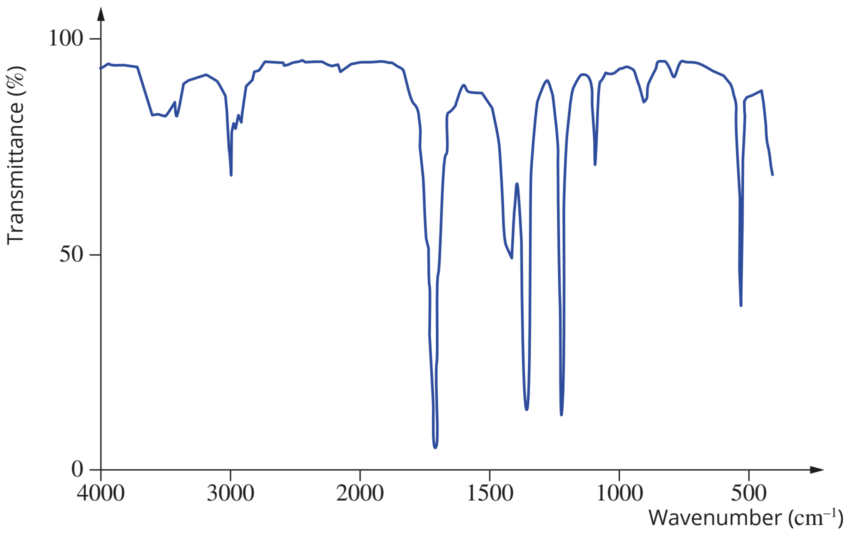
Chapter 12 Analysis of organic compounds by spectroscopic techniques

Section 12.1 Infrared spectroscopy

Worked example: Try yourself 12.1.1

INTERPRETING THE IR SPECTRUM OF AN UNKNOWN COMPOUND

Use the infrared spectrum of the unidentified compound to identify the functional groups present. The molecular formula of the compound is C_3H_6O. You will need to refer to the IR absorption data in Table 12.1.4.



Thinking	**Working**
Identify the absorption bands that correspond to the absorption bands of bonds in the IR absorption data table.	There is a strong, narrow band at approximately 1700 cm^{-1}, which corresponds to the absorption by a carbonyl, C=O, group. There is a small, narrow band at approximately 2900 cm^{-1}, which corresponds to the absorption by a C–H group.
Identify the functional group or groups that are present.	The spectrum shows absorption bands corresponding to the presence of C=O carbonyl group and C–H groups. This suggests the molecular formula of CH_3COCH_3.

12.1 Key questions

1 **a** Vibrational
  b Valence electron movement
  c Valence electron movement

2 **a** Microwave
  b Infrared
  c Radio
  d Gamma rays

3 **a** O–H at 3200–3550 cm^{-1} and C–O at 1000–1300 cm^{-1}
  b N–H at 3350–3500 cm^{-1} and C=O at 1670–1750 cm^{-1}
  c N–H at 3350–3500 cm^{-1}
  d O–H at 2500–3300 cm^{-1}, C=O at 1670–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
  e C=O at 1670–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
  f C=O at 1670–1750 cm^{-1}

4 The absorption bands from C–O and C–C bonds are located in the fingerprint region below 1400 cm^{-1}. Many molecules contain these bonds in various functional groups, and so they give few clues to the structure of a compound. The exact wavenumber of C–O and C–C absorption bands are highly specific to an individual molecule and can be used to compare the molecule to a reference standard for positive identification.

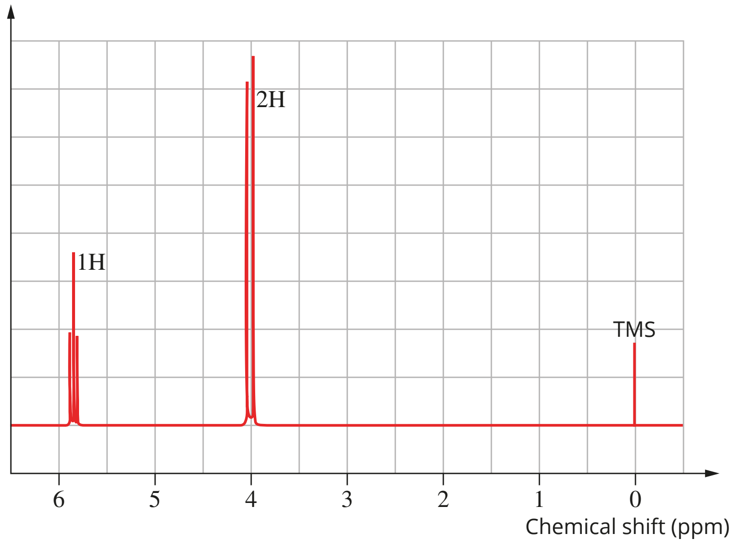
5 **a** O–H acids at approx. 3000 cm^{-1}, C=O at approx. 1700 cm^{-1}
  b C–H at approx. 2800 cm^{-1}, C=O at approx. 1700 cm^{-1}
  c O–H alcohols at approx. 3300 cm^{-1}, C–H at approx. 2800 cm^{-1}
  d N–H at approx. 3400 cm^{-1}, C–H at approx. 2900 cm^{-1}

Section 12.2 Nuclear magnetic resonance spectroscopy

Worked example: Try yourself 12.2.1

INTERPRETATION OF A ^{1}H NMR SPECTRUM

The proton NMR spectrum of a compound with a molecular formula of $C_2H_3Cl_3$ is shown below. Relative peak areas are shown on the spectrum.



Identify this compound using the information provided in the NMR spectrum.

Thinking	**Working**
What information does the formula provide about the compound?	Two molecules are possible from the formula: either 1,1,1-trichloroethane or 1,1,2-trichloroethane.
Summarise the information provided in the NMR spectrum in a table.	See table below
Identify the number of different hydrogen environments.	There are two signals so there must be two different hydrogen environments.

Chemical shift	Peak splitting	Relative peak area
4.0	doublet (2-line pattern)	2
5.8	triplet (3-line pattern)	1

If possible, use the chemical shifts in Table 12.2.1 to identify the types of protons. Remember the ranges are broad.	The table does not give information about compounds containing two chloro groups, so continue on to the next step.
Use the relative peak area to deduce the number of hydrogen atoms in each environment.	The relative area peak areas of the signals at 5.8 and 4.0 ppm are 1:2, so the relative number of hydrogen atoms must be 1:2. The sum of hydrogen atoms in the formula is 3, which means that the peak areas are directly equal to the number of hydrogens in each environment. This also supports the splitting information, confirming that the molecule contains one –CH– group and one $–CH_2–$ group.
Use the peak splitting of the signals to identify the types of hydrogen environments.	The signal at 4.0 ppm is a doublet (2-line pattern). The number of lines in the pattern given by $n + 1$. This signal must be generated by an environment that has one neighbouring hydrogen atom, i.e. a –CH group. The signal at 5.8 ppm is a triplet (3-line pattern). The number of lines in the pattern is given by $n + 1$. This signal must be generated by an environment that has 2 neighbouring hydrogen atoms, i.e. a $–CH_2–$ group.
Use the information you gathered to identify the compound.	The molecular formula of the compound is $C_2H_3Cl_3$. The compound is either 1,1,1-trichloroethane or 1,1,2-trichloroethane. The splitting patterns and peak area indicates that the molecule contains a $–CH_2–$ group adjacent to a –CH– group. The molecule must be 1,1,2-trichloroethane because the structure fits the evidence from the spectrum.

12.2 Key questions

1 **a** The number of signals indicates the number of non-equivalent hydrogen environments.
  b The chemical shift of a signal indicates the type of hydrogen environment.
  c The relative peak areas indicate the relative number of hydrogen atoms in each proton environment.
  d The splitting pattern of a signal indicates the number of hydrogen atoms neighbouring a specific proton environment.

2 **a** **i** 2
  ii 3
  iii 4
  iv 4
  b **i** 2
  ii 4
  iii 4
  iv 3
  c A triplet (3-line pattern), a quartet (4-line pattern) and a singlet (1-line pattern).
  d 3:2

3 The signal is likely to be caused by $RCH{=}CHC\mathbf{H}_3$. This group has three hydrogen atoms, one neighbour and a typical chemical shift of 1.6–1.9 ppm.

4 **a** There are three peak sets, each representing a different proton environment.
  b From Table 12.2.1, the expected chemical shifts are:

$–COCH_3$	2.1–2.7 ppm
RCH_3	0.8–1.0 ppm
$–OCH_2R$	3.3 ppm

  c Relative number of protons for the peak sets
  A:B:C = 2:3:3

d Proton NMR peaks are split because of interaction of the magnetic fields on adjacent atom. The number of peaks associated with each proton environment is shown in the figure in part b. Using the $n + 1$ rule:
- The quadruple peaks at A indicate that there are three hydrogens attached to an adjacent atom.
- The single peak at B indicates that there are no hydrogens attached to the adjacent atom.
- The triplet at B indicates that there are two hydrogens attached to the adjacent atom.

e A = CH_2 group
B = methyl group of ester
C = methyl group of CH_3CH_2

f There will be four peaks in the ^{13}C NMR spectrum because there are four different carbon environments in the ethyl ethanoate molecule.

Section 12.3 Mass spectrometry

Worked example: Try yourself 12.3.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak at $m/z = 58$. Determine the molecular formula of the alkane and give its name.

Thinking	**Working**
The m/z value of the molecular ion is equal to the relative molecular mass of the molecule.	The relative molecular mass of the alkane is 58.
Identify the general formula for the molecule.	The general formula for an alkane is C_nH_{2n+2}.
Use the general formula to set up an equation linking the relative molecular mass to the relative atomic masses of the constituent atoms.	$M_r(C) = 12$ $M_r(H) = 1$ $(12 \times n) + (1 \times (2n + 2)) = 58$
Solve the equation for n.	$12n + 2n + 2 = 58$ $14n + 2 = 58$ $14n = 56$ $n = 4$
Use the value of n to find the molecular formula and the name.	C_4H_{10}, which is butane.

12.3 Key questions

1 **a** 114 g mol^{-1}
b 43
c $C_6H_{13}^+$
d Octane, C_8H_{18}

2 $C_2H_4{}^{79}Br_2^+$, $C_2H_4{}^{79}Br^{81}Br^+$, $C_2H_4{}^{81}Br_2^+$

3 **a** $CH_3CH_2CH_2Br$
b The peaks at $m/z = 122$ and $m/z = 124$ are due to the molecular ion containing Br but it might be the ^{79}Br or ^{81}Br isotopes.
c The two isotopes of bromine, ^{79}Br and ^{81}Br, are found in almost equal abundances so the peaks are almost equivalent in height.
d $CH_3CH_2CH_2^+$

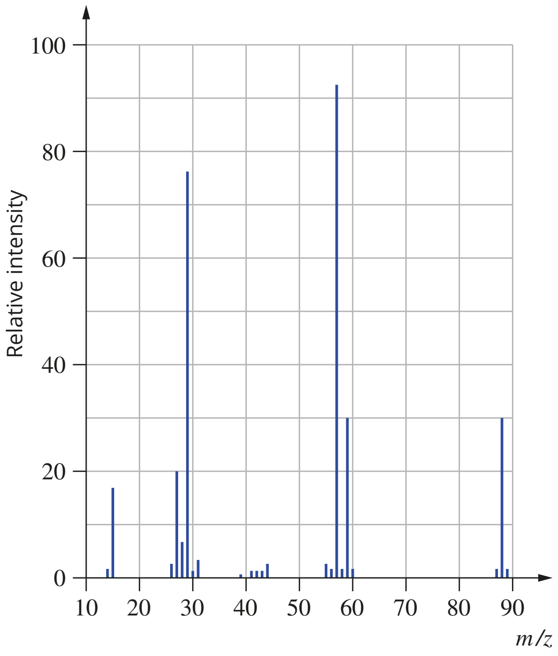
4 **a** Butanone
b Ethanamide

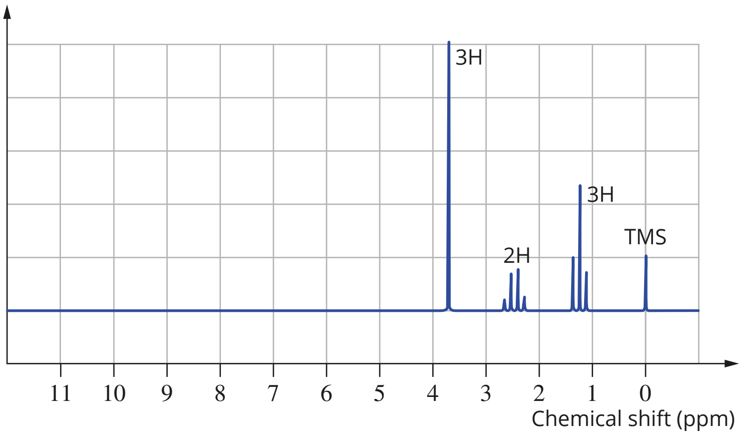
Section 12.4 Determination of molecular structure by spectroscopy

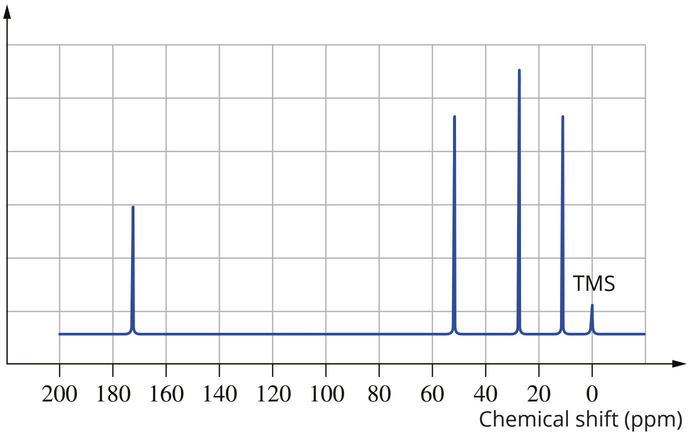
Worked example: Try yourself 12.4.1

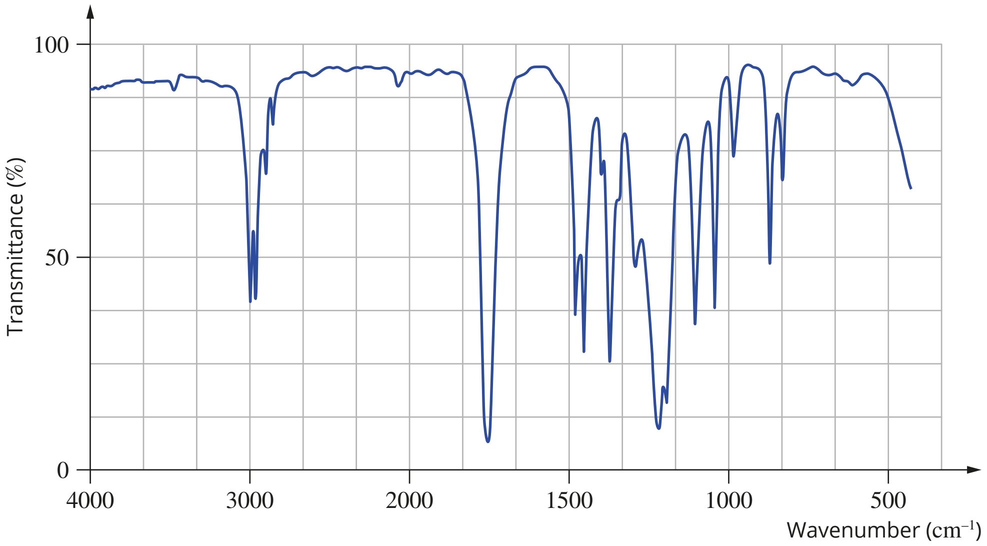
DEDUCING MOLECULAR STRUCTURE FROM SPECTROSCOPIC DATA

A sweet-smelling liquid has an empirical formula of C_2H_4O. Chemical tests show that the compound is not an aldehyde or ketone. Use this information and the mass, IR and NMR spectra provided to deduce the structure and name of the compound.





