Student book answers

Module 5: Equilibrium and acid reactions

Chapter 2: Qualitative equilibrium

Worked example 2.1

1 $\Delta H = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$

$\Delta H = [(16 \times -393) + (18 \times -285)] - [2 \times -250]$

$\Delta H = -10918$ kJ

$\Delta S = \Sigma\Delta S(\text{products}) - \Sigma\Delta S(\text{reactants})$

$\Delta S = [(18 \times +70) + (16 \times +214)] - [(2 \times + 361) + (25 \times + 205)]$

$\Delta S = -1163 \text{ J K}^{-1} \text{ mol}^{-1} = -1.1\ 63 \text{ kJ K}^{-1} \text{ mol}^{-1}$

$\Delta G = \Delta H - TS\ \Delta$

$\Delta G = -10918 - (298 \times -1.1\ \ 63)$

$\Delta G = -10571 \text{ kJ mol}^{-1}$

The reaction is spontaneous because the Gibbs free energy is negative.

2 $\Delta H = \Delta\Sigma H_f(\text{products}) - \Delta\Sigma H_f(\text{reactants})$

$\Delta H = [-1273] - [(6 \times -393) + (6 \times -285)]$

$\Delta H = 2795$ kJ

$\Delta S = \Sigma\Delta S(\text{products}) - \Sigma\Delta S(\text{reactants})$

$\Delta S = [+212 + (6 \times +205)] - [(6 \times +214) + (6 \times +70)]$

$\Delta S = -262 \text{ J K}^{-1} \text{ mol}^{-1} = -0.262 \text{ kJ K}^{-1} \text{ mol}^{-1}$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = 2795 - (298 \times -0.262)$

$\Delta G = 2873 \text{ kJ mol}^{-1}$

The reaction is not spontaneous because the Gibbs free energy is positive.

Check your understanding 2.1/2.2

1 In a forward reaction, reactants form products. In a reverse reaction, the products form reactants.

2 All the chemicals in the reaction are contained and no chemicals can enter or leave the reaction.

3 In static equilibrium, a chemical reaction occurs in one direction. Reactants continue to form products until one or both reactants are used up and the reaction stops. In dynamic equilibrium, as the products form some will react to form reactants again. Both reactants and products are present and constantly forming when the reaction is 'complete'.

4 Not all reactions are reversible. If the products are unable to react to form reactants, then the reaction will not be reversible. This usually occurs when the activation energy of the reverse reaction is very high.

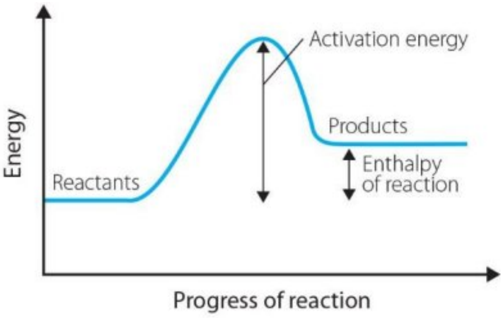
5 A double arrow is used to show that the reaction can occur in both directions.

6 The enthalpy change of a reaction is related to the bonds that are formed and broken as the reaction occurs. If the forward reaction results in a release of energy (exothermic), then the reverse reaction will have the opposite bonds breaking/forming, resulting in absorbing energy (endothermic). The magnitude of the two enthalpy values will be identical.

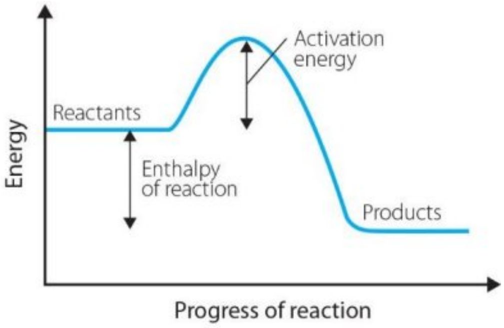
7 a $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$

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

c



d



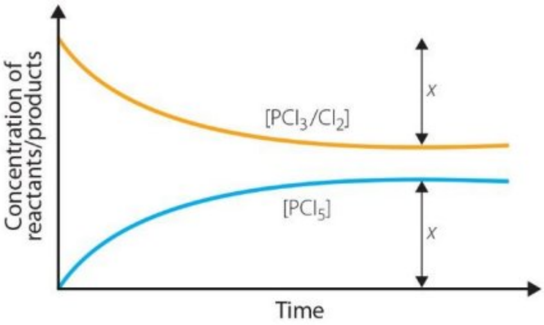
Check your understanding 2.3

1 For a dynamic equilibrium to be established, the chemical system must be closed and must involve a reversible reaction.

2 Steady state systems have constant properties. All dynamic equilibrium systems are also steady state systems. But a steady state system does not need to involve a reversible reaction to have constant properties, so therefore, not all steady state systems are dynamic equilibrium systems.

3 There would be no observable change for a system in dynamic equilibrium. Since both forward and reverse reactions occur at the same rate, there is a constant concentration of each species, so observable properties like colour, pressure and concentration would remain constant.

4



5 a $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

b $[CO(g)] = 1.0 \text{ mol L}^{-1}$, $[Cl_2(g)] = 1.0 \text{ mol L}^{-1}$, $[COCl_2(g)] = 0.2 \text{ mol L}^{-1}$

c At approximately 5 minutes, the lines are parallel, indicating that no further concentration change has occurred and equilibrium has been reached.

Check your understanding 2.4

1 If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way so as to partially counteract the imposed change.

2 The kinetic energy of the particles in the system will also decrease.

3 a Adding H_2 will see the system react to reduce this increased concentration, favouring the reverse reaction to use the extra H_2.

b Decreasing the temperature will see the system react to produce heat energy to increase the temperature; thus, the exothermic reaction will be favoured. Since the forward reaction is endothermic, the reverse reaction is exothermic. The reverse reaction will be favoured.

c Increasing the pressure will see the system react to produce less molecules to decrease the overall pressure of the system. Since there is a gas molecule ratio of 2:4, the reaction will shift to the left, turning 4 molecules into 2 and reducing the pressure of the system. The reverse reaction will be favoured.

4 Adding the carbonate ions in excess would drive the reaction to the right and decrease the concentration of the carbonate ions, also removing more silver ions in solution. Removal of the silver carbonate precipitate as it formed would drive the forward reaction, since the system would react to a decrease in concentration of the product. Increasing the rate of the forward reaction would counteract the removal of the precipitate product.

5 **a** Adding more ClO^- would drive the forward reaction to react to the increased hypochlorite ions. More HClO would form and more heat would be produced. The pH would increase as the concentration of H^+ decreased.

b Addition of heat would drive the endothermic reaction to absorb the extra heat. Since the forward reaction is exothermic, the reverse reaction would be favoured. This would see the system cool, decrease in pH as more H^+ formed, and more ClO^- would also form.

6 When the temperature of a system is increased, all particles gain more kinetic energy and the rate of both forward and reverse reactions will increase since there will be more successful collisions. However, the increase in temperature will affect the particles able to react in the endothermic reaction more than the exothermic reaction, so the endothermic reaction will be favoured. Since this reaction is exothermic, the reverse endothermic reaction will be favoured, causing the ammonia to be used up and more nitrogen and hydrogen to form.

Chapter review questions

1 A, C (if nothing is entering or leaving the beaker); D. B has CO_2 leaving the system so is not equilibrium; E is not equilibrium since no reaction occurs between oxygen and helium.

2 B (equal numbers of molecules on both sides). All others have uneven numbers of molecules so will be affected by pressure changes.

3 C – catalyst does not affect equilibrium position, only the rates of reaction.

4 D – an increase in temperature favours the endothermic reaction to oppose the increase in temperature by absorbing energy. The forward reaction is endothermic, so will be favoured and more products will form.

5 For a reaction to be reversible, the products need to be able to overcome the activation energy required for the reverse reaction to occur. If the activation energy of the reverse reaction is high, the reaction is usually not reversible.

6 **a**, **b** and **d** are all endothermic reactions. If heat is added, then the system will react to absorb the added heat by favouring the endothermic reaction. All of these examples will favour the forward reaction, producing more products.

c and **e** are exothermic reactions. If heat is added, the system will favour the endothermic reaction, which is the reverse reaction for these examples. In this case, the reverse reaction is favoured.

7 **a**

i With 9 gas molecules on the left and 10 gas molecules on the right, the system will favour the side of less molecules to oppose the increase in pressure. Hence, the reverse reaction is favoured.

ii To oppose the decrease in pressure, the system will favour the side of more molecules, so will move to the right.

b **i** With 2 molecules on either side, there will be no change when the pressure is changed.

ii No change, as with **b i**.

c **i** With 7 gas molecules on the left and 8 gas molecules on the right, the system will favour the side with less molecules to oppose the increase in pressure. Hence, the reverse reaction is favoured.

ii To oppose the decrease in pressure, the system will favour the side with more molecules, so will move to the right.

d **i** With 2 gas molecules on the left and 3 gas molecules on the right, the system will favour the side with less molecules to oppose the increase in pressure. Hence, the reverse reaction is favoured.

ii To oppose the decrease in pressure, the system will favour the side of more molecules, so will move to the right.

8 Removal of hydronium ions from the system will see a relative increase in the concentration of the reactants (HCO_3^- and H_2O). Collision theory says this will result in an increase in the number of successful collisions per unit time, thus increasing the rate of the forward reaction and shifting the equilibrium to the right.

9 **a** System reacts by shifting to the right to decrease the concentration of the N_2O_4, so more NO_2 would be produced.

b System reacts by shifting to the left to decrease the concentration of the NO_2, so more N_2O_4 would be produced.

c Adding heat will see the system react by moving in the endothermic direction to absorb the added heat. Since the forward reaction is endothermic, the reaction will shift to the right, producing more NO_2.

d Removing N_2O_4 will see the system move to replace the lost N_2O_4, so the reaction will shift to the left to produce more reactant.

e Increasing pressure will see the system react to decrease the pressure by moving to the side with less molecules. The system will move in the reverse direction since there is one gas molecule on the left, but two gas molecules on the right.

10 **a** Equilibrium on the graph is represented by parallel lines: 0–2 minutes, 3–5 minutes, 6–8 minutes and 9–12 minutes.

b Some of the $COCl_2$ was removed from the system.

c The pressure of the system was increased at 2 minutes, resulting in an immediate increase in concentration of all three substances. The system reacted by shifting to the side of less gaseous molecules to decrease the pressure. This resulted in the favouring of the production of $COCl_2$; hence, its concentration slowly increased. The Cl_2 and CO were used up, seen by a decrease in their concentration. At 3 minutes, equilibrium was re-established, as seen by the parallel lines on the graph showing no further change in concentration.

d At 8 minutes, the concentration of $COCl_2$ decreased, so the reaction shifted in favour of the Cl_2 and CO; hence, the reverse reaction was favoured. Increasing temperature results in the system shifting in the endothermic direction to absorb the extra heat; hence, the reverse direction is endothermic and the forward reaction (synthesis of $COCl_2$) is exothermic.

11 Initially the N_2O_4 reacted to form NO_2. After some time, the NO_2 began to form N_2O_4. When the rates of these two reactions were equal, equilibrium was formed. At the ‘change’, more NO_2 was added, which is seen by the immediate increase in concentration on the graph. To react to this change, the system moved to use up the extra NO_2 by shifting to the left, increasing the concentration of N_2O_4 and decreasing the concentration of NO_2. The change of each is related to the mole ratio; hence, the N_2O_4 increased by an amount, while the NO_2 decreased by double that amount. After some time, the rates of forward and reverse reaction equalised and equilibrium was re-established.

12 **a** Decreasing the volume will result in an increase in pressure since more molecules are in a smaller volume. The system will react by shifting to the side with less molecules, decreasing the pressure. The system will favour the reverse reaction since there are 2 gas molecules on the left and 3 gas molecules on the right.

b When the volume decreases and there are more molecules per volume, the concentration of each substance will increase. This will see an increase in both rates of reaction since more particles per volume will result in more collisions. However, the rate of the reverse reaction will be higher since the system opposes the pressure change.