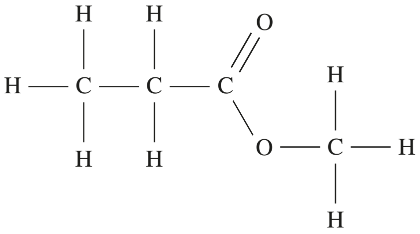




Thinking	**Working**
Use the mass spectrum to identify the molecular ion and relative molecular mass.	The peak with the largest mass-to-charge ratio is *m/z* = 88 so the relative molecular mass is 88. This molecular mass is twice as heavy as the empirical formula, so the molecular formula must be $C_4H_8O_2$.
Use the IR spectrum to identify functional groups present in the compound. (Refer to Table 12.2.1).	The IR spectrum shows a strong absorption band at 1700 cm^{-1}, suggesting the presence of a C=O bond, and hence a carbonyl group. The IR spectrum does not contain a strong, broad absorption in the range of 2500–3300 cm^{-1} that shows there is no O–H bond in the molecule.
Use the proton NMR spectrum to identify the different hydrogen environments. (Refer to Table 12.2.1.)	The NMR data is summarised in the following table. Chemical shift (ppm) / Splitting pattern / Relative peak area 1.1 / Triplet (3-line pattern) / 3 2.3 / Quartet (4-line pattern) / 2 3.7 / Singlet (1-line pattern) / 3 The spectrum contains three signals and so there are three different hydrogen environments. The sum of the relative peak areas is 8, which is consistent with the molecular formula, each unit of peak area corresponds to one hydrogen atom. The signal at 1.1 ppm is consistent with the signal produced by a $-CH_3$ group with two hydrogens in a neighbouring environment. The signal at 2.3 is consistent with the signal produced by a $-CH_2-$ group bonded to the carbon of an ester group, with three hydrogens in a neighbouring environment. The signal at 3.7 ppm is a singlet, indicating that there are no hydrogen atoms attached to adjacent atoms. The chemical shift is consistent with a methyl group singly bonded to an oxygen atom.
Use the carbon NMR spectrum to identify the different carbon environments. (Refer to Table 12.2.2.)	There are four signals in the carbon NMR spectrum and so the molecule contains four different carbon environments. The number of carbon environments corresponds to the number of carbons in the molecular formula, so each environment represents one carbon atom. The signal at 175 ppm is consistent with a carbon in a carbonyl group. The signal at 51 ppm is consistent with a carbon attached to an oxygen atom by a single bond to an oxygen. The signal at 27 ppm is consistent with a $R-CH_2-R$ group. The signal at 9 ppm is consistent with a methyl group, $R-CH_3$

The nested NMR data table from the third row:

Chemical shift (ppm)	Splitting pattern	Relative peak area
1.1	Triplet (3-line pattern)	3
2.3	Quartet (4-line pattern)	2
3.7	Singlet (1-line pattern)	3

Use the data from the spectra to deduce the structure of the compound.	From the data provided by the spectra it can be summarised that: • the molecular formula of the compound is $C_4H_8O_2$ • the compound has a carbonyl group, but no hydroxyl group • it is not an aldehyde or ketone • it is an ester • the compound has a CH_3CH_2– group attached to the carbon of a carbonyl group • the compound has a methyl group attached by a single bond to an oxygen atom. A structure consistent with this data is: 
Name the compound.	Methyl propanoate

12.4 Key questions

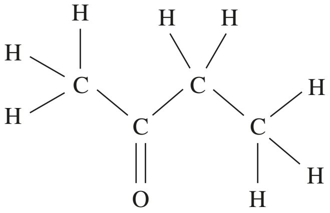
1 Strong absorption around 1750 cm^{-1} is consistent with the presence of C=O. A strong peak at 3000 cm^{-1} corresponds to the absorption of a –CH bond (it cannot be due to an OH of a carboxylic acid because the formula only contains one oxygen).

The proton NMR spectrum indicates:

Chemical shift	Peak splitting	Relative peak area
1.0	Triplet	3
2.1	Singlet	3
2.4	Quartet	2

There are three signals so there must be three hydrogen environments.
The chemical shift of 1.0 indicates R–CH_3.
The chemical shift of 2.1 indicates a C=O environment.
The chemical shift of 2.4 indicates $RCOCH_3$.
The signal at 1.0 is a triplet so the neighbouring environment must be CH_2.
The signal at 2.1 is a singlet so there are no neighbouring protons.
The signal at 2.4 is a quartet so it has a CH_3 neighbour.

The carbon NMR spectrum indicates four peaks and therefore four different carbon environments, so the formula is C_4H_8O. The structural formula is for butan-2-one.



2 $n(\text{C}) = \frac{48.6}{12} = 4.05$

$n(\text{H}) = \frac{8.2}{1.0} = 8.2$

$n(\text{O}) = \frac{43.2}{16} = 2.7$

Ratio of C:H:O = 1.5:3:1 = 3:6:2

The empirical formula is $C_3H_6O_2$.

In the mass spectrum, the largest molecular ion has a *m/z* value of 74. This is equal to the molecular mass of an element with the empirical formula of $C_3H_6O_2$.

In the IR spectrum, there is a narrow band at 1700 cm^{-1}, which indicates a C=O bond. There is a broad band at 3000 cm^{-1}, which indicates an –OH group of a carboxylic acid. This slightly masks the peak at 3000 cm^{-1} due to C–H bonds.

The proton NMR spectrum indicates three different hydrogen environments.

A chemical shift of 1.0 ppm is a triplet. A chemical shift of 2.0 ppm is quartet.

A chemical shift of 9 ppm is a singlet, indicating no neighbours and therefore a hydrogen of a carboxylic acid.

The carbon NMR spectrum shows that there are three different carbon environments.

The compound is a carboxylic acid with three carbons. Therefore, this is propanoic acid.

CHAPTER 12 **REVIEW**

INFRARED SPECTROSCOPY

1 Lowest C–Br, C–O, C–H, O–H highest

2 **a** Both spectra contain broad, strong absorption bands at 3300 cm^{-1}, which corresponds to the expected absorbance by alcohol O–H bonds. The spectra do not contain peaks at 1700 cm^{-1} and so they cannot be acids.

b The two spectra have different peaks in the fingerprint region and so cannot be of the same molecule.

3 **a** Broad absorption at 3200–3550 cm^{-1}

b Absorption at 3500 cm^{-1} and 1670–1750 cm^{-1}

c Absorption at 1670–1750 cm^{-1}

d Absorption at 700–800 cm^{-1}

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

4 TMS is used as a reference in NMR spectroscopy. The location of a signal is compared to the TMS signal and called the chemical shift. The chemical shift is in units of ppm.

5 **a** Methyl ethanoate

b Ethyl methanoate

c Propanoic acid

6 Proton NMR spectra can give an indication of the number of different proton environments. The peak splitting indicates the environments of neighbouring protons. The peak areas provide information about the number of equivalent hydrogen atoms. For example, CH_2 splits signals from hydrogens to adjacent atoms into 3 peaks. Carbon NMR spectra give an indication of the number of different carbon environments. Two peaks indicate two different carbon environments. Chemical shift data can be used to indicate the type of carbon environment (e.g. C=O).

For example, if C_3H_6O was propanone, all of the hydrogens would be found in a CH_3 bonded to a C=O environment; therefore, there would be only one peak in the proton NMR spectrum. The chemical shift data from the carbon NMR spectrum would show two peaks for the two carbon environments. One would correlate to a chemical shift indicating a CH_3 carbon environment and another to the C=O carbon environment.

7 **a**

Group	Shift (ppm)	Splitting	Peak area
$-CH_3$	0.9	triplet	6
$-CH_2-$	1.3	septet	2

b

Group	Shift (ppm)	Splitting	Peak area
$-CH_3$	0.9	triplet	3
$-CH_2-$	1.5	quartet	2

c

Group	Shift (ppm)	Splitting	Peak area
$-CH_3COO$	2.0	singlet	3
–**CH_2**OH	3.3	quartet	2
$-CH_2$**OH**	9	singlet	1

MASS SPECTROMETRY

8 Molecular ion has *m*/*z* of 44, and is $C_3H_8^+$, base ion has *m*/*z* of 29, 15 less than the molecular ion and is $C_2H_5^+$

9 C_4H_6

10 a C_4H_{10}

b C_3H_6O

c $C_2H_6N_2$

11 a i 98 corresponds to the molecular ion made up of two ^{35}Cl isotopes.

ii 100 corresponds to the molecular ion with one ^{35}Cl and one ^{37}Cl isotope.

iii 102 corresponds to the molecular ion with two ^{37}Cl isotopes

b The most abundant Cl isotope is ^{35}Cl therefore it has a higher peak.

c $ClCCH_3^+$

DETERMINATION OF MOLECULAR STRUCTURE BY SPECTROSCOPY

12 Propanal

13 2,2-Dimethylpropane

14 The mass spectrum shows a molecular ion with *m*/*z* of 88, meaning that the molecular formula is twice the empirical formula: $C_4H_8O_2$. The IR spectrum shows strong absorption bands at 1700 and 3000 cm^{-1}, suggesting the presence of acid hydroxyl and carbonyl groups. The compound is likely to be a carboxylic acid. The proton spectrum shows three signals, and so three hydrogen environments. The sum of the relative peak areas is the same as the number of hydrogen atoms in the formula. The signal at 1.1 ppm is doublet with relative peak area of 6, and represents two equivalent $–CH_3$ groups with one hydrogen in a neighbouring environment. The signal at 2.6 ppm is a 7-line pattern with relative peak area of 1, and represents a –CH– neighbouring two methyl groups. The singlet at 11.8 ppm represents a single carboxylic acid proton. The carbon spectrum shows only three signals, giving three carbon environments. The carbon at 184 ppm is most likely a carboxyl carbon. The carbon signal at 19 ppm represents carbons in methyl groups. The carbon signal at 35 ppm represents a carbon with two or more alkyl groups attached. All the information gives a semistructural formula of $(CH_3)_2CHCOOH$ and name of 2-methylpropanoic acid.

CONNECTING THE MAIN IDEAS

15 NMR spectroscopy is used to identify types of atoms within the molecule and can give information about their chemical environment and connectivity. IR spectroscopy is usually used to identify general functional groups in a molecule but can also be used for positive identification by analysing the fingerprint region compared to a reference. Mass spectrometry gives information about the molecular mass and possible fragments within a molecule, which can lead to confirmation of a suspected structure.

16 a Proton NMR spectroscopy gives a large amount of information about organic molecules. It can be used to identify the number and types of hydrogen chemical environments, the relative amounts of hydrogen atoms in each environment and the connectivity of adjacent environments. It is fairly difficult to confirm which functional groups are present in a molecule by proton NMR spectroscopy alone.

b IR spectroscopy is extremely useful for identifying functional groups. Many molecules have isolated or symmetrical hydrogen environments, which leads to simpler and less informative spectra. Carbon NMR spectroscopy can be used to identify sections of a molecule that contain no hydrogen environments. Mass spectrometry is useful to ensure that a proposed structure is correct. In many cases mass spectrometry is more powerful for the identification of molecules when the proton NMR spectroscopy is too complex to easily analyse.

17 The computer could look for specific ion peaks that would correspond to the molecular ions of illegal substances. It could then confirm the presence of these compounds by identifying the fragment ions of that compound.

Chapter 13 Analysis of organic compounds by chromatography

Section 13.1 Principles of chromatography

Worked example 13.1.1: Try yourself

CALCULATING R_f VALUES

Using Figure 13.1.5, calculate the R_f value of the red component.	
Thinking	**Working**
Record the distance the component has moved from the origin and the distance the solvent front has moved from the origin.	The distance the blue component has moved from the origin is 7.5 cm. The distance the solvent front has moved from the origin is 10 cm.
$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$	$R_f(\text{red component}) = \frac{7.5}{10}$ $= 0.75$

13.1 Key questions

1 The component at the top of the chromatogram has a greater rate of adsorption and desorption compared to components at the bottom of the chromatogram.

2 $R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$

3 **a** **i** Solvent **ii** Water coated onto paper
   b **i** Solvent **ii** Aluminium oxide or silica dioxide packed into column
   c **i** Solvent **ii** Layer of fine powder such as aluminium oxide onto plate

4 The sample would dissolve in the solvent rather than be carried along by the stationary phase.

Section 13.2 High-performance liquid chromatography

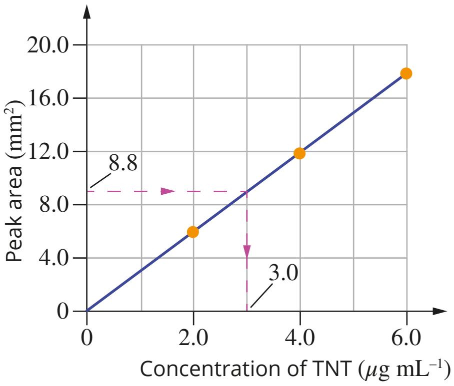
Worked example: Try yourself 13.2.1

CONCENTRATION OF A COMPONENT IN A MIXTURE

Trinitrotoluene (TNT) is often blended with other explosives to suit particular applications. A sample from a solution of an explosive mixture was injected onto an HPLC column using a water/methanol mobile phase. The peak corresponding to TNT had an area of 8.8 mm^2. The peak areas for three standard solutions were also measured, as shown in the table below.

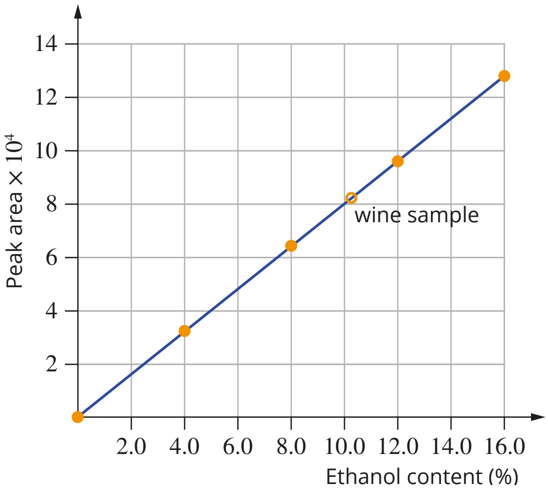
Determine the concentration of TNT in the sample solution in µg mL^{-1}.

TNT standards (µg mL^{-1})	**Peak area (mm^2)**
2.0	6.0
4.0	11.6
6.0	17.6

Thinking	**Working**
Construct a calibration curve by plotting peak area versus concentration.	 Calibration curve for TNT sample.
Use the calibration curve to find the concentration corresponding to the peak area of the sample.	A line can be drawn on the calibration curve from the peak area of the sample to find the corresponding concentration on the graph. The concentration of TNT in the sample solution is 3.0 µg mL^{-1}.

Extension question

a



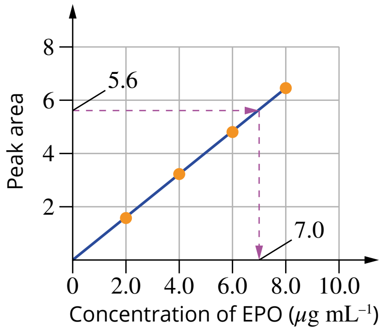
b 10.4%

c Techniques such as AA, GLC, HPLC, and UV spectroscopy do not directly produce measures of concentration. Standards must be used. More than one standard should be used and the unknown sample should lie between these standards. This is because a zero standard may be contaminated with trace amounts of the chemical being tested. Calibration graphs are often non-linear and multiple standards increase the chance of detecting incorrectly prepared solutions.