13 **a** When chickens pant, they expel extra $CO_2(g)$. This shifts the first equilibrium to the left to replace the $CO_2(g)$ but resulting in less $CO_2(aq)$. This results in less H_2CO_3 since the equilibrium ($H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$) shifts to the left. This results in the flow-on effect of less HCO_3^- and then CO_3^{2-} since the remaining equilibrium reactions are all driven to the left to replace decreased concentrations of reactants. Less CO_3^{2-} results in less $CaCO_3$ since the last equilibrium is driven to the left. Thus, less $CaCO_3$ means weaker eggshells.

b Carbonated water contains carbon dioxide in solution. Addition of $CO_2(aq)$ would drive all reactions to the right in turn, decreasing the concentration of the reactants formed from the addition of $CO_2(aq)$ in the first equilibrium. Thus, more $CaCO_3$ forms and the eggshells are stronger.

14 $\Delta H = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$

$\Delta H = (-132.51 + -205.0) - (-365.56)$

$\Delta H = 28.56$ kJ

$\Delta S = \Delta\Sigma S$ (products) $- \Delta\Sigma S$ (reactants)

$\Delta S = (113.4 + 146.4) - (151.08)$

$\Delta S = 108.72$ J K^{-1} mol^{-1}

$\Delta G = \Delta H - T\,\Delta S$

$\Delta G = 28.56 - (298 \times 108.72 \times 10^{-3})$

$\Delta G = -3.839$ kJ mol^{-1}

NH_4NO_3 will spontaneously dissolve in water at 298 K since ΔG is negative.

15 Oxygen is transported in the blood by haemoglobin (Hb). When oxygen gas combines with a haemoglobin molecule oxyhaemoglobin forms ($Hb{\cdot}4O_2$). This reaction is an equilibrium reaction: $Hb + 4O_2 \rightleftharpoons Hb4O_2$. When oxygen is high, the equilibrium favours the forward reaction and the production of oxyhaemoglobin. When oxygen levels are low, the equilibrium favours the reverse reaction, releasing oxygen gas for use by the body.

Student book answers

Module 5: Equilibrium and acid reactions

Chapter 3: Calculating the equilibrium constant

Worked example 3.1

1 $K_{eq} = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

2 $K_{eq} = \dfrac{[CO][H_2]}{[H_2O]}$

3 $K_{eq} = [O_2]$

4 $K_{eq} = \dfrac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]}$

5 $K_{eq} = \dfrac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$

Worked example 3.2

1a $K_{eq} = \dfrac{[CO][H_2O]}{[CO_2][H_2]} = \dfrac{0.17 \times 0.17}{2.00 \times 3.00} = 4.8 \times 10^{-3}$

b $K_{eq} = \dfrac{[S_2][H_2]^2}{[H_2S]^2} = \dfrac{3.5 \times 10^{-3} \times (7.0 \times 10^{-3})^2}{0.2^2} = 4.2 \times 10^{-6}$

2 $K_{eq} = \dfrac{[NH_3]^2}{[N_2][H_2]^3} \quad K_{eq2} = \dfrac{[NH_3]^8}{[N_2]^4[H_2]^{12}}$

$K_{eq2} = K_{eq}{}^4 = 39^4 = 2.3 \times 10^{-6}$

Check your understanding 3.1

1 **a** $K_{eq} = \dfrac{[\mathrm{Ag(NH_3)_2}^{+}]}{\left[\mathrm{Ag}^{+}\right][\mathrm{NH_3}]^2}$

b $K_{eq} = \dfrac{[\mathrm{ICl}]^2}{[\mathrm{Cl_2}][\mathrm{I_2}]}$

c $K_{eq} = \dfrac{[\mathrm{CH_3OH}][\mathrm{HCOOH}]}{[\mathrm{HCOOCH_3}]}$

d $K_{eq} = \dfrac{[\mathrm{CH_3OH}]}{[\mathrm{CO}][\mathrm{H_2}]^2}$

e $K_{eq} = \dfrac{[\mathrm{H_2}][\mathrm{CO_2}]}{[\mathrm{CO}][\mathrm{H_2O}]}$

f $K_{eq} = \dfrac{[\mathrm{NOCl}]^2}{[\mathrm{NO}]^2[\mathrm{Cl_2}]}$

g $K_{eq} = \dfrac{[\mathrm{CO}][\mathrm{H_2}]}{[\mathrm{H_2O}]}$

2 **a** $K_{eq} = \dfrac{\left[\mathrm{Br_3^-}\right]}{\left[\mathrm{Br^-}\right][\mathrm{Br_2}]}\ K_{eq2} = \dfrac{\left[\mathrm{Br^-}\right][\mathrm{Br_2}]}{\left[\mathrm{Br_3^-}\right]}$

$$K_{eq2} = \frac{1}{K_{eq}} = \frac{1}{18} = 0.056$$

b $K_{eq} = \dfrac{[\mathrm{Cl_2}][\mathrm{PCl_3}]}{[\mathrm{PCl_5}]}\ K_{eq2} = \dfrac{[\mathrm{PCl_5}]}{[\mathrm{Cl_2}][\mathrm{PCl_3}]}$

$$K_{eq2} = \frac{1}{K_{eq}} = \frac{1}{0.040} = 25$$

3 $K_{eq} = \dfrac{[\mathrm{NH_3}]^2}{[\mathrm{H_2}]^3[\mathrm{N_2}]}\ K_{eq2} = \dfrac{[\mathrm{NH_3}]}{[\mathrm{H_2}]^{\frac{3}{2}}[\mathrm{H_2}]^{\frac{1}{2}}}$

$$K_{eq2} = \sqrt{K_{eq}} = \sqrt{39} = 6.2$$

4 $$K_{eq} = \frac{[N_2O_4]^{\frac{1}{2}}}{[NO_2]} \quad K_{eq2} = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_{eq2} = \frac{1}{{K_{eq}}^2} = \frac{1}{(5.0\times10^{-3})^2} = 4.0\times10^4$$

Worked example 3.3

1 $$K_{eq} = \frac{[Cl_2][NO]^2}{[NOCl]^2} = \frac{1.43\times10^{-4}\times(5.24\times10^{-3})^2}{(2.07\times10^{-4})^2} = 0.09$$

2 **a** $2COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$

b $n(COF_2)$ decomposed = 1.0 − 0.040 = 0.96 mol

$$n(CO_2) = n(CF_4) = \frac{n(COF_2)}{2} = \frac{0.96}{2} = 0.48\text{ mol}$$

$$c(COF_2) = \frac{n}{V} = \frac{0.040}{5.0} = 0.0080\text{ mol L}^{-1}$$

$$n(CO_2/CF_4) = \frac{n}{V} = \frac{0.48}{5.0} = 0.096\text{ mol L}^{-1}$$

$$K_{eq} = \frac{[CF_4][CO_2]}{[COF_2]^2} = \frac{0.096\times0.096}{0.0080^2} = 144$$

Worked example 3.4

$$[N_2O_4] = \frac{n}{V} = \frac{0.500}{1.0} = 0.500\text{ mol L}^{-1}$$

	$[N_2O_4]$	$[NO_2]$
Initial	0.500	0
Change	−(0.5 × 0.048)	+0.048
Equilibrium	0.476	0.048

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.048^2}{0.476} = 4.8\times10^{-3}$$

Worked example 3.5

$$c(N_2O_4) = \frac{n}{V} = \frac{0.1}{1.00} = 0.10 \text{ mol L}^{-1}$$

$$c(NO_2) = \frac{n}{V} = \frac{0.25}{1.00} = 0.25 \text{ mol L}^{-1}$$

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.25^2}{0.10} = 0.625$$

Since $Q > K_{eq}$, the reaction is not at equilibrium. The reverse reaction will be favoured to reach equilibrium.

Worked example 3.6

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

$[CO] = [Cl_2] = x$

$$K_{eq} = \frac{[CO][Cl_2]}{[COCl_2]}$$

$$4.63\times10^{-3} = \frac{x\times x}{0.0864}$$

$x = [CO] = 0.0200 \text{ mol L}^{-1}$

Check your understanding 3.2/3.3

1 **a** $$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

Mixture A $K_{eq} = \frac{0.00117^2}{0.129} = 1.06\times10^{-5}$

Mixture B $K_{eq} = \frac{0.00185^2}{0.324} = 1.06\times10^{-5}$

Mixture C $K_{eq} = \frac{0.00284^2}{0.778} = 1.04\times10^{-5}$

b The reliability of the data is good. Two of the values are identical and the other is very close. A percentage range of 1.9% shows very good reliability.

2

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5OH$	H_2O
Initial	1.00	0.18	0	0
Change	−0.171	−0.171	+0.171	+0.171
Equilibrium	0.829	0.009	0.171	0.171

$$K_{eq} = \frac{[\mathrm{CH_3COOC_2H_5}][\mathrm{H_2O}]}{[\mathrm{CH_3COOH}][\mathrm{C_2H_5OH}]} = \frac{0.171 \times 0.171}{0.829 \times 0.009} = 3.9$$

3 $$K_{eq} = \frac{[\mathrm{CH_3OH}]}{[\mathrm{CO}][\mathrm{H_2}]^2} = \frac{4.17 \times 10^{-8}}{3.76 \times 10^{-3} \times (4.30 \times 10^{-3})^2} = 0.60$$

A catalyst has no effect on the magnitude of K_{eq}.

4

	H_2	CO_2	H_2O	CO
Initial	1.0	1.0	0	0
Change	−0.56	−0.56	+0.56	+0.56
Equilibrium	0.44	0.44	0.56	0.56

$$K_{eq} = \frac{[\mathrm{CO}][\mathrm{H_2O}]}{[\mathrm{CO_2}][\mathrm{H_2}]} = \frac{0.56 \times 0.56}{0.44 \times 0.44} = 1.6$$

5 **a** Well to the right

b Well to the left

c About in the middle

d Well to the left

e About in the middle

f Well to the right

g Well to the left

h Well to the right

6 **a**

$$Q = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{1.74^2}{0.14 \times 0.078} = 277$$

$Q > K_{eq}$ so the reaction is not at equilibrium. The reaction will proceed to the left to produce more reactants and lower the Q value.

b

$$Q = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{0.83^2}{0.32 \times 0.24} = 8.97$$

$Q < K_{eq}$ so the reaction is not at equilibrium. The reaction will proceed to the right to produce more products and raise the Q value.

7 **a** $$Q=\frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}=\frac{0.0030^2}{0.050\times0.025}=0.0072$$

$Q > K_{eq}$ so the reaction is not at equilibrium. The reaction will proceed to the left to produce more reactants and lower the Q value.

b $$Q=\frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}=\frac{0.0010^2}{0.35\times0.60}=4.76\times10^{-6}$$

$Q < K_{eq}$ so the reaction is not at equilibrium. The reaction will proceed to the right to produce more products and raise the Q value.

8 **a** $$K_{eq}=\frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$$

$$0.48=\frac{[\mathrm{NO_2}]^2}{0.15}$$

$[\mathrm{NO_2}] = 0.27\ \mathrm{mol\ L^{-1}}$

b $$K_{eq}=\frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$$

$$0.48=\frac{0.25^2}{[\mathrm{N_2O_4}]}$$

$[\mathrm{N_2O_4}] = 0.13\ \mathrm{mol\ L^{-1}}$

9 **a** $$K_{eq}=\frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}][\mathrm{I^-}]}$$

$$K_{eq}[\mathrm{I^-}]=\frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}]}$$

$$\frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}]}=K_{eq}[\mathrm{I^-}]=723\times7.00\times10^{-3}=5.06$$

$$\frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}]}=\frac{5.06}{1}$$

b

	I_2	I^-	I_3^-
Initial	1.00	0	0
Equilibrium	0.01	$x - 0.99$	0.99

$0.99 = 99\%$

$$K_{eq} = \frac{[I_3^-]}{[I_2][I^-]}$$

$$723 = \frac{0.99}{[0.01][x-0.99]}$$

$x - 0.99 = 0.137 \text{ mol L}^{-1}$

$[I^-] = 0.137 \text{ mol L}^{-1}$

10 a $[PCl_3] = [Cl_2] = 0.084 \text{ mol L}^{-1}$

$$K_{eq} = \frac{[Cl_2][PCl_3]}{[PCl_5]}$$

$$0.042 = \frac{0.084 \times 0.084}{[PCl_5]}$$

$[PCl_5] = 0.168 \text{ mol L}^{-1}$

b

$$K_{eq} = \frac{[Cl_2][PCl_3]}{[PCl_5]}$$

$$0.042 = \frac{[Cl_2][PCl_3]}{0.095}$$

$[Cl_2][PCl_3] = 0.00399$

$[Cl_2] = [PCl_3] = 0.063 \text{ mol L}^{-1}$

Worked example 3.7

$$\frac{1}{K_P} = P_{O_2} \times P_{H_2}{}^2 = 0.705^2 \times 2.21 = 1.10$$

$$K_P = 0.91$$

Check your understanding 3.4/3.5

1 **a** The system will adjust to absorb the extra heat, so it will favour the endothermic direction. Since the forward reaction is exothermic, the reverse reaction will be favoured. The concentration of reactants will increase, and products decrease. Hence, K_{eq} will decrease.

b The system will adjust to absorb the extra heat, so it will favour the endothermic direction. Since the forward reaction is endothermic, it will be favoured. The concentration of products will increase, and reactants decrease. Hence, K_{eq} will increase.

c The system will adjust to absorb the extra heat, so it will favour the endothermic direction. Since the forward reaction is exothermic, the reverse reaction will be favoured. The concentration of reactants will increase, and products decrease. Hence, K_{eq} will decrease.

d The system will adjust to absorb the extra head, so it will favour the endothermic direction. Since the forward reaction is endothermic, it will be favoured. The concentration of products will increase, and reactants decrease. Hence, K_{eq} will increase.

2 As the temperature increases, the K_{eq} value decreases, indicating an increase in the concentration of reactants. Hence, the reverse reaction is favoured. When temperature increases, the system adjusts to absorb the extra heat, so it moves in the endothermic direction. Hence, the reverse reaction is endothermic and the forward reaction is exothermic.

3 **a** $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_{sp} = [Ag^+][Cl^-]$

b $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$

$K_{sp} = [Al^{3+}][OH^-]^3$

4 **a** $$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]}$$

b $$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

5 **a** $$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

b $$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

6 $$K_p = \frac{P^{2}_{NO_2}}{P_{N_2O_4}} = \frac{0.693^2}{0.723} = 0.66$$

Chapter review questions

1 Solids and liquids do not vary in concentration; only substances that change concentration are included for a heterogeneous system.

2 The equilibrium constant is very small, so the reaction sits well to the left. There are significantly more reactants than products. This reaction only occurs to a very small extent since the K_{eq} number is so small.

3 $$K_a = \frac{\left[\mathrm{CH_3COO^-}\right]\left[\mathrm{H^+}\right]}{\left[\mathrm{CH_3COOH}\right]}$$

4 **a** $$K_{eq} = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

b $$K_{eq2} = \frac{1}{K_{eq}} = \frac{1}{1.1\times10^{-7}} = 9.1\times10^{6}$$

5 **a** Since the K_{eq} value is well above 10, the reaction lies well to the right. This means the nitric acid has almost completely dissociated and is thus a strong acid.

b Since the K_{eq} value is very small, this reaction lies well to the left. This means the lead chloride is not very soluble in water, since this equilibrium contains mostly reactants.

6 $$K_{eq} = \frac{[\mathrm{Cl_2}][\mathrm{CO}]}{[\mathrm{COCl_2}]} \quad K_{eq2} = \frac{[\mathrm{COCl_2}]^2}{[\mathrm{Cl_2}]^2[\mathrm{CO}]^2}$$

$$K_{eq2} = \frac{1}{K_{eq}{}^{2}} = \frac{1}{(5.0\times10^{-3})^2} = 4.0\times10^{4}$$

7 $$K_{eq}=\frac{[\mathrm{Fe(SCN)}^{2+}]}{[\mathrm{Fe}^{3+}][\mathrm{SCN}^{-}]}$$

$$K_{eq}=\frac{0.0094}{0.200\times0.00060}=78.3$$

$$K_{eq}=\frac{0.0290}{0.200\times0.0012}=120.8 * (outlier)$$

$$K_{eq}=\frac{0.0087}{0.100\times0.0011}=79.1$$

$$K_{eq}=\frac{0.0047}{0.100\times0.00060}=78.3$$

Average K_{eq} (excluding outlier) = 79

8 $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

	$COCl_2$	CO	Cl_2
Initial	0.050	0	0
Change	−0.0060	+0.0060	+0.0060
Equilibrium	0.044	0.0060	0.0060

Since volume = 1.0 L $[COCl_2] = 0.044\ \mathrm{mol\ L^{-1}}$ and $[CO] = [Cl_2] = 0.0060\ \mathrm{mol\ L^{-1}}$

$$K_{eq}=\frac{[\mathrm{Cl_2}][\mathrm{CO}]}{[\mathrm{COCl_2}]}=\frac{0.0060\times0.0060}{0.044}=8.2\times10^{-4}$$

9 $$K_{eq}=\frac{[\mathrm{Br_3^-}]}{[\mathrm{Br_2}][\mathrm{Br^-}]}$$

$$18=\frac{0.050}{[\mathrm{Br_2}]\times0.085}$$

$[Br_2] = 0.033\ \mathrm{mol\ L^{-1}}$

10 $$K_{eq}=\frac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2[\mathrm{O_2}]}$$

$$246=\frac{[\mathrm{SO_3}]^2}{0.600^2\times1.00}$$

$[SO_3] = 9.4\ \mathrm{mol\ L^{-1}}$

11 **a** $$Q = \frac{[O_2][NO]^2}{[NO_2]^2} = \frac{2.0 \times 1.0^2}{2.0^2} = 0.50$$

$Q < K_{eq}$ so the mixture is not at equilibrium.

b Since Q is lower than K_{eq}, the forward reaction will be favoured to increase the concentration of the products and increase the magnitude of Q.

12 $$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} = \frac{9.49 \times 10^{-4} \times 9.49 \times 10^{-4}}{0.0500} = 1.8 \times 10^{-5}$$

13

	N_2O_5	NO_2	O_2
Initial	0.10	0	0
Change	−(0.15/2) = −0.075	+0.15	+(0.15/4) = +0.0375
Equilibrium	0.025	0.15	0.0375

$$K_{eq} = \frac{[O_2][NO_2]^4}{[N_2O_5]^2} = \frac{0.0375 \times 0.15^4}{0.025^2} = 0.030$$

14 $$K_p = \frac{{P_{NO_2}}^4 \times P_{O_2}}{{P_{N_2O_4}}^2} = \frac{2.50^4 \times 0.142}{3.00^2} = 0.62$$

15 **a** $$Q = \frac{[H_2]^3[CO]}{[CH_4][H_20]}$$

b $$Q = \frac{0.50^3 \times 0.060}{0.045 \times 0.24} = 0.69$$

$Q < K_{eq}$ so mixture is not at equilibrium.

c (Answer to first question) – Since Q is lower than K_{eq}, the reaction will shift to the right to increase the concentration of products and increase the Q value.

d Since the temperature increases K_{eq} increases. When the temperature increases, the system reacts to absorb extra heat so favours the endothermic reaction. As K_{eq} increases, the concentration of products increases. Hence, the forward reaction is endothermic.

Module 5: Qualitative equilibrium

Chapter 4: Solution equilibria

Check your understanding 4.1/4.2

1 Water molecules or other molecules that form dipole bonds to the metal ion of an ionic salt.

2 Ionic lattices have a crystalline structure where positive and negative ions are arranged in an orderly fashion. Each positive ion is surrounded by negative ions; each negative ion is surrounded by positive ions.

3 Water is polar due to the unequal electronegativity between oxygen and hydrogen atoms. Each O—H bond forms a dipole with electrons more strongly attracted to the oxygen. The molecule has an overall dipole, causing it to be polar.

4 Water can form hydrogen bonds, or ion–dipole bonds with a range of substances, including ionic salts and covalent molecules.

5 Water molecules become attracted to the ions of an ionic salt. Water molecules are present in a fixed ratio to the ions in the solid. The ions and water molecules bond through ion–dipole bonding.

6 In sodium chloride, the energy required to separate the sodium and chloride ions is less than the energy released when the sodium and chloride ions are hydrated. In silver chloride, the energy required to separate the silver and chloride ions is greater than the energy that would be released upon ion hydration. Thus, silver chloride does not dissolve in water.

Worked example 4.1

1 a 30 g/100 g water

b 40 g/100 g water

c 80 g/100 g water

2 $NaNO_3$ as it has the highest mass dissolved.

3 Approximately 38 g would dissolve. The solution would be unsaturated since all the mass of solute has just dissolved.

Check your understanding 4.3/4.4

1 a The maximum mass of substance, in grams, that can dissolve in 100 g of a solvent at a given temperature

b Substances that have harmful effects on living creatures

2 A saturated solution can dissolve no more solute at that particular temperature. A supersaturated solution has more solute dissolved than a saturated solution at that particular temperature. A supersaturated solution only needs a small prompt to have the extra solute precipitate out.

3 a 56 g/100 g water

b Decreases in solubility from 18 g/100 g to 3 g/100 g.

c At 50°C potassium dichromate has solubility of 30 g/100 g, while at 90°C solubility increases to 69 g/100 g water.

d From 50°C and 90°C the graph is flat, showing no change in solubility. The solution is saturated so no further solute will dissolve.

4 At 70°C, the solubility is 30 g/100 g. If 100 g of water was used:

$MM(KClO_3) = 39.10 + 35.45 + (3 \times 16.00) = 122.55 \text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{30}{122.55} = 0.24 \text{ mol}$$

5 Leaching is the use of water to remove water soluble toxins. Placing the cut up cycad into running water dissolved the toxins and carried them away. This process could take from a few hours up to several days.

Worked example 4.2

1 Precipitate: cobalt sulfide

Neutrals species: $K_2S(aq) + Co(CH_3COO)_2(aq) \rightarrow 2KCH_3COO + CoS(s)$

Net ionic: $S^{2-}(aq) + Co^{2+}(aq) \rightarrow CoS(s)$

2 a Copper(II) hydroxide ($Cu(OH)_2$)

b No precipitate formed

c Lead sulfate ($PbSO_4$)

3 You could add sodium or potassium carbonate or sodium/potassium phosphate to form calcium carbonate or calcium phosphate, both of which are insoluble.

Check your understanding 4.5

1 The solid formed when two ionic solutions are mixed

2 An ion that is not involved in a reaction.

3 Soluble: sodium hydroxide, copper(II) sulfate, silver carbonate, lithium chloride

4 **a** Potassium nitrate and zinc chloride

b Ammonium carbonate and sodium sulfate

c Magnesium sulfate and copper(II) bromide

5 **a** $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

b $CuSO_4(aq) + 2KOH(aq) \rightarrow Cu(OH)_2(s) + K_2SO_4(aq)$

c NR

d $Na_2CO_3(aq) + FeSO_4 \rightarrow Na_2SO_4(aq) + FeCO_3(s)$

e $Zn(NO_3)_2(aq) + (NH_4)_2S(aq) \rightarrow ZnS(s) + 2NH_4NO_3(aq)$

f $K_2CO_3(aq) + CaCl_2(aq) \rightarrow 2KCl(aq) + CaCO_3(s)$

6 **a** Magnesium nitrate and sodium carbonate

$Mg(NO_3)(aq) + Na_2CO_3(aq) \rightarrow MgCO_3(s) + 2NaNO_3$

b Lead nitrate and potassium sulfate

$Pb(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow PbSO_4(s) + 2KNO_3$

c Silver nitrate and sodium bromide

$AgNO_3(aq) + NaBr(aq) \rightarrow AgBr(s) + NaNO_3(aq)$

7 B

A – Lead sulfate is a precipitate.

C – Barium sulfate is a precipitate.

D – Silver chloride is a precipitate.

8 **a** Add sodium hydroxide. If the solution contains barium ions, then no precipitate will form. If the solution contains lead ions, then insoluble lead hydroxide will form.

b Using Table 4.1, there is no precipitate test you can do to separate copper(II) ions and iron(II) ions.