13.2 Key questions

1 C. Compound B is likely to move more slowly through the column than compound A because it is more strongly absorbed. Since compound C is least strongly adsorbed on the stationary phase and most soluble in the mobile phase, it should pass through the column most rapidly.

2 **a**



b 7.0 μg mL^{-1}

3 An HPLC instrument does not directly produce measurements of concentration. R_t indicates the identity of components in a mixture. A calibration curve can then be used to determine the concentration of the component.

4 A, B, C, D. The water/methanol solvent used as the mobile phase in this analysis is polar. The more polar an alcohol, the more soluble it will be in this solvent and the more rapidly it will move through the column. In this case, A has the smallest retention time and will be the most polar.

As the length of the non-polar hydrocarbon group in an alcohol increases, the molecule becomes less polar overall. A must therefore be the smallest molecule, with the lowest molar mass, followed by B, and so on.

CHAPTER 13 REVIEW

PRINCIPLES OF CHROMATOGRAPHY

1 **a** 2
   b Purple
   c A and B only
   d R_f(red spot) = 0.28; R_f(green spot) = 0.83

2 **a** A: 0.59; B: 0.49; C: 0.38; D: 0.20; E: 0.13
   b A: leucine and/or isoleucine; B: β-phenylamine; C: proline and/or valine and/or tyrosine; D: threonine and/or hydroxyproline and/or serine and/or glycine; E: lysine and/or arginine and/or taurine
   c A: leucine and/or isoleucine; B: β-phenylamine; C: proline; D: serine; E: arginine
   d A two-way chromatogram produces better separation of components of complex mixtures, permitting easier isolation and identification.

3 **a** Stationary phase = powdered alumina (also accept powdered alumina on glass sheet). Mobile phase = water or ethanol. The mobile phase should be a polar solvent in order to dissolve the polar sample.
   b R_f leucine = $\dfrac{\text{distance leucine moved from origin}}{\text{distance solvent moved from origin}}$

$$R_f \text{ leucine} = \frac{0.29 \text{ cm}}{5 \text{ cm}} = 0.58$$

R_f value is same regardless of the distance travelled by solvent front

$$0.58 = \frac{\text{distance leucine moved from origin}}{13 \text{ cm}}$$

Distance from origin by leucine = 13 cm × 0.58 = 7.5 cm
   c The R_f values would not change. The movement of the component and solvent front both increase by the same proportion so there is no change in the R_f.
   d Taurine and glycine

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

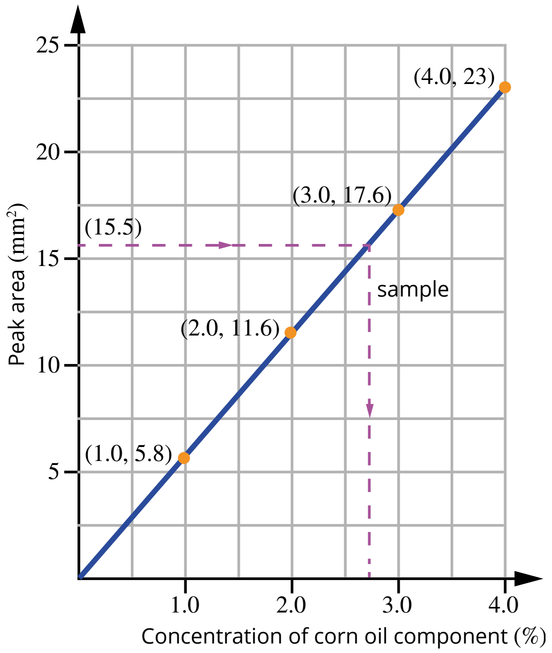
4 D. Reducing the pressure of the mobile phase.

5 **a** Obtain chromatograms of the blood sample and of standard solutions of testosterone. Use R_t values to identify the testosterone peak on the chromatogram of blood. Measure the testosterone peak areas. Construct a calibration curve and mark the blood testosterone peak area on it. Determine the testosterone concentration in the blood sample.
   b 48.0 ng L^{-1}

6 Molecules of serine and threonine are more polar than valine. They will therefore dissolve more readily in the polar liquid used in this technique. Valine will move most slowly through the column.

Because threonine has an extra methyl group in its side group, it will be less polar and move slower than serine.

7 Calibration curve:



A line can be drawn on the calibration curve from the peak area of the sample (15.5 mm^2) to find the corresponding concentration on the graph: 2.7%.

8 Compared with conventional column chromatography, HPLC is more sensitive, faster, resolves components better and it is able to detect colourless components readily.

9 **a** Retention time

b Retention time

c Peak area

CONNECTING THE MAIN IDEAS

10 Adsorption—the attraction of one substance to the surface of another.

Chromatography—a set of techniques used to separate and analyse the components in a mixture.

Desorption—the breaking of the bonds between a substance and the surface to which the substance is adsorbed.

Eluent—a liquid used as the mobile phase in chromatography.

Mobile phase—the phase that moves over the stationary phase in chromatography.

Stationary phase—a solid, or a solid that is coated in a viscous liquid, used in chromatography.

Retention time—the time taken for a component to pass through a chromatography column.

11 **a** Chemists can determine the number of components and the absorbance of components, from which concentration can be determined.

b 4

c Solid samples are dissolved in a suitable solvent. The liquid sample is injected into the top of an HPLC column. The stationary and mobile phases are chosen to achieve a good separation of the components in the sample. The sample components alternately adsorb onto the stationary phase and then desorb into the solvent as they are swept forward. The time taken to exit the column increases if the component strongly absorbs onto the stationary phase and has a low solubility in the mobile phase.

12 Paper chromatography would be used for the initial investigation because it is used to identify the components of a mixture whereas the thin-layer chromatography is more sensitive and is capable of greater resolution. A wider range of solvents can be used in thin-layer chromatography for further analysis.

Chapter 14 Analysis of organic compounds by volumetric analysis

Section 14.1 Principles of volumetric analysis

14.1 Key questions

1. B. Rinsing the burette with deionised water will slightly dilute the potassium hydroxide solution. This means more potassium hydroxide solution would need to be added to neutralise the methanoic acid. It would then appear that a greater amount of potassium hydroxide reacted; hence, it would appear that a greater amount of methanoic acid had reacted, resulting in a methanoic acid concentration higher than it actually is.
2. **a** A standard solution is a solution of accurately known concentration. A primary standard is a substance that is readily obtained in a pure form, has a known formula and can be stored without deteriorating or reacting with the atmosphere. It should also be cheap and have a high molar mass.
   b The equivalence point in a titration occurs when the reactants have been mixed in the mole ratio shown by the reaction equation. The end point occurs when the indicator changes colour.
   c A burette is a piece of equipment capable of delivering different volumes of a liquid accurately (generally up to 50.00 mL). Pipettes usually deliver only a fixed volume of liquid (e.g. 20.00 mL).
   d An aliquot is the volume of liquid delivered from a pipette. A titre is delivered by a burette and is the volume needed to reach the end point of a titration.
3. primary standard, volumetric flask, aliquot, pipette, indicator
4. **a** Methyl orange
   b Alizarin yellow
   c Phenol red
   d Methyl red
5. Yellow
6. **a** The equivalence point occurs in the range pH 3–11. Both indicators will change colour over this pH range. Both indicators will provide a sharp end point, i.e. they will change colour at the equivalence point with the addition a small volume (1 drop) of acid.
   b The equivalence point occurs in the pH range 3–7. Methyl orange provides a sharper end point over this pH range.
   c The equivalence point occurs in the pH range 7–11. Phenolphthalein provides the sharper end point.
   d Both indicators will provide a broad end point and neither would be suitable.

Section 14.2 Acid–base titrations of organic compounds

Worked example: Try yourself 14.2.1

VOLUMETRIC ANALYSIS OF ORGANIC ACIDS WITH STRONG BASES

The concentration of a solution of oxalic acid ($C_2H_2O_4$) was determined by titration with standard sodium hydroxide solution using phenolphthalein indicator.

A 20.00 mL aliquot of oxalic acid solution was titrated with a 1.00 M solution of sodium hydroxide. Titres of 22.10, 22.02, 18.80 and 22.06 mL, were required to reach the end point. What was the molar concentration of the oxalic acid solution? (Oxalic acid is diprotic; the end point occurred when both protons on each acid molecule reacted.)

Thinking	**Working**
Write a balanced chemical equation for the reaction.	Oxalic acid is a diprotic acid. An acid reacting with a base will produce a salt and water: $C_2H_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$
Determine the volume of the average titre.	The titre of 18.80 mL is discarded because it is not concordant, i.e. it is not within a range of 0.10 mL from the highest to lowest titre volumes. Average titre $= \frac{22.10+22.02+22.06}{3}$ $= 22.06$
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(NaOH) = c \times V$ $= 1.00 \times 0.022\,06$ $= 0.022\,06$ mol
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	Mole ratio $= \frac{n(C_2H_2O_4)}{n(NaOH)} = \frac{1}{2}$ So $n(C_2H_2O_4) = \frac{1}{2}\, n(NaOH)$ $= \frac{1}{2} \times 0.2206$ $= 0.011\,03$ mol
Determine the concentration of the unknown substance. Express your answer to the appropriate number of significant figures.	$c(C_2H_2O_4) = \frac{n}{V}$ $= \frac{0.011\,03}{0.020\,00}$ $= 0.5515M$ 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 $C_2H_2O_4 = 0.552$ M

Worked example: Try yourself 14.2.2

VOLUMETRIC ANALYSIS OF ORGANIC BASES WITH STRONG ACIDS

The concentration of a solution of ethanamine ($C_2H_5NH_2$) was determined by titration with a standard solution of hydrochloric acid, using methyl orange indicator.

A 20.00 mL aliquot of CH_3NH_2 solution was titrated with a 0.100 M solution of HCl. Titres of 21.50, 21.40 and 21.48 mL of HCl were required to reach the end point. What was the molar concentration of the ethanamine solution?

Thinking	**Working**
Write a balanced chemical equation for the reaction.	A weak organic base, such as ethanamine, reacts with an acid to form a salt: $C_2H_5NH_2(aq) + HCl(aq) \rightarrow C_2H_5NH_3Cl(aq)$
Determine the volume of the average titre.	The three titres are concordant, i.e. they are all within a range of 0.10 mL from the highest to lowest titre volumes. Average titre $= \frac{21.50+21.40+21.48}{3}$ $= 21.46$ mL
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(HCl) = c \times V$ $= 0.100 \times 0.02146$ $= 0.002146$ mol
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	Mole ratio $= \frac{n(C_2H_5NH_2)}{n(HCl)} = \frac{1}{1}$ = 0.002 146 mol So $n(C_2H_5NH_2) = n(HCl)$ = 0.002 146 mol
Determine the concentration of the unknown substance.	$c(C_2H_5NH_2) = \frac{n}{V}$ $= \frac{0.002\,146}{0.0200}$ $= 0.1073$ M 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 $C_2H_5NH_2$ = 0.107 M

14.2 Key questions

1 C. Acids are substances that can donate a proton, (hydrogen). Carboxylic acids contain the carboxyl function group (–COOH), which can be seen in option C. All other options cannot donate a hydrogen and are therefore incorrect.

2 **a** $CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$

b $n(KOH) = c \times V = 0.995 \times 0.021\,56 = 0.021\,45$ mol

c $n(CH_3COOH) = n(KOH) = 0.021\,45$ mol

d $c = \frac{n}{V} = \frac{0.021\,45}{0.025\,00} = 0.858$ M

e c (g L^{-1}) = c (M) × M = 0.858 × 60.0 = 51.5 g L^{-1}

3 $n(H_2SO_4) = c \times V = 0.386 \times 0.020\,00 = 0.007\,720$ mol

$n(CH_3CH_2NH_2) = 2 \times n(H_2SO_4) = 0.015\,44$ mol

$c(CH_3CH_2NH_2) = \frac{n}{V} = \frac{0.015\,44}{0.021\,02} = 0.7345 = 0.735$ M

4 **a** The 22.06 mL titre is not included in the calculation because it is not concordant.

Average titre = $\frac{21.06 + 21.00 + 21.08}{3}$ = 21.05 mL

$n(NaOH) = c \times V = 1.25 \times 0.02105 = 0.02631$

Reaction equation: $C_2H_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$

$n(C_2H_2O_4) = \frac{1}{2}\, n(NaOH) = \frac{1}{2} \times 0.02631 = 0.01316$ mol

$n(C_2H_2O_4) = \frac{n}{V} = \frac{0.01316}{0.02000} = 0.658$ M

b $M(C_2H_2O_4) = 90.0$ g mol^{-1}

mass of oxalic acid per litre = $c \times M = 0.658 \times 90.0 = 59.22$ g L^{-1}

$\% \frac{m}{m} = \frac{\text{mass of oxalic acid}}{\text{mass of 1 L}} \times 100 = \frac{59.22}{1000} \times 100 = 5.922 = 5.92$

Section 14.3 Redox titrations of organic compounds

Worked example: Try yourself 14.3.1

VOLUMETRIC ANALYSIS OF AN ALCOHOL

The concentration of a solution of methanol (CH_3OH) was determined by titration with a standard solution of acidified potassium permanganate ($KMnO_4$). The equation for the reaction is:

$$5CH_3OH(aq) + 4MnO_4^-(aq) + 12H^+(aq) \rightarrow 5HCOOH(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$$

A 10.00 mL aliquot of CH_3OH solution was titrated with a 0.125 M solution of $KMnO_4$. Titres of 14.13, 14.18 and 14.11 mL of HCl were required to reach the end point. What was the molar concentration of the methanol solution?

Thinking	**Working**
Determine the volume of the average titre.	Average titre $= \frac{14.13 + 14.18 + 14.11}{3}$ = 14.14 mL
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(MnO_4^-) = c \times V$ $= 0.125 \times 0.01414$ $= 0.001768$ mol
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that reacted with the standard solution.	Mole ratio $= \frac{n(CH_3OH)}{n(MnO_4^-)} = \frac{5}{4}$ so $n(CH_3OH) = \frac{5}{4} \times n(MnO_4^-) = 0.002209$ mol
Determine the concentration of the unknown substance. Express your answer to the appropriate number of significant figures.	$c(CH_3OH) = \frac{n}{V}$ $= \frac{0.002209}{0.01000}$ = 0.2209 M 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 CH_3OH = 0.201 M

14.3 Key questions

1 $CH_3CHOHCH_3(aq) \rightarrow CH_3COCH_3(aq) + 2H^+(aq) + 2e^-$

2 $n(HNO_3) = c \times V = 15.0 \times 0.0100 = 0.15$ mol

From equation: $n(Cu) = \frac{1}{4} n(HNO_3)$

$= \frac{1}{4} \times 0.15$

$= 0.0375$ mol

$m(Cu) = m \times M$

$= 0.0375 \times 63.5$

$= 2.38$ g

3 $n(MnO_4^-) = c \times V = 0.0200 \times 0.0250 = 0.000\,500$ mol

From equation: $n(H_2O_2) = \frac{5}{2} n(MnO_4^-)$

$= \frac{5}{2} \times 0.000\,500$

$= 0.001\,25$ mol

$c(H_2O_2) = \frac{n}{V}$

$= \frac{0.00125}{0.0200}$

$= 0.0625$ M

4 If the maximum concentration of vitamin C in fruit juice were 0.000 50 g mL^{-1}, titration of an aliquot of 50.00 mL of fruit juice with 0.0100 M iodine solution would give a maximum titre of 14.20 mL. The titration is a direct one using starch solution as the indicator. It involves the following steps.