Worked example 4.3

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

   $K_{sp} = [Ca^{2+}] \times [CO_3^{2-}]$

2. $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$

   $K_{sp} = [Pb^{2+}] \times [Cl^{-}]^2$

3. $Mg_3(PO_4)_2(s) \rightleftharpoons 3Mg^{2+}(aq) + 2PO_4^{3-}(aq)$

   $K_{sp} = [Mg^{2+}]^3 \times [PO_4^{3-}]^2$

Check your understanding 4.6

1. The equilibrium constant for a precipitation reaction system

2. The numerator contains the aqueous products; the denominator is a solid so it is not included in the equilibrium expression.

3. a. Sodium nitrate is soluble, so no equilibrium expression.

   b. Strontium sulfide is insoluble, so an equilibrium expression can be written.

   c. Silver acetate is slightly soluble, so an equilibrium expression can be written.

   d. Calcium bromide is soluble, so no equilibrium expression.

   e. Ammonium carbonate is insoluble, so an equilibrium expression can be written.

   f. Aluminium sulfite is insoluble, so an equilibrium expression can be written.

   g. Cadmium sulfide is insoluble, so an equilibrium expression can be written.

4. a. $ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$

      $K_{sp} = [Zn^{2+}] \times [S^{2-}]$

   b. $Ag_2CO_3(s) \rightleftharpoons 2Ag^{+}(aq) + CO_3^{2-}(aq)$

      $K_{sp} = [Ag^{+}]^2 \times [CO_3^{2-}]$

   c. $V(OH)_3(s) \rightleftharpoons V^{3+}(aq) + 3OH^{-}(aq)$

      $K_{sp} = [V^{3+}] \times [OH^{-}]^3$

5. No ionic compound is completely insoluble, so ‘sparingly soluble’ and ‘insoluble’ salts form an equilibrium between ions breaking away from the lattice and ions rejoining the lattice. Soluble salts completely ionise, so do not rejoin the lattice and do not form an equilibrium.

Worked example 4.4

1 $FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$

$$\frac{0.0006\text{ g}}{100\text{ g}} = 0.006\text{ g L}^{-1}$$

$MM(FeS) = 55.85 + 32.07 = 87.92\text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{0.006}{87.92} = 6.82 \times 10^{-5}\text{ mol}$$

$[FeS] = 6.82 \times 10^{-5}\text{ mol L}^{-1} = [Fe^{2+}] = [S^{2-}]$

$K_{sp} = [Fe^{2+}] \times [S^{2-}] = 6.82 \times 10^{-5} \times 6.82 \times 10^{-5} = 5 \times 10^{-9}$

2 $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$

$$\frac{0.002\ g}{100\ g} = \frac{0.002\ g}{100\ g}$$

$MM(Ca_3(PO_4)_2) = (3 \times 40.08) + (2 \times 30.97) + (8 \times 16.00) = 310.18\text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{0.02}{310.18} = 6.45 \times 10^{-5}\text{ mol}$$

$[Ca_3(PO_4)_2] = 6.45 \times 10^{-5}\text{ mol L}^{-1}$

$[Ca^{2+}] = 3 \times 6.45 \times 10^{-5} = 1.93 \times 10^{-4}\text{ mol L}^{-1}$

$[PO_4^{3-}] = 2 \times 6.45 \times 10^{-5} = 1.29 \times 10^{-4}\text{ mol L}^{-1}$

$K_{sp} = [Ca^{2+}]^3 \times [PO_4^{3-}]^2 = (1.93 \times 10^{-4})^3 \times (1.29 \times 10^{-4})^2 = 1 \times 10^{-19}$

Worked example 4.5

1 $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$

$[Ag^{+}] = [Cl^{-}] = s$

$K_{sp} = [Ag^{+}] \times [Cl^{-}] = s \times s$

$1.77 \times 10^{-10} = s^2$

$s = 1.33 \times 10^{-5}$

$[Ag^{+}] = [Cl^{-}] = 1.33 \times 10^{-5}\text{ mol L}^{-1}$

2 $Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^{-}(aq)$

$[Ba^{2+}] = s$ $\quad$ $[OH^{-}] = 2s$

$K_{sp} = [Ba^{2+}] \times [OH^{-}]^2 = s \times (2s)^2 = 4s^3$

$2.55 \times 10^{-4} = 4s^3$

$s = 0.0399$

$[Ba^{2+}] = 0.0399\ mol\ L^{-1}$

$[OH^-] = 2 \times 0.0399 = 0.0799\ mol\ L^{-1}$

3 $Cu_3(PO_4)_2(s) \rightleftharpoons 3Cu^{2+}(aq) + 2PO_4^{3-}(aq)$

$[Cu^{2+}] = 3s \qquad [PO_4^{3-}] = 2s$

$K_{sp} = [Cu^{2+}]^3 \times [PO_4^{3-}]^2 = (3s)^3 \times (2s)^2 = 108s^5$

$1.40 \times 10^{-37} = 108s^5$

$s = 1.67 \times 10^{-8}$

$[Cu^{2+}] = 3 \times 1.67 \times 10^{-8} = 5.01 \times 10^{-8}\ mol\ L^{-1}$

$[PO_4^{3-}] = 2 \times 1.67 \times 10^{-8} = 3.34 \times 10^{-8}\ mol\ L^{-1}$

Worked example 4.6

a $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$[Ag^+] = [Cl^-] = s$

$K_{sp} = [Ag^+] \times [Cl^-] = s \times s$

$1.77 \times 10^{-10} = s^2$

$s = 1.33 \times 10^{-5}$

$MM(AgCl) = 107.9 + 35.45 = 143.35\ g\ mol^{-1}$

$m = n \times MM = 1.33 \times 10^{-5} \times 143.35 = 0.00191\ g$

$[AgCl] = 0.00191\ g\ L^{-1}$

Solubility is less than 1 g L^{-1}, so silver chloride is insoluble.

b $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$

$[Ag^+] = 2s \qquad [SO_4^{2-}] = s$

$K_{sp} = [Ag^+]^2 \times [SO_4^{2-}] = (2s)^2 \times s = 4s^3$

$1.20 \times 10^{-5} = 4s^3$

$s = 0.0144$

$[Ag_2SO_4] = 0.0144\ mol\ L^{-1}$

$MM(Ag_2SO_4) = (2 \times 107.9) + 32.07 + (4 \times 16.00) = 311.87\ g\ mol^{-1}$

$m = n \times MM = 0.0144 \times 311.87 = 5.68\ g$

$[Ag_2SO_4] = 4.49\ g\ L^{-1}$

Since solubility is between 1–10 g L^{-1}, silver sulfate is sparingly soluble.

Worked example 4.7

$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^{-}(aq)$

$Q_{sp} = [Pb^{2+}] \times [Br^{-}]^2 = 0.0118 \times 0.236^2 = 6.57 \times 10^{-4}$

$Q_{sp} > K_{sp}$ so precipitation occurs

Check your understanding 4.7

1 **a** The relationship between the solubility product and the concentration of the ions

b Insoluble substances are those with a solubility of less than 1 g L^{-1}.

2 $Co(OH)_2(s) \rightleftharpoons Co^{2+}(aq) + 2OH^{-}(aq)$

$[Co^{2+}] = s \qquad [OH^{-}] = 2s$

$K_{sp} = [Co^{2+}] \times [OH^{-}]^2 = s \times (2s)^2 = 4s^3$

$s = 1.14 \times 10^{-5}$

$K_{sp} = 4 \times (1.14 \times 10^{-5})^3 = 5.93 \times 10^{-15}$

3 **a** $FeCO_3(s) \rightleftharpoons Fe^{2+}(aq) + CO_3^{2-}(aq)$

$[Fe^{2+}] = [CO_3^{2-}] = s$

$K_{sp} = [Fe^{2+}] \times [CO_3^{2-}] = s \times s$

$3.13 \times 10^{-11} = s^2$

$s = 5.59 \times 10^{-6}$

$[Fe^{2+}] = [CO_3^{2-}] = 5.59 \times 10^{-6}$ mol L^{-1}

b $Eu(OH)_3(s) \rightleftharpoons Eu^{3+}(aq) + 3OH^{-}(aq)$

$[Eu^{3+}] = s \qquad [OH^{-}] = 3s$

$K_{sp} = [Eu^{3+}] \times [OH^{-}]^3 = s \times (3s)^2 = 27s^4$

$9.38 \times 10^{-27} = 27s^4$

$s = 1.37 \times 10^{-7}$

$[Eu^{3+}] = 1.37 \times 10^{-7}$ mol L^{-1}

$[OH^{-}] = 3 \times 1.37 \times 10^{-7} = 4.10 \times 10^{-7}$ mol L^{-1}

4 **a** $CsIO_4(s) \rightleftharpoons Cs^+(aq) + IO_4^-(aq)$

$[Cs^+] = [IO_4^-] = s$

$K_{sp} = [Cs^+] \times [IO_4^-] = s \times s$

$s = 0.00227$

$[CsIO_4] = 0.00227 \text{ mol L}^{-1}$

$MM(CsIO_4) = 132.9 + 126.9 + (4 \times 16.00) = 323.8 \text{ g mol}^{-1}$

$m = n \times MM = 0.00227 \times 323.8 = 0.735 \text{ g}$

$[CsIO_4] = 0.735 \text{ g L}^{-1}$

Solubility is less than 1, so $CsIO_4$ is insoluble.

b $Sr(IO_3)_2(s) \rightleftharpoons Sr^{2+}(aq) + 2IO_3^-(aq)$

$[Sr^{2+}] = s \qquad [IO_3^-] = 2s$

$K_p = [Sr^{2+}] \times [IO_3^-] = s \times (2s)^2 = 4s^3$

$1.14 \times 10^{-7} = 4s^3$

$s = 0.00305$

$[Sr(IO_3)_2] = 0.00305 \text{ mol L}^{-1}$

$MM(Sr(IO_3)_2) = 87.61 + (2 \times 126.9) + 6 \times 16.00) = 437.41 \text{ g mol}^{-1}$

$m = n \times MM = 0.00305 \times 437.41 = 1.33 \text{ g L}^{-1}$

The solubility is between 1–10 g L^{-1}, so it is sparingly soluble.

5 $ZnF_2(s) \rightleftharpoons Zn^{2+}(aq) + 2F^-(aq)$

$$[ZnF_2] = \frac{10.0\ g}{500\ mL} = 20.0 \text{ g L}^{-1}$$

$MM(ZnF_2) = 65.38 + (2 \times 19.00) = 103.38 \text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{20.0}{103.38} = 0.193 \text{ mol}$$

$[ZnF_2] = 0.193 \text{ mol L}^{-1} = [Zn^{2+}]$

$[F^-] = 2 \times 0.193 = 0.386 \text{ mol L}^{-1}$

$Q_{sp} = [Zn^{2+}] \times [F^-]^2 = 0.193 \times 0.386^2 = 0.0288$

$Q_{sp} < K_{sp}$ so no precipitate forms.

Worked example 4.8

1 $MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$

$K_{sp} = [Mg^{2+}] \times [CO_3^{2-}]$

Solubility in 0.550 mol L^{-1} Na_2CO_3:

$[Mg^{2+}] = [MgCO_3] = s$

$[CO_3^{2-}] = (0.550 + s) \sim 0.550$

$K_{sp} = 6.82 \times 10^{-12} = s \times 0.550$

$s = 1.24 \times 10^{-11}$ mol L^{-1}

Solubility in 0.375 mol L^{-1}:

$[Mg^{2+}] = [MgCO_3] = s$

$[CO_3^{2-}] = (0.375 + s) \sim 0.375$

$K_{sp} = 6.82 \times 10^{-12} = s \times 0.375$

$s = 1.82 \times 10^{-11}$ mol L^{-1}

Thus, solubility is slightly higher in 0.375 mol L^{-1} Na_2CO_3.

2 $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

Qualitatively: when extra OH^- is added, the system reacts to decrease the concentration of OH^- so moves to the left. This decreases the solubility of copper(II) hydroxide.

Quantitatively:

Solubility in water:

$K_{sp} = [Cu^{2+}] \times [OH^-]^2$

$[Cu^{2+}] = s$ $\qquad$ $[OH^-] = 2s$

$2.2 \times 10^{-20} = s \times (2s)^2 = 4s^3$

$s = 1.77 \times 10^{-17}$

Solubility in 0.075 mol L^{-1} NaOH:

$[Cu^{2+}] = s$ $[OH^-] = (0.075 + s) \sim 0.075$

$2.2 \times 10^{-20} = s \times 0.075^2$

$s = 3.91 \times 10^{-18}$

Thus, the solubility is approximately 10^{10} times less soluble in 0.075 mol L^{-1} NaOH than in water.

Check your understanding 4.8

1 Adding a common ion to a saturated solution will decrease the solubility of the salt.

2 $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$

$[PbBr_2] = s$

$[Br^-] = 2s$

$[Pb^{2+}] = (0.10 + s) \sim 0.10$

$K_{sp} = [Pb^{2+}] \times [Br^-]^2$

$6.60 \times 10^{-6} = 0.10 \times (2s)^2 = 4s^2$

$s = 0.004 \text{ mol L}^{-1}$

3 In water, there are no extra nickel(II) ions so the equilibrium is maintained. When nickel(II) carbonate is added to nickel(II) nitrate, the extra nickel(II) ions will cause the system to react to decrease the concentration of nickel(II) ions by shifting to the left, decreasing the solubility of the nickel(II) carbonate.

4 $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

Solubility in water:

$[Mg^{2+}] = s$ $\quad$ $[OH^-] = 2s$

$K_{sp} = [Mg^{2+}] \times [OH^-]^2$

$5.61 \times 10^{-12} = s \times (2s)^2 = 4s^3$

$s = 1.12 \times 10^{-4}$

Solubility in 0.20 mol L^{-1} NaOH:

$[Mg^{2+}] = s\ [OH^-] = (0.20 + s) \sim 0.20$

$K_{sp} = s \times 0.20^2 = 5.61 \times 10^{-12}$

$s = 1.40 \times 10^{-10}$

It is approximately 8×10^5 times less soluble in 0.20 mol L^{-1} NaOH than in water.

5 $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$

$K_{sp} = [Ca^{2+}]^3 \times [PO_4^{3-}]^2$

Solubility in 0.30 mol L^{-1} Na_3PO_4:

$[Ca^{2+}] = 3s \qquad [PO_4^{3-}] = (0.30 + s) \sim 0.30$

$K_{sp} = 2.07 \times 10^{-29} = (3s)^3 \times 0.30^2$

$s = 2.1 \times 10^{-10}$

Solubility in 0.15 mol L^{-1} Na_3PO_4:

$[Ca^{2+}] = 3s \qquad [PO_4^{3-}] = (0.15 + s) \sim 0.15$

$K_{sp} = 2.07 \times 10^{-29} = (3s)^3 \times 0.15^2$

$s = 3.2 \times 10^{-10}$

Thus, less soluble in 0.30 mol L^{-1} by a factor of 1.5.

Chapter review questions

1 **a** A solution in which no more solute can be dissolved

b Substances that have harmful effects on living things

c The relationship between the solubility product and the concentration of each of the ions

d A solute that dissolves between the range 1 g L^{-1} to 10 g L^{-1}

2 The solubility product describes the equilibrium product for a system at equilibrium, represented by K_{sp}. The ionic product describes the reaction quotient for a system that is not at equilibrium, represented by Q_{sp}.

3 For many of the chemicals in Figure 4.7, the solubility of salts increases, but not all increase linearly. $NaNO_3$ and $Pb(NO_3)_2$ increase linearly, but $CaCl_2$ and $KClO_3$ increase, but not linearly. $Ce_2(SO_4)_3$ does not increase with temperature at all.

4 Leaching involves the use of water to dissolve water soluble toxins or unwanted salts. Objects are placed in water, setting up an equilibrium where the toxins/salts shift out of the object and into the water. When an equilibrium is set up, the object is removed from the solution and placed into fresh water. This process is repeated until the toxins/salts are removed.

5 Use of leaching to remove cycads was successful. Cycads were used as foods, which is not possible unless the toxins were removed. Their methods were very effective since they used running water to remove the toxins once they were leached out from the cycad pulp.

6 **a** Lead chloride is slightly soluble so will form a precipitate.

$2NaCl(aq) + Pb(NO_3)_2(aq) \rightarrow 2NaNO_3(aq) + PbCl_2(s)$

b No precipitate formed

c Barium sulfate

$Ba(OH)_2(aq) + Na_2SO_4(s) \rightarrow BaSO_4(s) + 2NaOH(aq)$

d Aluminium sulfite

$2AlCl_3(aq) + 3(NH_4)_2SO_3(aq) \rightarrow Al_2(SO_3)_3(s) + 6NH_4Cl$

e Copper(II) carbonate

$CuBr_2(aq) + Na_2CO_3(aq) \rightarrow 2NaBr_2(aq) + CuCO_3(s)$

7 **a** $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$

b $K_{sp} = [Mg^{2+}] \times [OH^-]^2$

c $K_{sp} = 0.00100 \times (3.74 \times 10^{-5})^2 = 1.41 \times 10^{-12}$

d $[Mg^{2+}] = s \qquad [OH^-] = 2s$

$K_{sp} = s \times (2s)^2 = 4s^3$

$s = 7.06 \times 10^{-5}$ mol L^{-1}

8 $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Fe^{2+}] \times [OH^-]^2$

$[Fe^{2+}] = s \quad [OH^-] = 2s$

$K_{sp} = 4.87 \times 10^{-17} = s \times (2s)^2 = 4s^3$

$s = 2.30 \times 10^{-6}$

$[Fe^{2+}] = 2.30 \times 10^{-6}$ mol L^{-1}

$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$

$K_{sp} = [Fe^{3+}] \times [OH^-]^3$

$[Fe^{2+}] = s \qquad [OH^-] = 3s$

$K_{sp} = 4.87 \times 10^{-17} = s \times (3s)^3 = 27s^4$

$s = 1.01 \times 10^{-10}$

$[Fe^{3+}] = 1.01 \times 10^{-10}$ mol L^{-1}

So, $Fe(OH)_2$ has the greater concentration of iron ions.

9 **a** $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$

As the temperature increases, the solubility also increases. If solubility increases, the forward reaction is favoured. If temperature is increased, the system reacts to decrease the temperature by moving in the endothermic direction. Hence, the heat of solution for silver sulfate is endothermic.

b $K_{sp} = [Ag^+]^2 \times [SO_4^{2-}]$

c $MM\ (Ag_2SO_4) = (107.9 \times 2) + 32.06 + (4 \times 16.00) = 311.86\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{14.1}{311.86} = 0.0452\ \text{mol}$$

$[Ag_2SO_4] = 0.0452\ \text{mol L}^{-1}$

d $[Ag^+] = 2 \times 0.0452 = 0.0904\ \text{mol L}^{-1}$

$[SO_4^{2-}] = 0.0452\ \text{mol L}^{-1}$

$K_{sp} = 0.0904^2 \times 0.0452 = 3.70 \times 10^{-4}$

10 $MM\,(MnCO_3) = 54.94 + 12.01 + (3 \times 16.00) = 114.95\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{(0.0065\ \times 10)}{114.95} = 5.65 \times 10^{-4}\ \text{mol}$$

$MnCO_3(s) \rightleftharpoons Mn^{2+}(aq) + CO_3^{2-}(aq)$

$K_{sp} = [Mn^{2+}] \times [CO_3^{2-}] = 5.65 \times 10^{-4} \times 5.65 \times 10^{-4} = 3.20 \times 10^{-7}$

11 **a** $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^-(aq)$

$MM(Ag_2CrO_4) = (2 \times 107.9) + (52.00) + (4 \times 16.00) = 331.8\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{0.0025}{331.8} = 7.53 \times 10^{-6}\ \text{mol}$$

$[Ag_2CrO_4] = 7.53 \times 10^{-6}\ \text{mol L}^{-1}$

b $K_{sp} = [Ag^+]^2 \times [CrO_4^{2-}]$

$[Ag^+] = 2 \times 7.53 \times 10^{-6} = 1.51 \times 10^{-5}\ \text{mol L}^{-1}$

$[CrO_4^{2-}] = 7.53 \times 10^{-6}\ \text{mol L}^{-1}$

$K_{sp} = (1.51 \times 10^{-5})^2 \times 7.53 \times 10^{-6} = 1.71 \times 10^{-15}$

c $[Ag^+] = (0.10 + s) \sim 0.10 \text{ mol L}^{-1}$

$[CrO_4^{2-}] = s$

$K_{sp} = [Ag^+]^2 \times [CrO_4^{2-}]$

$1.71 \times 10^{-15} = 0.10 \times s$

$s = 1.71 \times 10^{-14} \text{ mol L}^{-1}$

d Solubility is less in 0.10 mol L^{-1} silver nitrate than in water due to the common ion effect. The extra Ag^+ ions from the silver nitrate cause the equilibrium system to react to decrease the concentration of silver ions by driving the reaction to the left and decreasing the solubility of silver nitrate.

End-of-Module 5 Review

1 **a** $$K = \frac{[NO_2]^2}{[NO]^2 \times [O_2]}$$

b As the temperature increases, the value of K_{eq} decreases, so less products are being formed and the reaction has shifted to the left, favouring the formation of reactants. When temperature is increased, the system reacts to absorb the extra heat and decrease the temperature, shifting in the endothermic direction. Thus, the reverse reaction is endothermic and the forward reaction is exothermic.

c Low temperatures favour the formation of nitrogen dioxide in terms of equilibrium. Decreasing temperature favours the forward exothermic reaction, increasing the production of nitrogen dioxide. High pressure also favours the forward reaction as the system will react to decrease pressure by moving to the side of less molecules. With 3 gas molecules on the left and 2 on the right, the forward reaction is favoured.

d $$K = \frac{[NO_2]^2}{[NO]^2 \times [O_2]}$$

$$112 = \frac{[0.60]^2}{[NO]^2 \times 0.17}$$

$[NO] = 0.14 \text{ mol L}^{-1}$

2 **a**

	$HI(g)$	$H_2(g)$	$I_2(g)$
Initial (mol)	1.00	0	0
Change (mol)	−0.22	+0.11	+0.11
Equilibrium (mol)	0.78	0.11	0.11

b $$K = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{0.11 \times 0.11}{0.78^2} = 0.020$$

3 **a** Increased temperatures will cause the system to react to absorb the extra heat and decrease the temperature. The system will shift in the endothermic direction. Since the forward reaction is exothermic, the reverse reaction will be favoured, decreasing the production of ammonia.

b $$K_{eq2} = \frac{[H_2]^{3/2}[N_2]^{1/2}}{[NH_3]}$$

$$K_{eq2} = \sqrt{\frac{1}{K_{eq}}} = \sqrt{\frac{1}{9.60}} = 0.323$$

4 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$[SO_2] = \frac{n}{V} = \frac{0.18}{3} = 0.060 \text{ mol L}^{-1}$$

$$[O_2] = \frac{n}{V} = \frac{0.15}{3} = 0.050 \text{ mol L}^{-1}$$

	$SO_2(g)$	$O_2(g)$	$SO_3(g)$
Initial (mol L^{-1})	0.060	0.040	0
Change (mol L^{-1})	−0.040	−0.020	+0.040
Equilibrium (mol L^{-1})	0.020	0.020	0.040

$$K = \frac{[SO_3]^2}{[SO_2]^2 \times [O_2]} = \frac{0.040^2}{0.020^2 \times 0.020} = 200$$

5 A: Some nitrogen was added to the system, shown by the sharp increase in its concentration. The system reacted by shifting to the right to decrease the concentration of the nitrogen gas. Thus, the nitrogen and hydrogen decreased in concentration, and the concentration of ammonia increased.

B: The pressure of the system was increased, shown by the sharp increase in concentration of all gaseous species. The system reacted by moving to the side with less molecules to decrease the pressure. With 4 gas molecules on the left and 2 gas molecules on the right, the reaction moves to the right. Thus, the nitrogen and hydrogen decreased in concentration, and the concentration of ammonia increased.

C: When the temperature was increased the system reacted by shifting in the endothermic direction to absorb the extra heat. Since the graph shows an increase in the concentrations of nitrogen and hydrogen, the reverse reaction was favoured. Thus, the reverse reaction is endothermic and the forward reaction is exothermic.