1 Place the standard solution of iodine in a burette. Record the initial volume.

2 Place an aliquot of the juice in a conical flask.

3 Add 2 or 3 drops of indicator to the juice.

4 Titrate the juice with the iodine solution. Record the volume of solution used to reach the end point.

5 Repeat steps 1–4 to obtain three concordant titres (titres within 0.1 mL).

5 **a** The molar concentration of ethanol can be found by following these steps.

1 Write a balanced equation.

$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$

2 Calculate the amount of $Cr_2O_7^{2-}$ used in the titration.

$n(Cr_2O_7^{2-}) = 0.100 \text{ M} \times 0.017\,98 \text{ L} = 0.001\,798$ mol

3 From the equation, 3 mol of CH_3CH_2OH reacts with 2 mol of $Cr_2O_7^{2-}$.

$n(CH_3CH_2OH) = \frac{3}{2} \times n(Cr_2O_7^{2-})$

$= \frac{3}{2} \times 0.001\,798$

$= 0.002\,697$ mol

4 Calculate the amount of CH_3CH_2OH in the 500.0 mL flask. Remember that only 20.00 mL was removed from the 500.0 mL flask for the titration.

$n(CH_3CH_2OH)$ in 500.0 mL $= 0.002\,697 \times \frac{500.0}{20.00}$ mol

$= 0.067\,425$ mol

5 This is the same amount of CH_3CH_2OH as is present in the 10.00 mL sample. Calculate the concentration of CH_3CH_2OH in the 10.00 mL sample.

$c(CH_3CH_2OH)$ in the 10.00 mL sample $= \frac{0.067\,425 \text{ mol}}{0.0100 \text{ L}}$

$= 6.74$ mol L^{-1} (3 significant figures)

b $c(g\ L^{-1}) = c\ (M) \times M = 6.74 \times 46.0 = 310$ g L^{-1}

CHAPTER 14 REVIEW

PRINCIPLES OF VOLUMETRIC ANALYSIS

1 **a** Primary standard: has a very high level of purity; has a known formula; is stable, e.g. will not react with atmospheric gases (e.g. carbon dioxide, water vapour); has a high molar mass to minimise errors in weighing; is readily available; is relatively inexpensive.

b Accurately weigh an empty weighing bottle, add the primary standard and reweigh. Transfer the weighed sample to a volumetric flask using a dry glass funnel. Rinse out the weighing bottle and glass funnel using a wash bottle. Half fill the volumetric flask with water and shake to dissolve the sample. When the sample has dissolved, add water to the calibration mark and shake the flask again. Determine the concentration of the primary standard.

2 **a** 24.22, 24.20 and 24.16 mL

b 24.19 mL

3 The volumetric flask should be rinsed with deionised water, the pipette with hydrochloric acid, the burette with ethanamine ($CH_3CH_2NH_2$) solution and the conical flask with deionised water.

4 **a** Rinsing with water would dilute the standard solution.

b A smaller titre of the unknown solution would be required to react with the standard solution. This would then result in the concentration of the unknown solution being determined to be higher than it actually is.

5 Sodium hydroxide reacts with carbon dioxide and absorbs water from the atmosphere.

ACID-BASE TITRATIONS OF ORGANIC COMPOUNDS

6 **a** $n(C_3H_4O_4) = c \times V = 0.0615 \times 0.012\,82 = 0.000\,7884$ mol

b Mole ratio $= \frac{n(C_3H_4O_4)}{n(NaOH)} = \frac{1}{2}$

$\therefore n(NaOH) = 2 \times 0.000\,7884 = 0.001\,577$ mol

c $c(NaOH) = \frac{n}{V} = \frac{0.001\,577}{0.020\,00} = 0.078\,85 = 0.0789$ M

7 **a** Neither acidic nor basic

b Acidic

c Basic

d Acidic

8 **a** $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COON_4(aq) + H_2O(l)$

b $n(NaOH) = 0.9952 \text{ M} \times 0.020\,34 \text{ L}$

$= 0.02024$ mol

c Use the ratio of amounts of substances that were present in the 20.00 mL aliquot. From the equation in part a, 1 mol CH_3COOH reacts with 1 mol NaOH.

$$\frac{n(CH_3COOH)}{n(NaOH)} = \frac{1}{1}$$

$n(CH_3COOH)$ in 20.00 mL aliquot = 0.020 24 mol

d Calculate the concentration of the CH_3COOH in the 20.00 mL aliquot which is the same as the concentration in the vinegar, to the correct number of significant figures.

$$c(CH_3COOH) = \frac{0.020\,24 \text{ mol}}{0.020\,00 \text{ L}}$$

$$= 1.012 \text{ M}$$

REDOX TITRATIONS OF ORGANIC COMPOUNDS

9 $3CH_3CH_2CH_2CH_2OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3CH_2CH_2COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

10 **a** 1 Write a balanced equation. $C_6H_8O_6(aq) + I_2(aq) \rightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2I^-(aq)$

2 Calculate the amount of the given reactant, I_2. $n(I_2) = 0.0500 \text{ M} \times 0.028\,40 \text{ L} = 0.001\,42$ mol

3 From the equation, 1 mol vitamin C reacts with 1 mol I_2

$$\frac{n(C_6H_8O_6)}{n(I_2)} = \frac{1}{1}$$

$n(C_6H_8O_6) = 0.001\,42$ mol

4 Calculate the mass of vitamin C. $m(C_6H_8O_6) = 0.001\,42 \text{ mol} \times 176.124 \text{ g mol}^{-1}$
$= 0.2500 \text{ g}$
$= 0.250 \text{ g}$ (3 significant figures)

b $\% \ C_6H_8O_6 = \frac{0.2500}{1.306} \times 100$
$= 19.1\%$ (3 significant figures)

c Fillers, binders, sweeteners, flavours and colouring

11 **a** 1 Write a balanced equation.
$2Cr_2O_7^{2-}(aq) + 3C_2H_5OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$

2 Calculate the average titre.
Average titre $= \frac{9.20+9.16+9.22}{3} = 9.193 \text{ mL} = 0.009\,19 \text{ L}$

3 Calculate the amount of the $Cr_2O_7^{2-}$ present in the average titre.
$n(Cr_2O_7^{2-}) = 0.0500 \times 0.009\,19 \text{ L}$
$= 0.000\,4595 \text{ mol}$
$= 0.000\,460 \text{ mol}$ (3 significant figures)

b From the equation, 3 mol of CH_3CH_2OH reacts with 2 mol of $Cr_2O_7^{2-}$.
$\frac{n(CH_3CH_2OH)}{n(Cr_2O_7^{2-})} = \frac{3}{2}$
$n(CH_3CH_2OH)$ in 20.00 mL $= \frac{3 \times 0.000\,4595}{2}$ mol
$= 0.000\,689\,25 \text{ mol}$
$= 0.000\,690 \text{ mol}$

c Calculate the amount of CH_3CH_2OH in the 250.0 mL flask, remembering that only 20.00 mL was removed from the 250.0 mL flask for the titration. This is the amount of CH_3CH_2OH in the 10 mL beer sample.
$n(CH_3CH_2OH)$ in 250.00 mL $= 0.000\,689\,25 \times \frac{250.0}{20.00}$ mol
$= 0.008\,615 \text{ mol}$
$= 0.008\,62 \text{ mol}$ (3 significant figures)

d Calculate the mass of CH_3CH_2OH in the beer sample.
$m(CH_3CH_2OH) = 0.008\,615 \text{ mol} \times 46 \text{ g mol}^{-1}$
$= 0.3963 \text{ g}$
$= 0.396 \text{ g}$ (3 significant figures)

e 1 Calculate the mass of the 10.00 mL sample of beer, using the density given and the formula, density $= \frac{m}{V}$, so m = density × V.
$m(CH_3CH_2OH) = 1.10 \text{ g mL}^{-1} \times 10.00 \text{ mL}$
$= 11.00 \text{ g}$

2 Calculate the percentage by mass of CH_3CH_2OH in the sample of beer.
$\% \ CH_3CH_2OH = \frac{0.3963}{11.00} \times 100$
$= 3.60\%$ (3 significant figures)

No; this product would not conform with the regulations for low-alcohol beer.

12 **a** 1 Write a balanced equation for the titration.
$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

2 Calculate the amount of $S_2O_3^{2-}$ used in the titration.
$n(S_2O_3^{2-}) = 0.750 \text{ M} \times 0.025\,10 \text{ L}$
$= 0.018\,825 \text{ mol}$

3 From the equation, 1 mol I_2 reacts with 2 mol $S_2O_3^{2-}$.
$\frac{n(I_2)}{n(S_2O_3^{2}\ )} = \frac{1}{2}$
$n(I_2) = \frac{0.018\,825}{2}$
$= 0.009\,4125 \text{ mol}$
$= 0.009\,41 \text{ mol}$ (3 significant figures)

b 1 Write a balanced equation for the reaction where the bleach produces I_2.

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

2 From the equation, 1 mol of NaOCl produces 1 mol of I_2.

$$\frac{n(OCl^-)}{n(I_2)} = \frac{1}{1}$$

$n(OCl^-)$ = 0.009 4125 mol

= 0.009 4125 mol

= 0.009 41 mol (3 significant figures)

c 1 Calculate the mass of NaOCl in the 20.00 mL sample of mould killer.

m(NaOCl) = 0.009 4125 mol × 74.44 g mL^{-1}

= 0.7005 g

2 The mass of the 20.00 mL sample of mould-killer is 20.00 g, as the density of mould killer is 1.0 g mL^{-1}. Calculate the percentage of NaOCl in the sample of mould killer.

$$\% \text{ NaOCl} = \frac{0.7005}{20.00} \times 100$$

= 3.5% (2 significant figures)

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

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

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

d $n(MnO_4^-)$ = 0.0200 M × 0.01295 L

= 0.000 259 mol

From the equation, 5 mol of Fe^{2+} reacts with 1 mol of MnO_4^-.

$$\frac{n(Fe^{2+})}{n(MnO_4^-)} = \frac{5}{1}$$

$n(Fe^{2+})$ in each 20.00 mL aliquot = 5 × 0.000 259 mol

= 0.001 295 mol

= 0.001 30 mol

e Remember that only 20.00 mL was removed from the 250.0 mL flask for the titration.

$$n(Fe^{2+}) \text{ in 250.0 mL} = 0.00130 \times \frac{250.0}{20.00} \text{ mol}$$

= 0.016 1875 mol

= 0.0162 mol (3 significant figures)

f From part **e**, this is the amount of Fe^{2+} in 10 tablets, which equals the amount of $FeSO_4$ in 10 tablets. Calculate the mass of $FeSO_4$ in the 10 tablets, and then the mass of Fe^{2+} in 1 tablet.

$m(FeSO_4)$ in 10 tablets = 0.016 1875 mol × 151.847 g moL^{-1}

= 2.4580 g

$$m(FeSO_4) \text{ in 1 tablet} = \frac{2.4580 \text{ g}}{10}$$

= 0.246 g (3 significant figures)

g Low results, due to loss of vitamin paste during transfer, or aliquots being less than the correct volume.

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

b 1 Calculate the amount of the given reactant, MnO_4^-.

2 From the equation, 5 mol of Fe^{2+} reacts with 1 mol of MnO_4^-.

$$\frac{n(Fe^{2+})}{n(MnO_4\ )} = \frac{5}{1}$$

$n(Fe^{2+})$ = 5 × 0.006 066 mol

= 0.003 033 mol

3 The 0.200 g wire sample was dissolved, making up a 25.0 mL solution, which was titrated.

$n(Fe^{2+})$ in 25.0 mL solution = 0.00303 mol (3 significant figures)

c $$\% \text{ Fe} = \frac{0.003\,033 \text{ mol} \times 55.847 \text{ g mol}^{-1}}{0.200 \text{ g}} \times 100$$

= 84.7% (3 significant figures)

d The end point is readily recognised by the first permanent tinge of pink caused by excess permanganate ions.

e Wear safety glasses and a laboratory coat; hold pipette close to the top when fitting the pipette filler.

CONNECTING THE MAIN IDEAS

15 **a** $(MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)) \times 4$

$(\text{alcohol}(aq) + H_2O(l) \rightarrow \text{carboxylic acid}(aq) + 4H^+(aq) + 4e^-) \times 5$

$4MnO_4^-(aq) + 5 \times \text{alcohol}(aq) + 12H^+(aq) \rightarrow 4Mn^{2+}(aq) + 5 \times \text{carboxylic acid}(aq) + 11H_2O(l)$

Mole ratio = $\frac{n(\text{alcohol})}{n(MnO_4^-)} = \frac{5}{4}$

b $n(KMnO_4) = c \times V$

$= 0.1971 \times 0.02000$

$= 0.003942$

$n(\text{alcohol}) = \frac{5}{4} \times n(KMnO_4)$

$= \frac{5}{4} \times 0.003942$

$= 0.004928$ mol

$m(\text{alcohol}) = c \times V$

$= 14.00 \times 0.02111$

$= 0.02955$ g

$M(\text{alcohol}) = \frac{m}{n}$

$= \frac{0.02955}{0.004928}$

$= 59.98$ g mol^{-1}

c Propan-1-ol

16 **a** $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ multiply by 2

$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$ multiply by 5, then add the equations

$2MnO_4^-(aq) + 16H^+(aq) + 10e^- + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g) + 10e^-$

Simplify:

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

b $n(Na_2C_2O_4) = \frac{0.161}{134}$ mol

From the equation: $n(MnO_4^-) = \frac{2}{5} \times n(C_2O_4^{2-})$

$= \frac{2}{5} \times \frac{0.161}{134}$ mol

$= 0.000481$ mol

$c(MnO_4^-) = V$

$= \frac{0.000481}{0.0267}$ M

$= 0.0180$ M

Chapter 15 Structure and bonding in food molecules

Section 15.1 Amino acids

15.1 Key questions

1 A. The carboxyl group is carbon number 1. Therefore, A is the only amino acid where the second carbon is not the central carbon attached to both the amine functional group and the carboxyl functional group.

2 **a** Asparagine
  b Tyrosine
  c Aspartic acid
  d Methionine

3 The human body only manufactures some of the required amino acids. The other amino acids, called essential amino acids, are provided in our food. Animal protein provides all these essential amino acids. Vegetable protein is often deficient in one or more essential amino acids.

4 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.

5

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 15.2 The formation of proteins

15.2 Key questions

1

Tripeptide	Three amino acids joined by peptide links in a polypeptide chain
R group	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

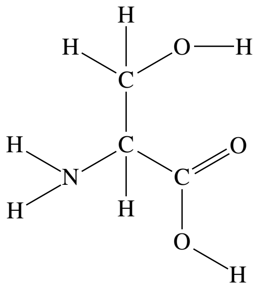
2 **a** A, amino group; B, peptide or amide link or bond or group; C, R group; D, carboxyl group
  b Alanine, serine, leucine

3 C. B is incorrect because five peptide bonds (–CONH–) can be seen. Therefore, this polypetide contains six amino acids.

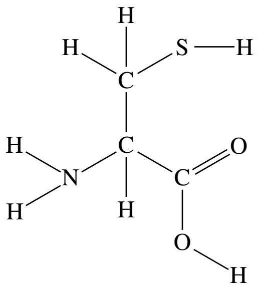
A is incorrect because there are two R groups that contain a carboxyl group plus the carboxyl group on the terminal amino acid. Therefore, there are three carboxyl groups .

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 15.3 Primary and secondary structures of proteins

15.3 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 9, 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 15.4 Tertiary and quaternary structures of proteins

15.4 Key questions

1 B, C and D. Hydrogen bonds between the polar –NH group in one peptide link and the polar –C=O group in another peptide link can form at regular intervals to form the alpha helix and beta pleated sheets that make up the secondary structure. Hydrogen bonds can also form between R groups that contain –O–H, –N–H or –C=O functional groups that make up the tertiary structure. The quaternary structure involves two or more polypeptides bonded together through a variety of bonds, one of which could be hydrogen bonds. Therefore, B, C and D are all correct.