6 The left axis ($[H_2S]$ increases) is valid since it shows an increase in hydrogen sulfide concentration. The horizontal axis (pressure increases) shows that the concentration of hydrogen sulfide decreases as pressure increases. Le Chatelier's principle states that an increase in pressure will see the system move to the side of less molecules. The reaction shown has more gas molecules on the left (3 left, 2 right) so the reaction should shift to the right and decrease the concentration of hydrogen sulfide. The right axis shows that as temperature increases the concentration of hydrogen sulfide also increases. Since the reaction is exothermic, an increase in temperature would see the reaction shift in the endothermic (reverse) direction to absorb the extra heat. This would see an increase in the concentration of hydrogen sulfide.

Hence, this graph is a reasonable representation. All axes show correct information about the equilibrium system and how it adjusts to changes.

7 **a** Changing the volume of the container will see no change in the equilibrium constant since the ratio of reactants and products will remain constant even if the concentration changes. The rates of forward and reverse reactions remain equal.

b Increasing the temperature will see the system shift in the endothermic (forward) direction to absorb the extra heat. Since temperature affects the rates of both reactions differently, the rate of forward and reverse reaction will not be equal so the K value will change. The K value will increase as more products form.

8 $Ag_2C_2O_4(s) \rightleftharpoons 2Ag^+(aq) + C_2O_4(aq)$

Qualitatively:

Adding silver ions when dissolving in the silver nitrate will see the system react to decrease the concentration of silver ions by shifting to the left, decreasing the solubility of silver oxalate in silver nitrate when compared to water.

Quantitatively:

Solubility in water: $K_{sp} = [Ag^+]^2 \times [C_2O_4^{2-}]$

$[Ag^+] = 2s$ $[C_2O_4^{2-}] = s$

$5.40 \times 10^{-12} = s \times (2s)^2 = 4s^3$

$s = 1.11 \times 10^{-4}$ mol L^{-1}

Solubility in 0.150 mol L^{-1} $AgNO_3$:

$K_{sp} = [Ag^+]^2 \times [C_2O_4^{2-}]$

$[Ag^+] = (0.15 + 2s) \sim 0.15$ $[C_2O_4^{2-}] = s$

$5.40 \times 10^{-12} = s \times 0.15^2$

$s = 2.4 \times 10^{-10}$ mol L^{-1}

Thus, it is approximately 4.6×10^5 times less soluble in silver nitrate than in water.

9 D

10 **a** $K = \dfrac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$

b According to Le Chatelier's principle, the system adjusts to minimise the change experienced by the system. Hence, it favours the reaction that absorbs the heat (i.e. it favours the endothermic reaction). Since reaction mixture becomes a deeper brown, the formation of NO_2 must be an endothermic reaction. The reaction, as written, is endothermic.

c According to Le Chatelier's principle, the system adjusts to minimise the change experienced by the system. When volume is halved, the concentration of the gases increases; hence, the system adjusts to decrease the concentration of gases present, and hence also the reverse reaction is favoured. The colour becomes a lighter brown since the $[NO_2]$ decreases.

d The equilibrium expression for the reaction (K_2) is:

$$K_2 = \frac{[N_2O_4]^{\frac{1}{2}}}{[NO_2]}$$

The equilibrium expression for the original reaction (K_1) was:

$$K_1 = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_2 = \sqrt{\frac{1}{K_1}} = \sqrt{\frac{1}{4.7\times10^{-3}}} = 14.6$$

11 **a** $\left[CH_3OH\right] = \dfrac{n_{\mathrm{CH_3OH}}}{V_{\text{reaction vessel}}} = \dfrac{0.255}{15.0} = 0.0170 \text{ mol L}^{-1}$

At equilibrium, $[\mathrm{CH_3OCH_3}] = [\mathrm{H_2O}] = x$

$$K = \frac{[\mathrm{CH_3OCH_3}]\times[\mathrm{H_2O}]}{[\mathrm{CH_3OH}]^2} = \frac{x^2}{0.0170^2}$$

$$x = \sqrt{5.74\times0.0170^2} = 0.0407 \text{ mol L}^{-1}$$

$[\mathrm{CH_3OCH_3}] = 0.0407 \text{ mol L}^{-1}$

$$n_{\mathrm{CH_3OCH_3}} = \left[\mathrm{CH_3OCH_3}\right]\times V_{\text{reaction vessel}} = 0.0407\times15.0 = 0.611 \text{mol}$$

b $n_{\text{methanol that decomposed}} = 2 \times n_{\text{dimethyl ether that was produced}} = 2 \times 0.611 = 1.222\,\text{mol}$

$n_{\text{methanol initially}} = n_{\text{methanol at equilibrium}} + n_{\text{methanol that decomposed}}$

$n_{\text{methanol initially}} = 0.255 + 1.222 = 1.477\ \text{mol}$

Student book answers

Module 6: Acid/base reactions

Chapter 5: Properties of acids and bases

Check your understanding 5.1

1 **a** Hydrofluoric acid

b Sulfuric acid

c Carbonic acid

2 **a** HBr

b HCN

c HNO_3

3 **a** Potassium hydroxide

b Calcium hydroxide

c Iron(III) oxide

4 **a** LiOH

b $Co(OH)_2$

c MgO

5 **a** Dihydroxido | oxido | sulfur

$(OH)_2$ | O | S

b Dihydroxido | dioxido | sulfur

$(OH)_2$ | O_2 | S which matches **iii** H_2SO_4

Check your understanding 5.2

1 Indicator colour change, feel, taste

2 The solution may be highly corrosive or caustic or could be contaminated with another chemical.

3 An acid is a substance that produces hydrogen ions in solution. A base is a substance that contains OH^- or O^{2-} ions in solution or by reaction with water.

4 When a hydrogen ion attaches to a water molecule it is called a hydronium ion. The hydronium ion is the more correct term, since all hydrogen ions in aqueous solutions would be present as hydronium ions.

5 An amphoteric oxide is one that can act as both an acid and a base (e.g. Al_2O_3, ZnO).

6 **a** $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

b $H_3PO_4(aq) + 3H_2O(l) \rightarrow 3H_3O^+(aq) + PO_4^{3-}(aq)$

c $Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

d $NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-(aq)$

7 Student responses will vary. Refer to results of Investigation 5.1.

Check your understanding 5.3

1 **a** Acid + base → salt + water

b Acid + carbonate → salt + water + carbon dioxide gas

c Acid + metal → salt + hydrogen gas

2 The reaction of an acid and a base to give salt and water

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

3 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

4 **a** Carbonate ion is CO_3^{2-} and the hydrogen carbonate ions is HCO_3^{2-}.

b The reactions produce the same products so are not different.

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

b $H_2SO_4(aq) + ZnO(aq) \rightarrow ZnSO_4(aq) + H_2O(l)$

c $2HF(aq) + Mg(OH)_2(s) \rightarrow MgF_2(aq) + 2H_2O(l)$

d $H_3PO_4(aq) + 3NH_3(aq) \rightarrow (NH_4)_3PO_4(aq)$

e $2CH_3COOH(aq) + Na_2O(aq) \rightarrow 2CH_3COONa(aq) + H_2O(l)$

f $CaO(aq) + 2NH_4NO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2NH_3(aq) + H_2O(l)$

6 **a** $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$

b $2CH_3COOH(aq) + Ca(OH)_2(aq) \rightarrow Ca(CH_3COO)_2(aq) + 2H_2O(l)$

c $6HNO_3(aq) + 2Fe(s) \rightarrow 2Fe(NO_3)_3(aq) + 3H_2(g)$

d $2HCl(aq) + Zn(s) \rightarrow Zn(Cl)_2(aq) + H_2(g)$

e $2HF(aq) + CaHCO_3(s) \rightarrow CaF_2(aq) + H_2O(l) + CO_2(g)$

f $2HNO_3(aq) + CuCO_3(s) \rightarrow Cu(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

Check your understanding 5.4

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

b Bond between H^+ and O in OH^- is being formed.

c Since strong acid and bases are fully ionised there is only bond formation so energy is being released. This reaction will always be exothermic.

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

2 a Change in enthalpy is the energy change per mole of specific reactant or product when the reaction occurs at constant pressure.

b The standard enthalpy of neutralisation is the enthalpy change when solutions of an acid and alkali react together under standard conditions (25°C and 100 kPa) to produce exactly 1 mole of water.

3 When using solid reactants, there is bond breaking that occurs as the substance dissolves to form ions, while in aqueous solutions, ions are already present.

4 a $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$

b $\Delta T = 0.70°C$

$q = mC\Delta T = 200 \times 4.18 \times 0.70 = 585.2\ J = 0.585\ kJ$

c $n_{HCl} = n_{KOH} = 0.100 \times 0.100 = 0.0100$ mol

$n_{H_2O} = 0.0100$ mol

$$\Delta H \text{ per mol } H_2O = \frac{0.585}{0.0100} = 58.5\ kJ\ mol^{-1}$$

d $\Delta T = 0.70°C$ The temperature rise would be by the same amount as the volume has been doubled and the number of moles has been doubled so these effects would cancel each other out.

5 a Examples could include using toothpaste, using antacids to relieve indigestion, baking, neutralising soils to improve plant growth, neutralising wastewater from mines and factories or chemical spills.

b Equations will depend on example given.

6 Adding acids such as gypsum and powdered sulfur will reduce alkalinity.

7 $H_2SO_4(aq) + 2NH_3(aq) \rightarrow (NH_4)_2SO_4(aq)$

8 a Blue flowers indicate acidic soil.

b Adding an alkaline substance, such as calcium hydroxide, to the soil will produce pink flowers.

9 a Naturally occurring water is almost neural or just slightly acidic so if significant environmental damage could occur if highly acid or alkaline water was allowed to enter natural systems.

- **b** Acidity can be neutralised using an alkali, such as calcium oxide, caustic soda or soda ash.

10 Sodium carbonate or sodium hydrogen carbonate is widely used to neutralise acid spills in preference to sodium hydroxide since they are much less caustic and more environmentally acceptable.

Check your understanding 5.5

1 Acids are sour-tasting substances. Bases counteract the effects of acids.

2 A operational definition is related to properties of a substance that can be observed in the laboratory, while a conceptual definition is related to what the substance is.

3 Lavoisier proposed that oxygen was the component in a compound responsible for the compound being an acid, while Davy proposed that hydrogen was the key component that gives an acid its properties.

4 **a** Arrhenius proposed that an acid was a substance that ionised in solution to produce hydrogen ions (H^+) and that a base was a substance that in solution produced hydroxide ions (OH^-).

b Ammonia gas reacts with an acid to produce a salt, and neither OH^- ions nor water are present.

c The nature and role of the solvent was not considered in the Arrhenius model. The model does not work when an organic solvent is used since many acids and bases do not dissociate. According to this model, all salts produced by reactions of an acid and base should be neutral. In reality this is not the case. Not all bases are soluble, thus OH^- ions cannot be produced and when bases are dissolved in non-aqueous solvents no hydroxide ion is present in the resulting solution. This means an OH^- ion is not necessary for a substance to be identified as a base.

5 **a** The theory proposed that ammonia accepts a proton to form an ammonium ion (NH_4^+) and is acting as a base. HCl is acting as an acid since it donates a proton to form a chloride ion (Cl^-).

b An acid is a substance that donates one or more protons or hydrogen ions (H^+) and a base is defined as a substance that accepts one or more protons.

c For example: $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

HCl is an acid since it donates a proton to the water molecule, which accepts it, so H_2O acts as a base.

6 $H_2O(l) + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

One water molecule donates a proton (acid), while another molecule accepts a proton (base).

7 NH_4Cl is acting as the acid because it donates a proton to form NH_3. OH^- is acting as the base because it accepts a proton to form H_2O.

8 The Brønsted–Lowry model requires the presence of a solvent that has a hydrogen attached to an oxygen or nitrogen (e.g. water, ammonia, acetic acid). However, it does not explain the acid–base behaviour of substances in non-aqueous solvents where a proton is not involved. Another limitation is that the Brønsted–Lowry model cannot explain reactions between acidic oxides such as CO_2, SO_2, SO_3 and basic oxides like CaO, BaO, MgO, which take place even where there is no solvent. There are also substances such as BF_3 and $AlCl_3$, which are known to act as acids but do not have a hydrogen present, so they cannot donate a proton.

9 A Lewis acid is any atom, ion or molecule that can accept electrons, while a Lewis base is any atom, ion or molecule capable of donating electrons. The definition does not require a solvent nor a H^+.

10 a While all Brønsted–Lowry acids and bases are Lewis acids and bases, the reverse is not true.

b BF_3 reacts with ammonia. The boron in the BF_3 molecule is a Lewis acid because it accepts a non-bonding electron pair from the nitrogen in NH_3, which is a Lewis base, forming the compound BF_3NH_3. Here it is not a proton being donated or accepted, so according to the Brønsted–Lowry definition this would not be an acid–base reaction.

Chapter review questions

1 An agreed chemical nomenclature system allows a common understanding and language to be used, providing a key communication tool.

2 a Phosphoric acid (acid)

b Nitric acid (acid)

c Copper(II) oxide (base)

d Ammonia (base)

3 a CH_3COOH

b H_2SO_3

c K_2O

d NH_4OH

4 Alkalis are only those bases that are soluble, so alkalis are a subset of all bases.

5 a $H_2SO_4(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$

b $HF(aq) + H_2O(l) \rightarrow H_3O^+(aq) + F^-(aq)$

c $NaO(s) + H_2O(l) \rightarrow Na^+(aq) + 2OH^-(aq)$

d $KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$

6 a i According to the table, solution A is highly acidic, while solution B could be anywhere in the range from highly acidic to neutral. It is probable that solution A is more acidic.

ii Use some blueberry indicator on solution B. If it does not turn red, then the assumption is correct.

b w and y could be neutral but further testing would be required to confirm if they were.

7 **a** $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$

b $3HCl(aq) + Al(OH)_3(s) \rightarrow AlCl_3(aq) + 3H_2O(l)$

c $H_2SO_4(aq) + Mg(s) \rightarrow MgSO_4(aq) + H_2(g)$

d $2CH_3COOH(aq) + MgCO_3(s) \rightarrow (CH_3COO)_2Mg(aq) + CO_2(g) + H_2O(l)$

e $H_3PO_4(aq) + 3NaHCO_3(s) \rightarrow Na_3PO_4(aq) + 3CO_2(g) + 3H_2O(l)$

8 Add an acid such as HCl. If bubbles of gas are produced, then the solution is calcium carbonate.

9 $HNO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

$\Delta T = 1.77°C$ $V = m = 75$ mL

$q = mC\Delta T = 75 \times 4.18 \times 1.77 = 554.9$ J $= 0.555$ kJ

$n_{HNO_3} = 0.206 \times 0.050 = 0.0103$ mol

$n_{NaOH} = 0.412 \times 0.025 = 0.0103$ mol

$n_{H_2O} = 0.0103$ mol

$$\Delta H \text{ per mol } H_2O = \frac{0.555}{0.0103} = 53.9 \text{ kJ mol}^{-1}$$

10 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$\Delta T = 14°C$ $V = m = 1000$ mL

$q = mC\Delta T = 1000 \times 4.18 \times 14 = 58520$ J $= 58.52$ kJ

$n_{HCl} = n_{NaOH} = 2 \times 0.500 = 1.0$ mol

$n_{H_2O} = 1.0$ mol

$$\Delta H \text{ per mol } H_2O = \frac{58.5}{1.0} = 58.5 \text{ kJ mol}^{-1}$$

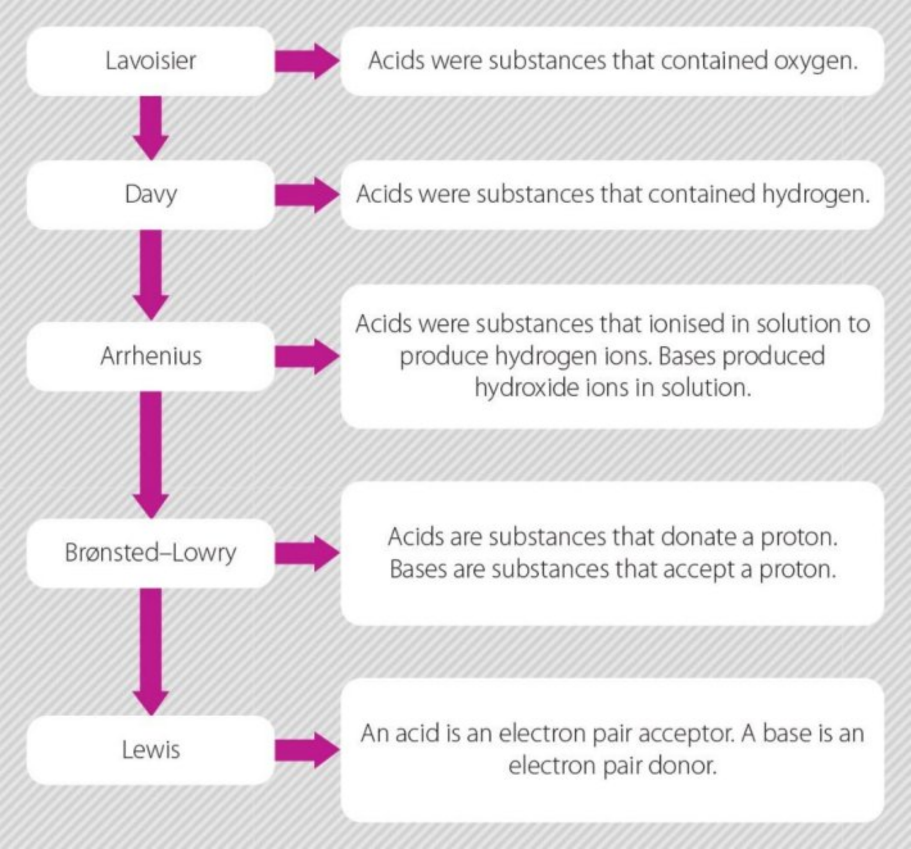
11 Many of the foods we eat and drink are acidic and acid is produced when the bacteria in the mouth consume sugar from the food eaten. This acid reacts with tooth enamel causing demineralisation. Toothpaste is alkaline and used to neutralise the acids in the mouth as well as removing food particles that produce acids when they decay, thus helping to prevent tooth decay.

12 Students responses will vary.

13 The statement is accurate. Indicators change colour as the acidity and alkalinity of a solution changes. When an indicator is added to an acid it turns one colour, then as a base is added to the acid solution the indicator will begin to change to the colour of the alkaline solution. If more acid is added to this solution, it will again begin to change to the acid colour. Investigation 5.1 demonstrated this using a natural indicator.

14 The next reaction for neutralisation is $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$. Strong acids and bases completely dissociate in aqueous solution, so the net reaction applies to all these reactions. Therefore. the enthalpy change will be independent of the actual acid and base used.

15



Acids were substances that contained oxygen.

Acids were substances that contained hydrogen.

Acids were substances that ionised in solution to produce hydrogen ions. Bases produced hydroxide ions in solution.

Acids are substances that donate a proton. Bases are substances that accept a proton.

An acid is an electron pair acceptor. A base is an electron pair donor.

16 Arrhenius proposed that an acid was a substance that ionised in solution to produce hydrogen ions (H^+) and that a base was a substance that in solution produced hydroxide ions (OH^-). Brønsted–Lowry proposed that an acid is a substance that donates one or more protons or hydrogen ions (H^+) and that a base is a substance that accepts one or more protons. While the definition of an acid did not change significantly, the definition of a base was quite different. This allowed substances that did not produce OH^- ions but accepted protons to be defined as bases thus overcoming the difficulty with ammonia as a base using the Arrhenius definition.

17 In the reaction between a carbonate and water, the carbonate ion accepts a proton so according to Brønsted–Lowry, the carbonate ion is a base.

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

18 Acids and bases are most commonly encountered in aqueous solutions and also usually involve a transfer of the hydrogen ion, so the limitations of the Brønsted–Lowry theory do not affect typical situations and application of acids and bases; therefore, it is still commonly used.

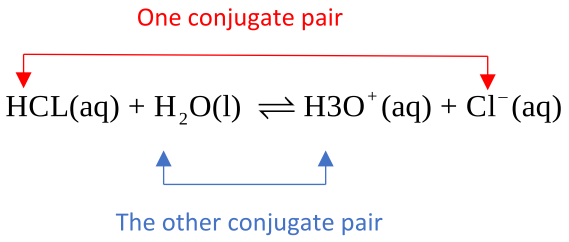
Module 6: Acid/base reactions

Chapter 6: Using Brønsted–Lowry theory

Check your understanding 6.1

1 Members of a conjugate acid–base pair differ by the presence or absence of a H^+.

For example:



HCl/Cl^- is a conjugate pair and H_2O/H_3O^+ is a conjugate pair.

2 A conjugate acid is produced when a base accepts a proton; for example, $NH_3 \rightarrow NH_4^+$ (conjugate acid). While a conjugate base is produced when an acid donates a proton; for example, $HCl \rightarrow Cl^-$ (conjugate base).

3 An amphiprotic substance is one that can gain or lose a H^+ so it can act as both an acid and a base.

4 **a** HNO_3/NO_3^-; H_2O/H_3O^+

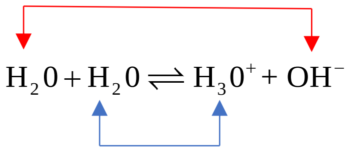
b $NH_4^+/NH_3/H_2O/H_3O^+$

c HSO_4^-/SO_4^{2-}; O_2^-/OH^-

d $H_2PO_4^-/HPO_4^{2-}$; CO_3^{2-}/HCO_3^-

e $HC_2H_3O_2/C_2H_3O_2^-/HS^-/H_2S$

5



6 **a** H_2CO_3

b H_2O

c $H_2PO_4^-$

7 a HCO_3^-

b OCN^-

c PO_4^{3-}

8 NH_4Cl is acting as the acid because it donates a proton to form NH_3. OH^- is acting as the base because it accepts a proton to form the conjugate acid H_2O.

9 Earlier definitions limited bases to substances that would form oxide (O_2^-) ions or hydroxide (OH^-) ions in solution. HCO_3^- or CO_3^{2-} do not produce these ions in water. The Brønsted–Lowry definition of a base accepting a proton can explain the behaviour because the carbonate ions can accept a proton to form $H_2CO_3^-$ or HCO_3^- respectively.

Worked example 6.1

1 $pH = \log_{10}[H^+]$

$pH = \log_{10}(1.0 \times 10^{-3})$

$pH = 3$

2 $pH = \log_{10}[H^+]$

$pH = \log_{10}(1.2 \times 10^{-5})$

$pH = 4.92$

3 $[H^+] = 10^{-pH}$

$[H^+] = 10^{-6} = 0.000001 \text{ mol L}^{-1}$

4 $[H^+] = 10^{-pH}$

$[H^+] = 10^{-11.7} = 2.00 \times 10^{-12} \text{ mol L}^{-1}$

Check your understanding 6.2

1 pH is a scale based on concentration of hydrogen ions. $pH = -\log_{10}[H^+]$

2 The pH scale provides a measure acidity or alkalinity of a solution.

3 a Hydrogen ion is H^+ and is a proton. The hydrogen ion cannot exist as an entity in aqueous solution so it forms a coordinate covalent bond with a water molecule to produce the hydronium ion H_3O^+.

b In an aqueous solution $[H^+] = [H_3O^+]$, while $pH = -\log_{10}[H^+] = -\log_{10}[H_3O^+]$.

4 Universal indicator produces a range of colours in solutions depending on whether the solution is acidic or basic.

5 a pH measures the concentration of hydrogen ions in the solution. The lower the pH, the more acidic the solution is. The higher the pH, the more basic the solution is. As the H^+ ion increases in concentration the OH^- ion decreases in concentration.

b When $pH = 7$ then $[H^+] = [OH^-]$

6 **a** pH 1–3

b pH 7

c pH 8–10

d pH 11–13

7 pH can be measured using an indicator and a pH probe or meter.

Using an indicator is simple, relatively quick and easy and can be used for solutions and solids; however, it does not give a high degree of accuracy. Using a probe requires a solution; it does provide a high degree of accuracy, provided it has been calibrated correctly.