2

Bond type	**Required components in R group**	**Amino acid examples**
Hydrogen bonds	Contains –O–H, –N–H and –C=O	Serine, threonine, histidine
Dipole–dipole interactions	Any polar group such as those containing –S–H, –O–H or –N–H	Cysteine, asparagine
Ionic interactions	Contains $–NH_3^+$ and another group that contains $–COO^-$	Aspartic acid, glutamic acid, lysine, arginine
Covalent cross-links	Cysteine side groups react to form a disulfide bridge (–S–S–)	Cysteine
Dispersion forces	Any non-polar group	Alanine, leucine, phenylalanine

3 Bonds that hold together the secondary and tertiary structure of insulin are sensitive to excessive heat. An increase in temperature will cause these bonds to break, causing the insulin to lose its shape. When a protein loses its shape, it loses its function.

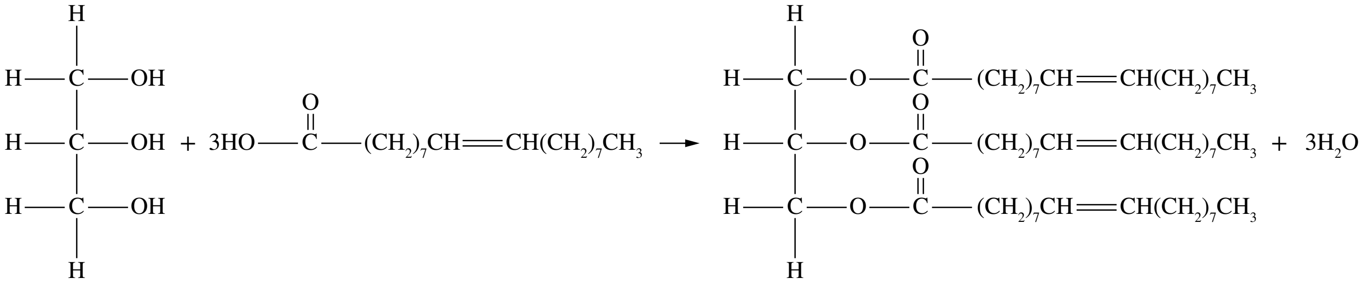
Section 15.5 **Fats and oils**

15.5 Key questions

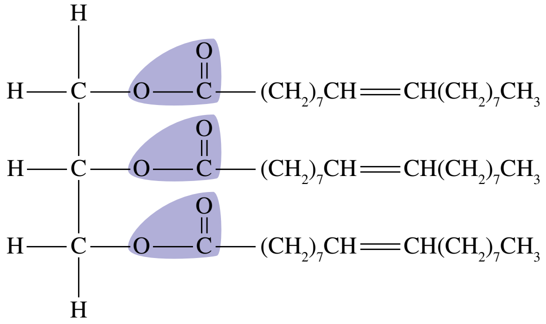
1 B. As hydrocarbon chain length increases, the melting point of fatty acids increases as the strength of dispersion forces increases. Unsaturated fatty acids have lower melting points because the chains can no longer come as close to one another and form dispersion forces of similar strength of saturated fatty acids. In the examples given, B is the molecule likely to have the lowest melting point because it is the fatty acid with the shortest chain length.

2 Hydroxyl and carboxyl

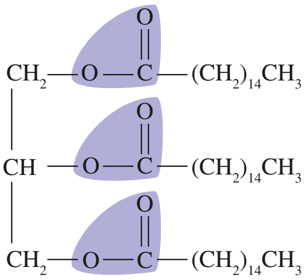
3 **a**



b



4 **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.

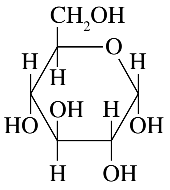
5 **a** Saturated
b Monounsaturated
c Saturated
d Polyunsaturated
e Polyunsaturated
f Saturated
g Saturated
h Monounsaturated

Section 15.6 Carbohydrates

15.6 Key questions

1 B, D, F and G. Starch is a polysaccharide formed from glucose monosaccharide units. It is the storage molecule of glucose in plants and is found in two forms: amylose and amylopectin. Amylose is largely insoluble in water due to the shape of the molecule, which leaves the hydroxyl groups facing each other rather than being in contact with water. Amylopectin is more soluble in water because its branching shape leaves the –OH groups exposed and able to interact with water. Therefore, B, D, F and G are all correct.

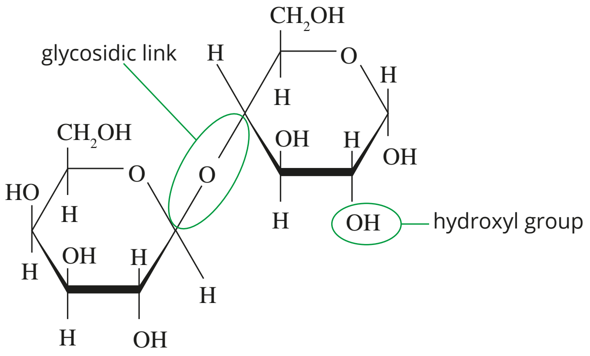
2 The glucose molecule has five polar OH groups that form hydrogen bonds with water. As a result, glucose is highly soluble in water.



glucose

3 **a** Glucose is a monosaccharide. Maltose is made up of two monosaccharide molecules bonded together. Starch is a polymer of monosaccharide molecules.
  b Condensation
  c Hydroxyl functional group

4 **a** A hydrolysis reaction is one in which water is a reactant.
  b



5 **a** Cellulose
  b Glycogen
  c Starch
  d Lactose

6 The orientation of the hydroxyl group on the first carbon in α-glucose points ‘downwards’ and in β-glucose it points ‘upwards’.

Section 15.7 Vitamins

15.7 Key questions

1 B, F and G . A is incorrect because vitamins are required in the diet in small amounts for the body to function properly and prevent specific diseases but not in similar amounts to proteins.

C is incorrect because different vitamins have different structures and therefore solubilities.

D is incorrect because even fat-soluble vitamins can contain hydroxyl groups, just not many.

E is incorrect because fat-soluble vitamins have many different functions.

2 Insoluble, non-polar, soluble, dispersion forces

3 **a** Vitamin K
  b Vitamin K is fat soluble so is able to be stored in fatty tissue and used when necessary.

CHAPTER 15 **REVIEW**

AMINO ACIDS

1 C. A is incorrect because R groups can contain additional atoms to C, H, O and N (such as sulfur).

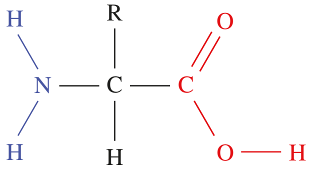
B is incorrect because there are nine essential amino acids. Because humans do not have the capacity to produce them, they need to be included in the diet.

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

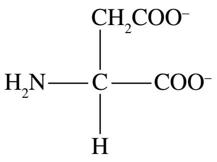


4 **a** **i** Carboxyl

ii Amino

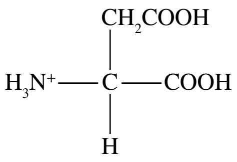
b A zwitterion is a molecule that contains positive and negative charges but has no charge overall.

c **i**



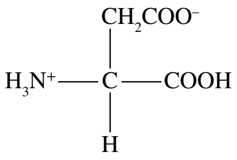
$$H_2N-\overset{\displaystyle CH_2COO^-}{\underset{\displaystyle H}{C}}-COO^-$$

ii



$$H_3N^+-\overset{\displaystyle CH_2COOH}{\underset{\displaystyle H}{C}}-COOH$$

iii



$$H_3N^+-\overset{\displaystyle CH_2COO^-}{\underset{\displaystyle H}{C}}-COOH$$

Either carboxyl protons may be lost.

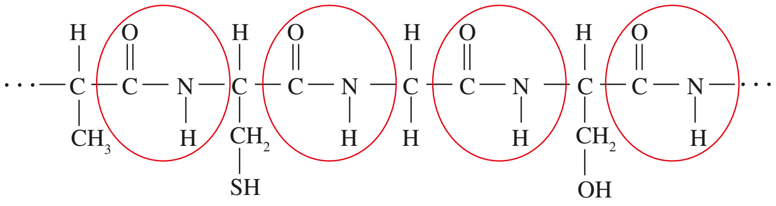
THE FORMATION OF PROTEINS

5 **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 H_2NCHCH_3COOH, $H_2NCH(CH_2SH)COOH$, H_2NCH_2COOH, $H_2NCH(CH_2OH)COOH$

PRIMARY AND SECONDARY STRUCTURES OF PROTEINS

6 **a** Covalent bond/peptide bond/amide bond
  b Hydrogen bond
  c α-helix

7 β-sheets are formed when two adjacent strands of peptide lie in a plane and form hydrogen bonds between their respective backbones.

TERTIARY AND QUATERNARY STRUCTURES OF PROTEINS

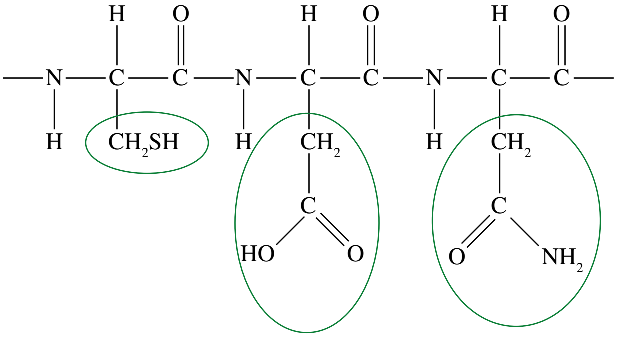
8 D. A is incorrect because it refers to the level of organisation of alpha helices, which is found in the secondary structure.

B is incorrect because the sequence of amino acids is the primary structure.

C is incorrect because amino acids bond via peptide bonds in the primary structure.

D is correct because the quaternary structure involves bonding between two or more peptides through a variety of bonds.

9



10 The activity of an enzyme, which is a type of protein, is dependent 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.

11 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

FATS AND OILS

12 C. C is correct because omega-3 and omega-6 fatty acids are required in the diet because they cannot be produced in the body from other sources.

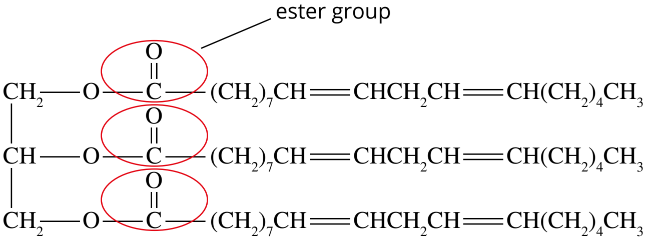
A is incorrect because carbohydrates are the source of energy for cells.

B is incorrect because omega-3 and omega-6 fatty acids are not stored in the body, which is why they need to be consumed.

D is incorrect because omega-3 and omega-6 fatty acids can be solids or oils.

13 **a** Saturated fatty acids have single bonds between carbon atoms.
  b Monounsaturated fatty acids have a single carbon to carbon double bond.
  c Polyunsaturated fatty acids have multiple double bonds.

14 **a** Glycerol
  b



  c Ester group (circled in part **b**)
  d Polyunsaturated
  e The fat is likely to be a liquid at room temperature. Decreasing saturation results in relatively greater spacing between the hydrocarbon chains in the fatty acids and, therefore, reduced dispersion forces.

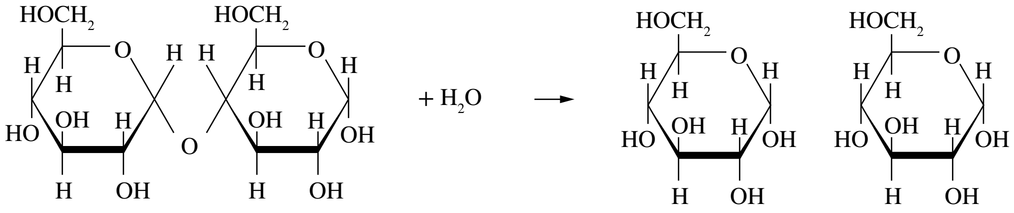
15 Some of the double bonds in sunflower oil are converted to single bonds via a catalysed addition reaction with hydrogen.

16 The term ‘omega’ refers to the last carbon in the fatty acid chain. The number 3 or 6 indicates the position of the double bond in the unsaturated fatty acid in relation to this carbon. That is, the double bone in omega-3 fatty acids is the on the third carbon along from the omega carbon.

CARBOHYDRATES

17 B. Aspartame contains about the same about of energy as an equal mass of sucrose however is nearly 200 times sweeter so can be used in lower amounts. Therefore, B is the most correct answer.

18



19 Glycogen is the main storage polysaccharide in animals. Therefore, it fulfills the same role in animals that starch does in plants.

20 When the body digests food and absorbs glucose, the glucose is transported by the blood to the liver where it is converted to glycogen, a storage polysaccharide. The glycogen is slowly hydrolysed between meals to maintain a fairly constant concentration of glucose in the blood for use by tissues such as those in the brain.

21 **a** Carbon dioxide
  b Glucose
  c Disaccharide
  d Glycosidic
  e Polysaccharide

VITAMINS

22 B

23 **a** Vitamin C
- **b** Vitamin D
- **c** Vitamin D
- **d** Vitamin D
- **e** Vitamin D
- **f** Vitamin C
- **g** Vitamin C
- **h** Vitamin C
- **i** Vitamin D
- **j** Vitamin D
- **k** Vitamin C
- **l** Vitamin C

CONNECTING THE MAIN IDEAS

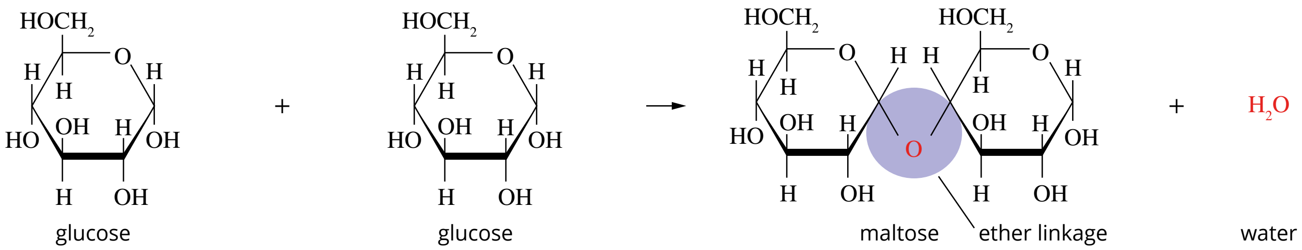
24 **a** Soluble
- **b** Insoluble
- **c** Soluble
- **d** Insoluble
- **e** Soluble
- **f** Insoluble

25 **a** Carboxyl and hydroxyl groups; lipids
- **b** Two hydroxyl groups; carbohydrates
- **c** Carboxyl and amino groups; proteins

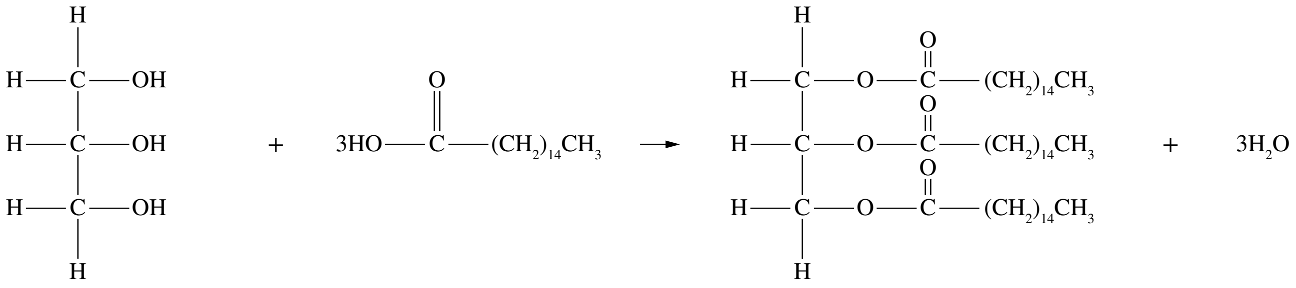
26 **a** Condensation reactions involve the linking together of two small molecules and the elimination of a small molecule, usually water. Hydrolysis reactions consume water and they can often be regarded as the reverse of condensation reactions.

b Vital biochemical processes include condensation reactions (e.g. synthesis of lipids, proteins and polysaccharides) and hydrolysis reactions (e.g. digestion).

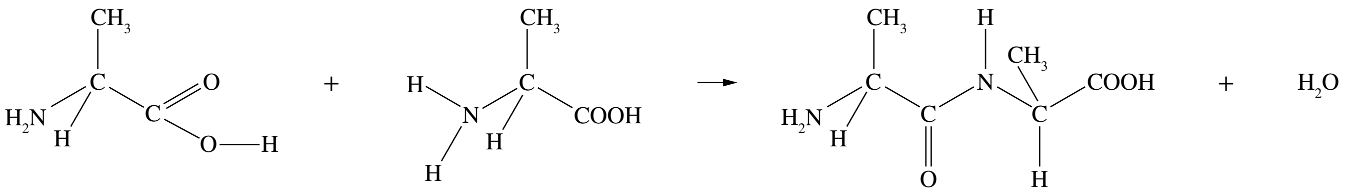
c **i**



ii



iii



Chapter 16 Metabolism of food in the human body

Section 16.1 Metabolism of food

16.1 Key questions

1 proteins, condensation, water, hydrolytic, monosaccharides, glycerol, triglyceride

2 **a** Micronutrient
  b Macronutrient
  c Macronutrient
  d Micronutrient
  e Micronutrient
  f Macronutrient

3 B . A is incorrect because the body obtains energy from the oxidation (not hydrolysis) of carbohydrates, proteins and triglycerides.

C is incorrect because energy is absorbed when large molecules are formed from small molecules.

D is incorrect because the condensation reactions described require energy.

B is the only correct statement.

4 Enzymes catalyse many of the important digestion reactions. They are essential for the hydrolysis of large molecules obtained from food into smaller molecules.

5 The products of digestion are more water soluble so they can pass into the bloodstream more readily to be transported around the body.

6 Action of saliva in the mouth → action of hydrochloric acid in the stomach → action of enzymes in the small intestine → action of bacteria in the large intestine

7 $\text{Polysaccharide} \xrightarrow{\text{hydrolysis}} \text{monosaccharides} \xrightarrow{\text{condensation}} \text{polysaccharide}$

$\text{Triglyceride} \xrightarrow{\text{hydrolysis}} \text{glycerol and fatty acids} \xrightarrow{\text{condensation}} \text{triglyceride}$

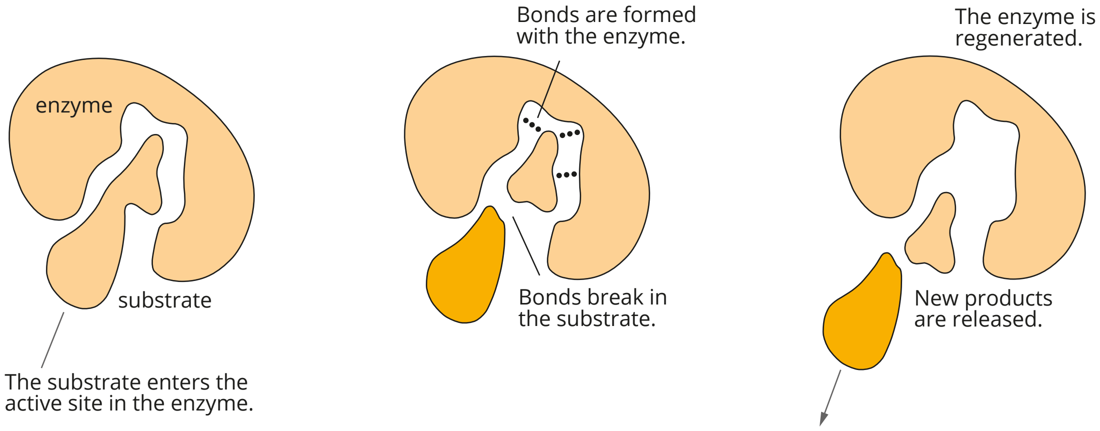
$\text{Protein} \xrightarrow{\text{hydrolysis}} \text{amino acids} \xrightarrow{\text{condensation}} \text{protein}$

Section 16.2 Action of enzymes

16.2 Key questions

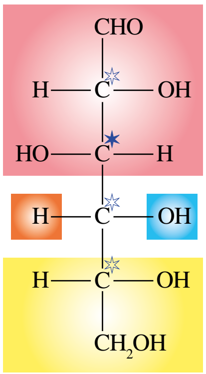
1 D. Enzymes only catalyse one type of reaction. Glucokinase is specific for the oxidation of sugar and will not catalyse other reactions. Enzymes are biological catalysts and work by lowering the activation energy. All enzymes are proteins.

2 **a**



b Hydrogen bonds, ion–dipole interaction, dipole–dipole interactions, ionic interactions

3 There are four chiral centres in D-glucose.



4 **a** True
b True
c False
d True
e False

5 **a** Both
b Enzymes
c Enzymes
d Both
e Both

6 **a** A pair of molecules that are optical isomers of each other. Different structural arrangements that are non-superimposable mirror images.
b Either a metal ion or an organic molecule that binds to the enzyme to assist with the catalytic process.
c The reactant in an enzyme catalysed reaction.
d The earliest model used to describe how enzymes catalyse biochemical reactions. In the lock-and-key model a reactant (substrate) enters a hollow in an enzyme called its active site, producing the enzyme-substrate complex. Only substrates with specific three-dimensional shapes can interact at the active site, so only one enantiomer of a pair of optical isomers (mirror images) may be involved in catalysis.
e An organic molecule that must associate with an enzyme as well as the substrate for catalysis to occur.
f A flexible hollow or cavity in an enzyme that is able to form intermolecular bonds with a substrate molecule.

7 C. A is incorrect because the coenzyme may be changed after the reaction, whereas the enzyme is unchanged.

B is incorrect because coenzymes are non-protein substances.

D is incorrect because the coenzyme may be changed after the reaction.

C is correct because the active site of the enzyme has a unique shape that is complementary to only one enantiomer and not the other.

Section 16.3 Enzymes—dependence on pH and temperature

16.3 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 9, the concentration of OH^- ions is high. The $-COOH$ group will donate a proton to become a $-COO^-$ group. In a solution of pH 3, 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 R group	**Is the R group acidic or basic or neither?**	**Is the R group 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** Enzyme activity is an indication of the amount of substrate converted to product per unit time. Enzyme activity can be influenced by a number of reaction conditions, including solution pH, temperature and substrate concentration.

b 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.

c 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.

Section 16.4 Hydrolysis of carbohydrates

16.4 Key questions

1 **a** $C_6H_{12}O_6$

b Glycosidic links

2 Maltose, amylopectin, amylose, cellulose

3 **a** Maltose is digested in the small intestine by maltase.

b Cellulose is not digested by humans and passes through the digestive tract unchanged. Only animals that have cellulase can digest cellulose.

b Starch is digested into maltose by amylase in the mouth (buccal cavity).

d Lactose is digested in the small intestine by lactase.

4 **a** Amylose

b Wheat grain

c Broccoli

d Strawberry

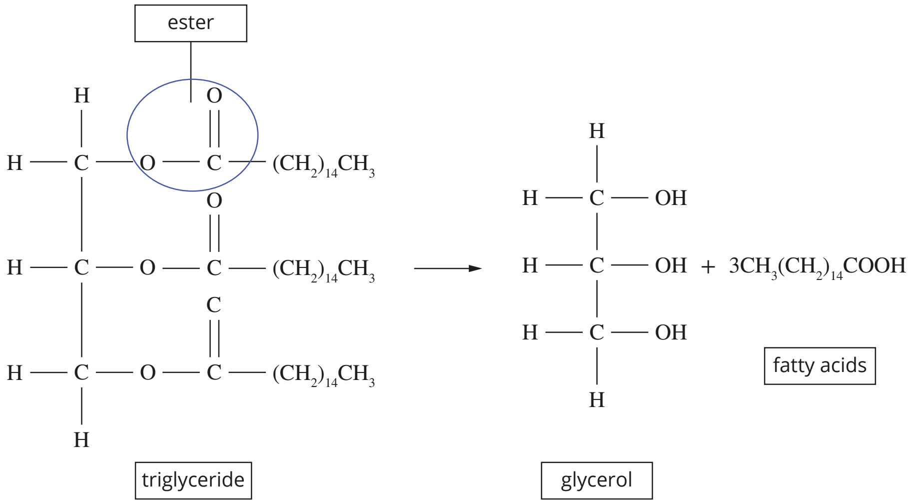
e Whole milk

5 low, slowly, low, slowly, minimal

Section 16.5 Hydrolysis of fats and oils

16.5 Key questions

1



2 **a** The process by which a triglyceride is broken down to fatty acids and glycerol
  b The process by which oxygen reacts with unsaturated triglycerides producing molecules that cause an unpleasant taste in oil and fats
  c The process by which a fat globule is broken into many smaller particles that can be dispersed in an aqueous environment
  d The process in which fatty acids and glycerol combine to form a triglyceride

3 small intestine, emulsifies, hydrolyses, glycerol, adipose

4 **a** False. Rancidity is more likely to occur when a triglyceride is unsaturated.
  b True
  c False. Antioxidants react with free radicals, preventing their further propagation
  d True
  e False. Rancidity occurs when a triglyceride reacts with oxygen in a process called autoxidation, which involves the formation of free radicals.
  f True

CHAPTER 16 REVIEW

METABOLISM OF FOOD

1 **a** All
  b Triglyceride
  c Polysaccharide
  d Triglyceride
  e All
  f Protein
  g Triglyceride
  h Triglyceride

2 If insulin were given orally, the protein would be broken down in the process of digestion before it could be absorbed into the blood.

3

	Names of links between units	**Functional groups formed when links break**	**Monomer or smallest components**
Carbohydrate	glycosidic	hydroxyl	glucose
Fat	ester	hydroxyl and carboxyl	fatty acids and glycerol
Protein	peptide/amide	amino and carboxyl	amino acid

ACTION OF ENZYMES

4 **a** Enzymes in the body include:
- pepsin, which hydrolyses peptide bonds of certain amino acids
- DNA polymerase, which replicates and repairs DNA
- lactase, which breaks down the sugar lactose in the small intestine
- salivary amylase, which breaks down polysaccharides in the mouth.

b Almost all the chemical reactions occurring in living organisms are controlled by enzymes. Enzymes speed up the reactions that are essential for life processes by as much as 10^{10} times; reactions that do not contribute to the functioning of a creature are not catalysed and occur at much slower rates.

c The shape and functional groups in the active site of the enzyme allow it to bind only with certain substrates so that only a specific reaction is catalysed. In a similar way, a lock will only open using a key of a certain shape.

5 **a** True

b True

c False

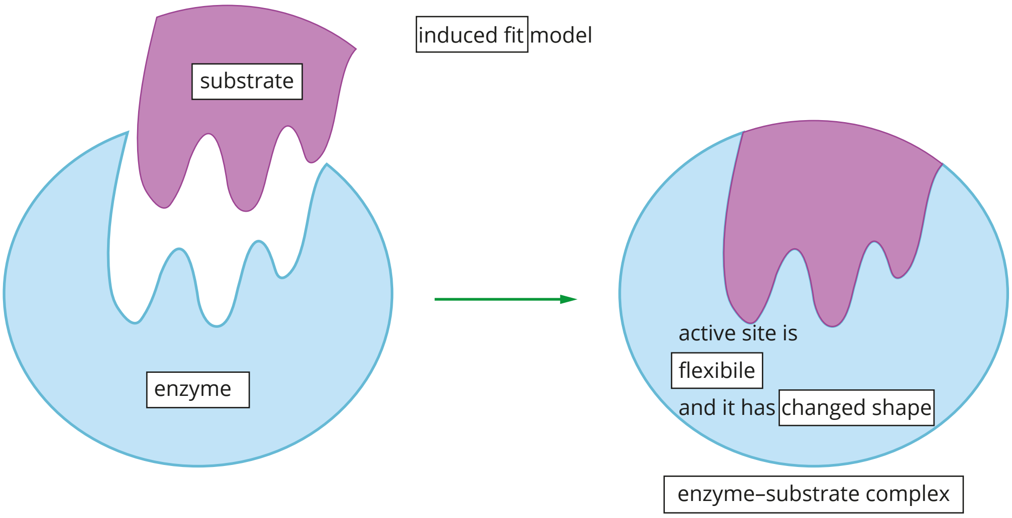
d False

e True

f True

g True

6



7 **a** The active site of an enzyme binds the substrate facilitating the catalysis of the substrate reaction. The active site is selective for binding only a specific substrate and catalysing a single reaction.

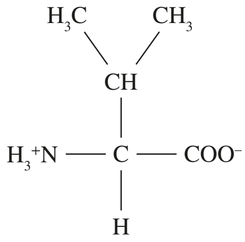
b The amino acid side chains of the active site bind the substrate via a combination of interactions including hydrogen bonds, ionic interactions, dispersion forces and covalent disulfide bonds.

ENZYMES—DEPENDENCE ON pH AND TEMPERATURE

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. A is correct because under highly acidic conditions, an amino acid is protonated at the amino group ($–NH_3^+$) and protonated at the carboxyl group (–COOH).

10



11 **a** Denaturation occurs when there is a change to the structure and shape of an enzyme that prevents it from functioning.

b Denaturation usually involves the disruption of the bonds that hold the enzyme's protein chain in a particular shape, by the 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 on the existence of a suitable hollow or cavity within the molecule, the tertiary structure is crucial to the enzyme's operations.

12 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.

HYDROLYSIS OF CARBOHYDRATES

13 Enzymes in saliva act on starch.
Hydrochloric acid and enzymes in the stomach act on food.
Enzymes in the small intestine act on food.
Bacteria in the large intestine act on dietary fibre.

14 Some people are unable to produce lactase so they cannot digest lactose. Instead, lactose sits and ferments in the digestive tract where the gas it produces can cause bloating and cramps.

15 Humans lack the enzyme (cellulase) that catalyses the hydrolysis of cellulose to form glucose.

16 The surface area of oats is relatively low. The husk of the oats has not been removed. The impact on blood sugar levels will be slow.

HYDROLYSIS OF FATS AND OILS

17 $RH \rightarrow R\bullet + H\bullet$
$R\bullet + O_2 \rightarrow ROO\bullet$
$ROO\bullet \rightarrow ROOH$
$ROOH \rightarrow$ unpleasant products

CONNECTING THE MAIN IDEAS

18 During condensation reactions, small molecules join together to form larger molecules. Large food molecules undergo hydrolysis to form smaller molecules.

a Condensation
b Condensation
c Condensation
d Hydrolysis
e Hydrolysis
f Hydrolysis

19 **a** Ester
b Glycosidic (ether)
c Amide/peptide
d Glycosidic (ether)
e Ester

20 water-soluble, only one, decreased, lower,

21 **a** Vitamin C prevents the propagation of free radicals in the autoxidation process in the decomposition of lipids. It is the hydroxyl groups present in the molecule that facilitate this role.

b Vitamin C is found naturally in a number of fruits and vegetables such as citrus fruits and leafy green vegetables.

Chapter 17 The energy content of food

Section 17.1 Food—an energy source

Worked example: Try yourself 17.1.1

CALCULATING THE ENERGY VALUE OF FOODS

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

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

Thinking	Working
Use Table 17.1.2 to determine the available energy for each nutrient type.	Carbohydrate: $17\,kJ\,g^{-1}$ Protein: $17\,kJ\,g^{-1}$ Fat: $37\,kJ\,g^{-1}$
Assuming that there is 100 g of the sample, multiply each percentage of nutrient by the available energy per gram for the nutrient type.	Carbohydrate: $53.0\,g \times 17\,kJ\,g^{-1} = 901\,kJ$ Protein: $8.0\,g \times 17\,kJ\,g^{-1} = 136\,kJ$ Fat: $4.0\,g \times 37\,kJ\,g^{-1} = 148\,kJ$
Find the sum of the energies for the three nutrient types and divide by 100 to find the energy value in $kJ\,g^{-1}$.	Energy value $= \frac{901 + 136 + 148}{100}$ $= 12\,kJ\,g^{-1}$ (2 significant figures)

17.1 Key questions

1

Energy in joules (J)	Energy in kilojoules (kJ)
100	0.100
1.0×10^4	10
10.0	1.00×10^{-2}
1.00×10^3	1.00
0.10	1.0×10^{-4}

2 A. Glucose, fructose and galactose are all monosaccharides, whereas starch is a polysaccharide.

3 cellular, exothermic, oxidised, oxygen, released, anaerobic, less

4 B. When energy is lost to the surroundings in a combustion reaction, the result is smaller than expected. This does not explain why the heat of combustion would be larger than the available energy.

5 Available energy from Table 17.1.2:

carbohydrates	$17\,kJ\,g^{-1}$
proteins	$17\,kJ\,g^{-1}$
fats	$37\,kJ\,g^{-1}$

Energy per nutrient in 100 g of cheese:

carbohydrates $2.0 \times 17 = 34\,kJ$

proteins $26.7 \times 17 = 453.9\,kJ$

fats $33.3 \times 37 = 1232.1\,kJ$

$$\text{Total energy per gram of cheese} = \frac{34 + 453.9 + 1232.1}{100}$$

$$= 17.2\,kJ\,g^{-1}$$

$$= 17\,kJ\,g^{-1}$$

Section 17.2 Introducing calorimetry

Worked example: Try yourself 17.2.1

CALCULATING THE HEAT ENERGY TRANSFERRED TO WATER FROM BURNING FOOD

A sample of burning food is used to heat 200 mL of water. Calculate the heat energy, in kilojoules, that has been transferred if the temperature of the water increases from 15.5°C to 30.0°C.

Thinking	**Working**
Change the volume of water in millilitres to mass of water in grams. Remember that the density of water is 1.00 g mL^{-1}.	1 mL of water has a mass of 1 g, so 200 mL of water has a mass of 200 g.
Calculate the change in temperature, ΔT, by subtracting the initial temperature from the final temperature: $\Delta T = T_{\text{final}} - T_{\text{initial}}$	$\Delta T = T_{\text{final}} - T_{\text{initial}}$ $= 30.0 - 15.5$ $= 14.5°\text{C}$
Calculate the heat energy transferred to the water, in joules, using the formula: $q = m \times C \times \Delta T$	$q = m \times C \times \Delta T$ $= 200 \times 4.18 \times 14.5$ $= 12\,122\ \text{J}$
Express the quantity of energy, in kJ, to the appropriate number of significant figures. Remember that to convert from Joules to kilojoules, you divide by 10^3.	$q = \frac{12\,122}{1000}$ $=12.1\ \text{kJ}$ (3 significant figures)

Worked example: Try yourself 17.2.2

ESTIMATING THE ENERGY CONTENT OF A SAMPLE OF FOOD

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

Thinking	**Working**
Calculate the heat energy absorbed by the water in Joules, using the formula: $q = m \times C \times \Delta T$	$q = m \times C \times \Delta T$ $= 200 \times 4.18 \times 35.0$ $= 29\,260\ \text{J}$
Express the quantity of energy in kJ. Remember that to convert from joules to kilojoules, you divide by 10^3.	$q = \frac{29260}{1000}$ $= 29.260\ \text{kJ}$
Calculate the mass of the food that was burned by subtracting the final mass from the initial mass: $\Delta m = m_{\text{inital}} - m_{\text{final}}$	$\Delta m = m_{\text{inital}} - m_{\text{final}}$ $= 2.500 - 1.160$ $= 1.340\ \text{g}$
Calculate the energy content of the food by dividing the energy transferred to the water by the change in mass during combustion: Energy content = $\frac{q}{\Delta m}$	Energy content $= \frac{q}{\Delta m}$ $= \frac{29.260}{1.340}$ $= 21.8\ \text{kJ g}^{-1}$ (3 significant figures)

17.2 Key questions

1

Final temperature – initial temperature	ΔT
Specific heat capacity	C
Initial mass – final mass	Δm
Heat energy	q
Time	t

2 **a** The density of water is $1.00\,\mathrm{g\,mL^{-1}}$, so the mass of 100 mL of water is 100 g.

$$\begin{aligned} q &= m \times C \times \Delta T \\ &= 100 \times 4.18 \times 15.2 \\ &= 6353.6\,\mathrm{J} \\ &= 6.35\,\mathrm{kJ} \end{aligned}$$

b The density of water is $1.00\,\mathrm{g\,mL^{-1}}$, so the mass of 500 mL of water is 500 g.

$$\begin{aligned} q &= m \times C \times \Delta T \\ &= 500 \times 4.18 \times (28.0 - 16.0) \\ &= 25\,080\,\mathrm{J} \\ &= 25.1\,\mathrm{kJ} \end{aligned}$$

c

$$\begin{aligned} q &= m \times C \times \Delta T \\ &= 1500 \times 4.18 \times (30.0 - 20.0) \\ &= 62\,700\,\mathrm{J} \\ &= 62.7\,\mathrm{kJ} \end{aligned}$$

3 $q = 4.50\,\mathrm{kJ} = 4.5 \times 10^3\,\mathrm{J}$

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

$$\begin{aligned} \Delta T &= \frac{q}{m \times C} \\ &= \frac{4.50 \times 10^3}{250 \times 4.18} \\ &= 4.306\,^\circ\mathrm{C} \end{aligned}$$

$$\begin{aligned} T_{\text{final}} &= T_{\text{initial}} + \Delta T \\ &= 18.0 + 4.3 \\ &= 22.3\,^\circ\mathrm{C} \end{aligned}$$

4

$$\begin{aligned} q &= m \times C \times \Delta T \\ &= 500 \times 4.18 \times 38.3 \\ &= 80\,047\,\mathrm{J} \\ &= 80.0\,\mathrm{kJ} \end{aligned}$$

$$\begin{aligned} \text{Energy content} &= \frac{E}{m(\text{biscuit})} \\ &= \frac{80.0}{5.00} \\ &= 16.0\,\mathrm{kJ\,g^{-1}} \end{aligned}$$

5

$$\begin{aligned} \text{Energy content} &= \frac{E}{m(\text{corn chips})} \\ m(\text{corn chips}) &= \frac{E}{\text{energy content}} \\ &= \frac{34.7}{22.0} \\ &= 1.58\,\mathrm{g} \end{aligned}$$

6 **a** Bomb
b Solution
c Solution
d Bomb
e Solution
f Bomb

7 insulating, released, lost, lid, increases, endothermic

Section 17.3 Calibration of calorimeters

Worked example: Try yourself 17.3.1

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY ELECTRICAL CALIBRATION

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

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

Worked example: Try yourself 17.3.2

CALCULATING THE CALIBRATION FACTOR OF A CALORIMETER BY CHEMICAL CALIBRATION

A bomb calorimeter was calibrated by the complete combustion of 1.245 g of benzoic acid ($M(C_6H_5COOH) = 122.0\ \text{g mol}^{-1}$; $\Delta H_c = -3227\ \text{kJ mol}^{-1}$). The temperature of the water in the calorimeter rose from 17.50°C to 24.70°C during the calibration. Determine the calibration factor of the calorimeter.

Thinking	**Working**
Determine the amount, in moles, of benzoic acid that undergoes complete combustion. Use the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{1.245}{122.0}$ $= 0.01020$ mol
Calculate the thermal energy released by the complete combustion of the benzoic acid in the calorimeter. Use the equation $E = n \times \Delta H_c$, noting that the energy will be in kJ.	$E = n \times \Delta H_c$ $= 0.01020 \times 3227$ $= 32.93$ kJ
Calculate the temperature change during the calibration. Use the equation: $\Delta T = T_{\text{final}} - T_{\text{initial}}$	$\Delta T = T_{\text{final}} - T_{\text{initial}}$ $= 24.70 - 17.50$ $= 7.20$°C
Calculate the calibration factor by dividing the energy by change in temperature. Use the equation: $CF = \frac{E}{\Delta T}$	$CF = \frac{E}{\Delta T}$ $= \frac{32.93}{7.20}$ $= 4.57\ \text{kJ}\,°\text{C}^{-1}$

Worked example: Try yourself 17.3.3

CALCULATING THE ENERGY CONTENT OF A SAMPLE OF FOOD USING A BOMB CALORIMETER

7.00 g of pizza biscuits were burnt in a bomb calorimeter. The calibration factor of the bomb calorimeter was 8.45 kJ °C^{-1}. During the combustion of the biscuits, the temperature of the water rose by 17.75°C. The mass of the ash left over at the end of the experiment was negligible. Calculate the energy content of the biscuits in kJ g^{-1}.

Thinking	**Working**
Calculate the heat energy released by the food, in kJ, using the equation: $E = CF \times \Delta T$	$E = CF \times \Delta T$ $= 8.45 \times 17.75$ $= 150$ kJ
Calculate the energy content of the food using the equation: Energy content $= \frac{E}{m}$ Express your answer to the correct number of significant figures.	Energy content $= \frac{E}{m}$ $= \frac{150}{7.00}$ $= 21.4$ kJ g^{-1} (3 significant figures)

Worked example: Try yourself 17.3.4

CALCULATING THE ENTHALPY OF COMBUSTION OF A PURE COMPOUND USING A BOMB CALORIMETER

1.164 g of oleic acid (molar mass 284.0 g mol^{-1}) was completely burned in a bomb calorimeter. The calibration factor of the calorimeter was 10.20 kJ °C^{-1}. During the combustion of the oleic acid, the temperature of the water rose by 4.51°C. Calculate the enthalpy of combustion of oleic acid in kJ mol^{-1}.

Thinking	**Working**
Calculate the amount of reactant in moles, using the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{1.164}{284.0}$ $= 0.004\,099$ mol
Calculate the heat energy released, in kJ, using the equation: $E = CF \times \Delta T$	$E = CF \times \Delta T$ $= 10.20 \times 4.51$ $= 46.0$ kJ
Calculate the energy released per mole using the equation: $\Delta H_c = \frac{E}{n}$	$\Delta H_c = \frac{E}{n}$ $= \frac{46.0}{0.004\,099}$ $= 1.12 \times 10^4$ kJ mol^{-1}
State the enthalpy of combustion with the correct sign, remembering that combustion is an exothermic process.	ΔH_c(oleic acid) $= -1.12 \times 10^4$ kJ mol^{-1} (3 significant figures)

Worked example: Try yourself 17.3.5

CALCULATING THE HEAT OF SOLUTION

The heat of solution of sucrose, $C_{12}H_{22}O_{11}$ (M = 342.0 g mol^{-1}) can be determined by solution calorimetry. When 41.587 g of sucrose was dissolved in 200 mL of water in a calorimeter, the temperature decreased by 1.65°C. The calibration factor of the calorimeter was 396.4 J °C^{-1}. Calculate the heat of solution of sucrose.	
Thinking	**Working**
Calculate the amount of reactant in moles, using the equation: $n = \frac{m}{M}$	$n = \frac{m}{M}$ $= \frac{41.587}{342.0}$ = 0.1216 mol
Calculate the heat energy released, in kJ, using the equation: $E = CF \times \Delta T$	$E = CF \times \Delta T$ = 396.4 × 1.65 = 654 J = 0.654 kJ
Calculate the energy released per mole, using the equation: $\Delta H = \frac{E}{n}$	$\Delta H = \frac{E}{n}$ $= \frac{0.654}{0.1216}$ = 5.38 kJ mol^{-1}
State the heat of solution with the correct sign, remembering that a temperature increase indicates an exothermic process and a temperature decrease indicates an endothermic process.	ΔH(sucrose) = +5.38 kJ mol^{-1} (3 significant figures)

17.3 Key questions

1 **a** Bomb, solution
  b Solution
  c Bomb, solution
  d Bomb
  e Bomb
  f Bomb, solution

2 B

Time = 4 × 60 = 240 s

$$CF = \frac{VIt}{\Delta T} = \frac{4.5 \times 5.2 \times 240}{8.5}$$

$$= 661\ \text{J °C}^{-1}$$

3

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$
$$= 17.500 - 16.600$$
$$= 0.900\text{°C}$$
$$CF = \frac{VIt}{\Delta T}$$
$$= \frac{4.40 \times 1.25 \times 90.5}{0.900}$$
$$= 553\ \text{J °C}^{-1}$$
$$= 0.553\ \text{kJ °C}^{-1}$$

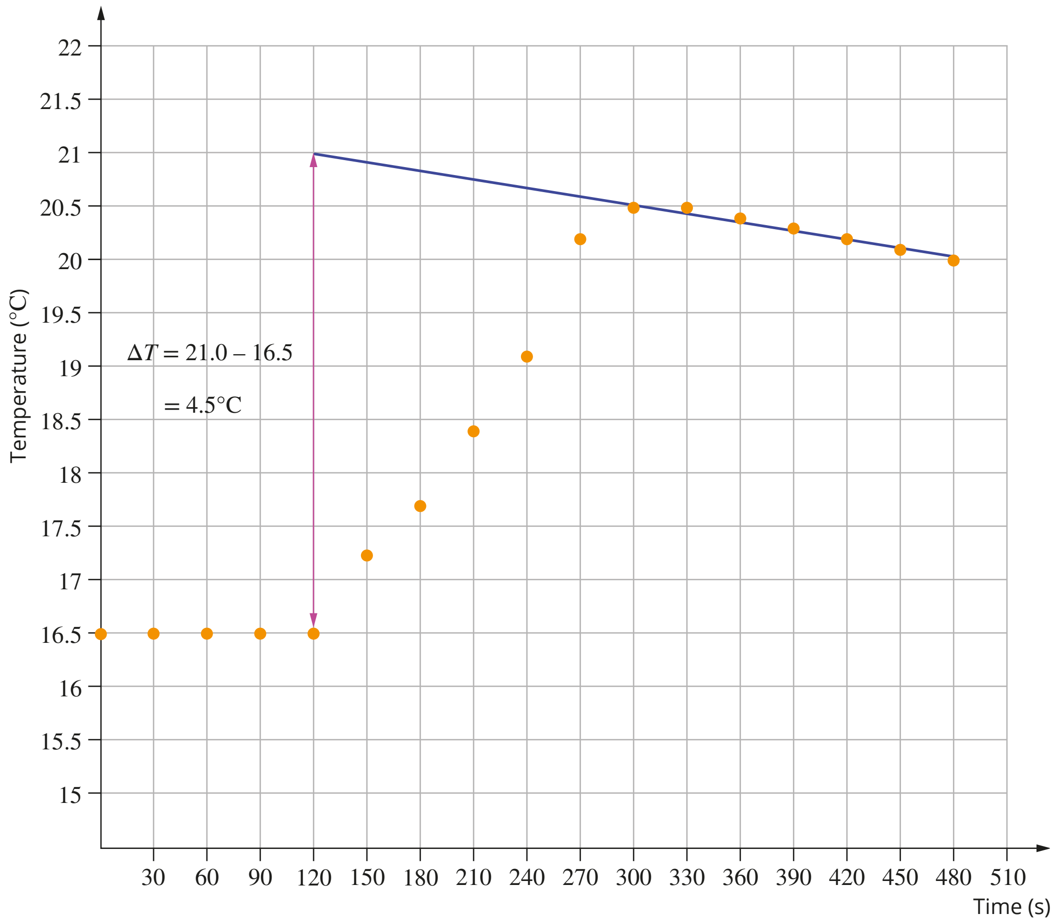
4 **a**

$$CF = \frac{VIt}{\Delta T}$$
$$= \frac{3.50 \times 3.00 \times 240}{1.80}$$
$$= 1400\ \text{J °C}^{-1}$$
$$= 1.40\ \text{kJ °C}^{-1}$$

b $E = CF \times \Delta T$
$= 1.40 \times 14.8$
$= 20.72\ \text{kJ}$

$$\text{Energy content} = \frac{E}{m} = \frac{20.72}{5.00} = 4.14\ \text{kJ g}^{-1}$$

5



From the graph $\Delta T = 21 - 16.5 = 4.5$°C

$$CF = \frac{VIt}{\Delta T} = \frac{6.50 \times 3.80 \times 150}{4.5} = 823\ \text{J °C}^{-1}$$

6 $n(C_6H_5COOH) = \frac{0.153}{122.0} = 0.00125\ \text{mol}$

$E(\text{from benzoic acid}) = \Delta H \times n$
$= 3227 \times 0.00125$
$= 4.05\ \text{kJ}$

$$CF = \frac{E}{\Delta T} = \frac{4.05}{5.80} = 0.698\ \text{kJ °C}^{-1} = 698\ \text{J °C}^{-1}$$

7 B. Options A, C and D refer to foods that are a mixture of many different components. Consequently, their mass cannot be converted to moles as they are not pure substances. Ascorbic acid is a pure substance with the chemical formula $C_6H_8O_6$.

8 $n(\text{citric acid}) = \frac{1.45}{192.0}$

$= 0.00755\ \text{mol}$

$E = CF \times \Delta T$

$= 601 \times 24.63$

$= 14803\ \text{J}$

$= 14.8\ \text{kJ}$

Heat energy per mole $= \frac{E}{n}$

$= \frac{14.8}{0.00755}$

$= 1960\ \text{kJ mol}^{-1}$

$= 1.96 \times 10^3\ \text{kJ mol}^{-1}$

9 $n(\text{sucrose}) = \frac{39.94}{342.0}$

$= 0.1168\ \text{mol}$

$E = CF \times \Delta T$

$= 420.1 \times 1.50$

$= 630.15\ \text{J}$

$\Delta H = \frac{E}{n} = \frac{630.15}{0.1168}$

$= +5396\ \text{J mol}^{-1}$

$= +5.40\ \text{kJ mol}^{-1}$

The heat of solution of sucrose is $+5.40\ \text{kJ mol}^{-1}$

CHAPTER 17 REVIEW

FOOD—AN ENERGY SOURCE

1 B. B is correct because aerobic respiration produces carbon dioxide and water.

A is incorrect because glycogen is the storage molecule of glucose in animals.

C is incorrect because oxygen is a reactant in aerobic respiration.

D is incorrect because lactic acid and ethanol are both produced from anaerobic respiration in animals and plants.

2 Energy = mass of nutrient × available energy for that nutrient.

A. 15 g protein: $15 \times 17 = 255$ kJ

B. 8 g fat: $8 \times 37 = 296$ kJ

C. 20 g carbohydrate: $20 \times 17 = 340$ kJ

D. 5 g fat and 10 g protein: $5 \times 37 + 10 \times 17 = 355$ kJ

Option D produces the most energy.

3 almonds, higher, 1998, 1850

4 Available energy from Table 17.1.2:

carbohydrates	$17\ \text{kJ g}^{-1}$
proteins	$17\ \text{kJ g}^{-1}$
fats	$37\ \text{kJ g}^{-1}$

Energy per nutrient in 100 g of stuffed pepper:

carbohydrates	$16 \times 17 = 272$ kJ
proteins	$13 \times 17 = 221$ kJ
fats	$6.0 \times 37 = 222$ kJ

Total energy per gram of stuffed pepper $= \frac{272 + 221 + 222}{100}$

$= 7.15\ \text{kJ g}^{-1}$

$= 7.2\ \text{kJ g}^{-1}$

INTRODUCING CALORIMETRY

5 The density of water is 1.00 g mL^{-1}, so the mass of 50.0 mL of water is 50.0 g.

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

$= 50.0 \times 4.18 \times (29.8 - 18.5)$

$= 2361.7$ J

$= 2.36$ kJ

6 B. A is incorrect because the material that is generating the heat warms the water. Therefore, the specific heat capacity for water is used.

C is incorrect because the energy generated (q) is measured in joules.

D is incorrect because the change in temperature of the water being warmed or cooled by the sample is used.

B is the only correct answer because the mass of the material being heated is used.

7 $q = 136$ kJ $= 1.36 \times 10^5$ J

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

$$\Delta T = \frac{q}{mC} = \frac{1.36 \times 10^5}{500 \times 4.18}$$

$= 65.1$°C

$T_{\text{final}} = T_{\text{initial}} + \Delta T$

$= 15.0 + 65.1$

$= 80.1$°C

8 $q = m \times C \times \Delta T$

$= 200 \times 4.18 \times 13.2$

$= 11\,035.2$ J

$= 11.0$ kJ

mass of peanut combusted $= m_{\text{initial}} - m_{\text{final}}$

$= 1.200 - 0.750$

$= 0.450$ g

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

$$= \frac{11.0}{0.450}$$

$= 24.5$ kJ g^{-1}

9 Energy in one biscuit $= 12.8 \times 17.0$

$= 217.6$ kJ

$= q$

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

$= 60.0 - 20.0$

$= 40.0$°C

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

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

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

$= 1301$ g

1000 g of water occupies a volume of 1 L:

$V(H_2O) = 1.30$ L

CALIBRATION OF CALORIMETERS

10 a
- Connect the heater of the bomb calorimeter into an electirc circuit with a voltmeter and an ammeter in the circuit.
- Add an accurately measured and recorded volume of water to a calorimeter and measure and record the temperature of the water.
- Turn on the power supply and read the current and voltage for a predetermined time, such as 120 s. Record these values.
- Measure and record the highest temperature reached of the water.
- Turn off and disconnect the electrical circuit.

b
- Add the same volume of fresh water as used for the calibration.
- Record the initial temperature of the water in the calorimeter.
- Add the preweighed food to be burnt into the calorimeter and connect the oxygen supply and ignition device.
- Ignite the food using the ignition device.
- Monitor the temperature of the water until the temperature no longer increases.
- Record the highest temperature reached in the calorimeter.

11 $CF = \frac{VIt}{\Delta T}$

$= \frac{4.05 \times 2.75 \times 150}{3.40}$

$= 491\ \text{J}\ °\text{C}^{-1}$

12 a $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

b Energy change = calibration factor × temperature change

$E = 1250\ \text{J}\ °\text{C}^{-1} \times 1.78°\text{C}$

$= 2225\ \text{J}$

$= 2.23$ kJ is released by 1.00×10^{-3} mol

c 1.00×10^{-3} mol released 2.23 kJ

1 mol will release $\frac{2.23}{1.00 \times 10^{-3}}$

So $\Delta H = -2230\ \text{kJ mol}^{-1}$

$= -2.23\ \text{MJ mol}^{-1}$

d $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l);$

$\Delta H = -2.23\ \text{MJ mol}^{-1}$

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

b Calculate the energy input:

$E = VIt$

$E = 5.90 \times 1.50 \times 60.0$

$= 531\ \text{J}$

Calculate the calibration factor:

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

$= \frac{531\ \text{J}}{0.456°\text{C}}$

$= 1164.5\ \text{J}\ °\text{C}^{-1}$

$= 1.16\ \text{kJ}\ °\text{C}^{-1}$

c $E = CF \times \Delta T$

$= 1.1645\ \text{kJ}\ °\text{C}^{-1} \times 0.672°\text{C}$

$= 0.7825\ \text{kJ}$

$= 783\ \text{J}$

d Calculate the amount of KNO_3:

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

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

Calculate ΔH for the equation, using stoichiometry.

0.01 mol absorbed 783 J

1 mol will absorb $\frac{783}{0.01}$ J. So $\Delta H = +78\,300\text{ J mol}^{-1}$

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

Write the thermochemical equation.

$KNO_3(s) \rightarrow K^+(aq) + NO_3^-(aq)\ \Delta H = +78.3\text{ kJ mol}^{-1}$

14 $n(C_6H_5COOH) = \frac{2.405}{122.0}$

$= 0.01971\text{ mol}$

$E(\text{from benzoic acid}) = \Delta H \times n$

$= 3227 \times 0.01971$

$= 63.61\text{ kJ}$

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

$= 26.35 - 17.50$

$= 8.85°C$

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

$= \frac{63.61}{8.85}$

$= 7.19\text{ kJ °C}^{-1}$

15 $E = CF \times \Delta T$

$= 14.32 \times 28.98$

$= 415.0\text{ kJ}$

$\text{Energy content} = \frac{\text{energy}}{\text{mass}}$

$= \frac{415.0}{20.0}$

$= 20.8\text{ kJ g}^{-1}$

16 $CF = \frac{VIt}{\Delta T}$

$= \frac{8.20 \times 4.25 \times 120}{1.02}$

$= 4100\text{ J °C}^{-1}$

$= 4.10\text{ kJ °C}^{-1}$

$n(\text{glucose}) = \frac{4.50}{180.0}$

$= 0.0250\text{ mol}$

$E = CF \times \Delta T$

$= 4.10 \times 16.74$

$= 68.6\text{ kJ}$

Remember that combustion reactions are always exothermic, with a negative value for ΔH.

$\Delta H_c = \frac{E}{n}$

$= \frac{68.6}{0.0250}$

$= -2.75 \times 10^3\text{ kJ mol}^{-1}$

17 Energy released = energy content × mass

$= 18.0 \times 25.0$

$= 450\,\text{kJ}$

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

$$= \frac{450}{15.40}$$

$= 29.2°\text{C}$

18 $n(C_6H_5COOH) = \dfrac{1.375}{122.0}$

$= 0.01127\,\text{mol}$

$E(\text{from benzoic acid}) = \Delta H \times n$

$= 3227 \times 0.01127$

$= 36.37\,\text{kJ}$

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

$$= \frac{36.37}{7.89}$$

$= 4.61°\text{C}$

$T_{\text{final}} = T_{\text{initial}} + \Delta T$

$= 16.70 + 4.61$

$= 21.31°\text{C}$

19 $E = CF \times \Delta T$

$= 25.3 \times 10.0$

$= 253\,\text{kJ}$

$$n = \frac{E}{\Delta H}$$

$$= \frac{253}{10031}$$

$= 0.0252\,\text{mol}$

$m = n \times M$

$= 0.0252 \times 256.0$

$= 6.46\,\text{g}$

CONNECTING THE MAIN IDEAS

20 combustion, water, increase, calibrating, temperature, energy

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

$= 5.02°\text{C}$

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

22 $CF = \dfrac{VIt}{\Delta T}$

$$= \frac{6.15 \times 4.50 \times 4.00 \times 60}{2.00}$$

$= 3321\,\text{J}\,°\text{C}^{-1}$

$= 3.32\,\text{kJ}\,°\text{C}^{-1}$

Energy transferred $= CF \times \Delta T$

$= 3.32 \times 33.9$

$= 112\,582\,\text{J}$

$= 113\,\text{kJ}$

$$\text{Energy content} = \frac{\text{energy}}{\text{mass}} = \frac{113}{5.00} = 22.5\ \text{kJ g}^{-1}$$

23 **a** Available energy from Table 17.1.2:

carbohydrates	$17\ \text{kJ g}^{-1}$
proteins	$17\ \text{kJ g}^{-1}$
fats	$37\ \text{kJ g}^{-1}$

Energy per nutrient in 70 g of donut:

carbohydrates	$28.0 \times 17 = 476\ \text{kJ}$
proteins	$4.5 \times 17 = 76.5\ \text{kJ}$
fats	$14.0 \times 37 = 518\ \text{kJ}$

$$\text{Total energy per gram of donut} = \frac{476 + 76.5 + 518}{70} = 15.29\ \text{kJ g}^{-1} = 15\ \text{kJ g}^{-1}$$

b $E = CF \times \Delta T$

$= 13.2 \times 11.2$

$= 147.84\ \text{kJ}$

$$\text{Energy content} = \frac{\text{energy}}{\text{mass}} = \frac{147.84}{10.0} = 14.8\ \text{kJ g}^{-1}$$

24 C. When the temperature inside the calorimeter increases, heat will escape if the insulation is not adequate. This will result in a final temperature that is lower than it should be and a calibration factor that is larger than it should be.

25
1. The student has forgotten to divide the energy by the change in temperature when calculating the calibration factor.
2. The student has then multiplied the calibration factor by ΔT, which is correct, but the value is too large due to the earlier mistake.
3. The energy has been divided by the mass of the water, instead of the mass of the honey to calculate the energy content.
4. Conversion to kJ is incorrect. Energy content in J g^{-1} should be divided by 1000, not 100.
5. The final statement suggests that energy is given out when the honey dissolves when it is actually taken in as can be seen by the drop in temperature. Therefore dissolving honey in water is actually an endothermic reaction.

The student's calculations should be as follows:

$$CF = \frac{5.40 \times 2.60 \times 180}{2.3} = 1098.8\ \text{J}$$

Heat energy per gram to dissolve the honey:

$E = CF \times \Delta T$

$= 1098.8 \times 1.7$

$= 1868\ \text{J}$

$$\text{Energy per gram} = \frac{1868}{19.80} = 94.3\ \text{J g}^{-1}$$

94.3 J of energy is taken in when 1 g of honey dissolves. This is an endothermic reaction.

26 B. The graph shows that the insulation is inadequate, so as heat is being added to the calorimeter, it is also being lost through the insulation. To allow for this the graph needs to be extrapolated back to the time when heating began ($t = 120$ s) and ΔT calculated at this point.

Because this method was not used, the value of ΔT was too small, so when the calibration factor is calculated using $CF = \frac{VIt}{\Delta T}$ the calibration factor is larger than it should be. Any enthalpy changes calculated using this calibration factor will also be too large, as $E = CF \times \Delta T$.

27

Mistake or error	**Calibration factor is too small**	**No effect on calibration factor**	**Calibration factor is too large**
The lid is left off during calibration.			✓
Less water is used in the calorimeter for the calibration than for subsequent measurements.	✓		
During electrical calibration, the voltmeter had a systematic error making it read too low.	✓		
During chemical calibration, the mass of benzoic acid was recorded as less than its actual value.	✓		

28 **a** Calibration factor $= \frac{E}{\Delta T} = \frac{VIt}{\Delta T} = \frac{6.10 \times 4.05 \times 240}{13.90} = 427\,\text{J °C}^{-1}$

b Energy produced by combustion:

$E = CF \times \Delta T$

$= 427 \times (48.20 - 18.50)$

$= 1.27 \times 10^4\,\text{J}$

$= 12.7\,\text{kJ}$

Mass loss of jelly babies

$= 5.147 - 4.207$

$= 0.940\,\text{g}$

Energy content of jelly babies:

$\frac{E}{m} = \frac{12.7}{0.940}$

$= 13.5\,\text{kJ g}^{-1}$

c Major sources of error for any calorimetric analysis are loss of heat to the surroundings due to inefficient insulation, inaccurate temperature recording or inaccurate volume measurement.