8 **a** $\text{pH} = \log_{10}[\text{H}^+]$

$\text{pH} = \log_{10}(1.0 \times 10^{-2})$

$\text{pH} = 2$

b $\text{pH} = \log_{10}[\text{H}^+]$

$\text{pH} = \log_{10}(1.75 \times 10^{-2})$

$\text{pH} = 1.76$

9 **a** $[\text{H}^+] = 10^{-\text{pH}}$

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

b $[\text{H}^+] = 10^{-\text{pH}}$

$[\text{H}^+] = 10^{-10.4} = 3.98 \times 10^{-11} \text{ mol L}^{-1}$

Check your understanding 6.3

1 Nitric acid – $HNO_3(aq)$

Sulfuric acid – $H_2SO_4(aq)$

Sodium hydroxide – $NaOH(aq)$

2 **a** $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

b $H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

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

d $H_3PO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + H_2PO_4^-(aq)$

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$

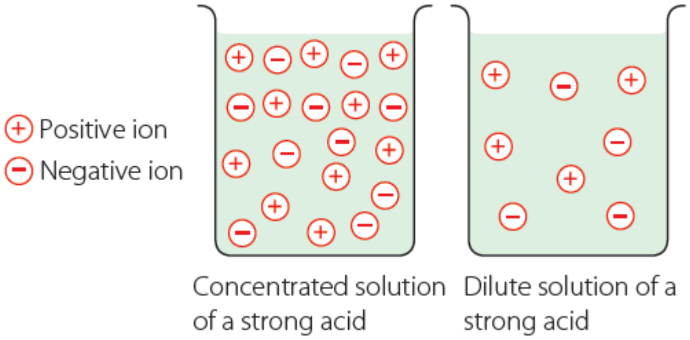
3 **a** $Ba(OH)_2(aq) \rightarrow Ba_2+(aq) + 2OH^-(aq)$

b $CaO(aq) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

c $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

4 **a** Strength refers to the degree to which an acid or base ionised in water. A strong acid or base ionises completely in water, while only some of the particles of a weak acid or base ionise/dissociate. Concentration is a measure of the number of particles that are present in a given amount of solution. A concentrated solution has many more particles than a dilute solution.

b



5 **a** The pH of a strong acid will be lower than the pH of a weak acid because there are more hydrogen ions.

b The pH of a strong base will be larger than the pH of a weak base of the same concentration.

6 **a** Diprotic acids can donate two protons when they ionise in water.

b The pH of a diprotic acid is smaller because there are more hydrogen ions present in the solution.

Worked example 6.2

1 KOH is a strong base so $[OH^-] = [KOH] = 0.04 \text{ mol L}^{-1}$

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

$K_w = [H^+][0.04] = 1 \times 10^{-14}$

Hence, $[H^+] = \dfrac{1\times10^{-14}}{0.04} = 2.5 \times 10^{-13}$

$pH = -\log[H^+] = 12.6$

2 $[H^+] = 10^{-pH} = 10^{-9.5} = 3.16 \times 10^{-10}$

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

$K_w = [3.16 \times 10^{-10}][OH^-] = 1 \times 10^{-14}$

Hence, $[OH^-] = \dfrac{1\times10^{-14}}{3.10\times10^{-10}} = 3.16 \times 10^{-5}$

$[OH^-] = [NaOH] = 3.16 \times 10^{-5}$ mol L^{-1}

3 $[OH^-] = 4.7 \times 10^{-8}$ mol L^{-1}

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

$K_w = [H^+][4.7 \times 10^{-8}] = 1 \times 10^{-14}$

Hence, $[H^+] = \dfrac{1\times10^{-14}}{4.7 \times 10^{-8}} = 2.1 \times 10^{-7}$ mol L^{-1}

$[HCl] = 2.1 \times 10^{-7}$ mol L^{-1}

Check your understanding 6.4

1 $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

2 **a** $K_w = [H^+][OH^-] = 1 \times 10^{-14}$

b $H_2O(l)$ is not included in the in the expression since its concentration is very large and does not change significantly in the reaction.

3 **a** $[H_3O^+] = 10^{-5}$ mol L^{-1}, $[OH^-] = 10^{-9}$ mol L^{-1}

b $[H_3O^+] = 10^{-13} = 0.1$ mol L^{-1}, $[OH^-] = 10^{-1}$ mol L^{-1}

c $[H_3O^+] = 10^{-3}$ mol L^{-1}, $[OH^-] = 10^{-11}$ mol L^{-1}

4 **a** $[HNO_3] = [H^+] = 0.01$ mol L^{-1}

pH = $-\log[H^+] = 2$

b $[NaOH] = [OH^-] = 0.1$ mol L^{-1}

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

$K_w = [H^+][0.1] = 1 \times 10^{-14}$

Hence, $[H^+] = \dfrac{1\times10^{-14}}{0.1} = 10^{-13}$

pH = $-\log[H^+] = 13$

c pH = 0

d pH = 0.64

e pH = 12

5 **a** pH = 11.5, so $[H^+] = 10^{-11.5}$

$$[OH^-] = \frac{10^{-14}}{10^{-11.5}} = 10^{-2.5} = 0.0032 \text{ mol L}^{-1}$$

b pH = 3; $[H^+] = 10^{-3}$; [HCl] = 0.001 mol L^{-1}

c pH = 10; $[H^+] = 10^{-10}$; $[OH^-] = \frac{10^{-14}}{10^{-10}} = 10^{-4} = 0.0001 \text{ mol L}^{-1}$

$$[Ca(OH)_2] = \frac{1}{2} \times 0.0001 = 0.00005 \text{ mol L}^{-1}$$

Worked example 6.3

1 $[OH^-] = 0.001 \text{ mol L}^{-1}$; $pOH = -\log[OH^-] = 3$

2 $[OH^-] = 7.2 \times 10^{-3} \text{ mol L}^{-1}$; $pOH = -\log[OH^-] = 2.1$

3 pOH = 8; $[OH^-] = 10^{-pOH} = 10^{-8} \text{ mol L}^{-1}$

4 pOH = 1.17; $[OH^-] = 10^{-pOH} = 10^{-1.17} = 6.76 \times 10^{-2} \text{ mol L}^{-1}$

5 pOH = 11.2; $[OH^-] = 10^{-pOH} = 10^{-11.2} = 6.31 \times 10^{-12} \text{ mol L}^{-1}$

$[OH^-] = [NaOH] = 6.31 \times 10^{-12} \text{ mol L}^{-1}$

Worked example 6.4

1 $[KOH] = [OH^-] = 0.004 \text{ mol L}^{-1}$

$pOH = -\log[OH^-] = 2.4$; pH + pOH = 14

pH = 14 − 2.4 = 11.6

2 $[HCl] = [H^+] = 0.023 \text{ mol L}^{-1}$; $pH = -\log[H^+] = 1.6$

pH + pOH = 14

pOH = 14 − 1.6 = 12.4

3 pH = 10.5; pOH = 14 − 10.5 = 3.5

$[OH^-] = 10 - pOH = 10 - 3.5 = 3.16 \times 10^{-4} \text{ mol L}^{-1}$

$$[Ba(OH)_2] = \frac{1}{2} \times 3.16 \times 10^{-4} = 1.58 \times 10^{-4} \text{ mol L}^{-1}$$

Worked example 6.5

1 pH = 1; solution is diluted by a factor of 1000, which means a change in pH by 3 units so concentration of H_3O^+ will decrease and pH will increase.

pH = 4

2 pOH = 11.5; solution is diluted by a factor of 100, which means a change in pOH by 2 units, concentration of OH^- will decrease and pOH will increase.

pOH = 13.5

3 pOH = 10.4; pH + pOH = 14

$pH = 14 - 10.4 = 3.6$; $[H^+] = 10^{-3.6} = 2.51 \times 10^{-4}$ mol L^{-1}

$c_1 = 2.51 \times 10^{-4}$ mol L^{-1}, $V_1 = 250$ mL, $c_2 = ?_,\ V_2 = 20$ mL

$2.51 \times 10^{-4} \times 250 = c_2 \times 20$

$$c_2 = \frac{(2.51 \times 10^{-4} \times 250)}{20} = 3.14 \times 10^{-3} \text{ mol L}^{-1}$$

$pH = -\log(3.14 \times 10^{-3}) = 2.5$

Check your understanding 6.5

1 **a** $pOH = -\log[OH^-]$

b pH + pOH = 14

2 **a** $[OH^-] = 9.4 \times 10^{-2}$ mol L^{-1}

$pOH = -\log[OH^-] = 1.03$

b $pOH = 3.21$; $[OH^-] = 10^{-pOH} = 10^{-3.21} = 6.17 \times 10^{-4}$ mol L^{-1}

3 **a** $[OH^-] = 10^0$ mol L^{-1} = 1 mol L^{-1}; $[H_3O^+] = 0^{-14}$

b $[OH^-] = 10-11$ mol L^{-1} ; $[H_3O^+] = 10^{-3}$

c $[H_3O^+] = 10^{-8}$ mol L^{-1}; $[OH^-] = 10^{-6}$ mol L^{-1}

4 **a** $[HCl] = [H^+] = 1.27$ mol L^{-1}; $pH = -\log[H^+] = -0.10$

b $[NaOH] = [OH^-] = 0.052$ mol L^{-1}

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

$K_w = [H^+][0.052] = 1 \times 10^{-14}$

$$\text{Hence, } [H^+] = \frac{1 \times 10^{-14}}{0.052} = 1.9 \times 10^{-13}$$

$pH = -\log[H^+] = 12.7$

5 **a** $[HNO_3] = [H^+] = 0.0175\ \text{mol L}^{-1}$; $\text{pH} = -\log[H^+] = 1.76$

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

$\text{pOH} = 14 - 1.76 = 12.2$

b $[Ba(OH)_2] = 0.033\ \text{mol L}^{-1}$; $[OH] = 2 \times 0.033 = 0.066\ \text{mol L}^{-1}$

$\text{pOH} = -\log[OH^-] = 1.2$

6 **a** $\text{pOH} = 11$; $\text{pH} = 14 - 11 = 3$

$[H^+] = 10^{-3}\ \text{mol L}^{-1} = [HCl] = 0.001\ \text{mol L}^{-1}$

b $\text{pH} = 10$; $\text{pOH} = 14 - 10 = 4$

$$[OH^-] = 10^{-4}\ \text{mol L}^{-1};\ [Ba(OH)_2] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5}\ \text{mol L}^{-1}$$

7 A concentrated solution has more hydrogen ions than a dilute solution, so a concentrated solution will have a lower pH than a dilute solution of the same substance.

8 **a** pH = 8; dilution factor is 100, so pH is increased by 2 units. pH = 10

b pH = 5; initial volume is 100 mL, final volume is 1000 mL so dilution factor is 10. pH = 6

c $[KOH] = [OH^-] = 5.0 \times 10^{-4}\ \text{mol L}^{-1}$

$c_1 = 5.0 \times 10^{-4}\ \text{mol L}^{-1}$, $V_1 = 250$ mL, $c_2 = ?$, $V_2 = 650$ mL

$5.0 \times 10^{-4} \times 250 = c_2 \times 650$

$$c_2 = \frac{(5.0 \times 10^{-4} \times 250)}{650} = 1.9 \times 10^{-4}\ \text{mol L}^{-1}$$

$\text{pH} = -\log(1.9 \times 10^{-4}) = 3.7$

Worked example 6.6

1 $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$[H_3O^+] = 10^{-pH} = 10^{-2.22}$

Therefore, $[H_3O^+] = 6.03 \times 10^{-3}$ mol $L^{-1} = [NO_2^-]$

$$K_a = \frac{[H_3O^+]^2}{[HNO_2]} = \frac{(6.03 \times 10^{-3})^2}{0.050}$$

$K_a = 7.26 \times 10^{-4}$

2 $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+ + CH_3COO^-$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= 1.7 \times 10^{-5}$$

$$= \frac{[H_3O^+]^2}{0.2}$$

$[H_3O^+]^2 = 1.7 \times 10^{-5} \times 0.2 = 0.0000034$

$[H_3O^+] = \sqrt{0.0000034} = 0.00184$

$pH = -\log[H_3O^+] = 2.73$

Worked example 6.7

1 pH = 2.87; $[H_3O^+] = 10^{-2.87} = 0.00135$ mol L^{-1}

$[HCOO^-] = 0.00135$ mol L^{-1}

$$\% \text{ ionisation} = \frac{[A^-]}{[HA]} \times \frac{100}{1} = \frac{0.00135}{0.1} \times 100 = 1.35\%$$

2 pH = 2.08; $[H_3O^+] = 10^{-2.08} = 0.00832$ mol L^{-1}

$[NO_2^-] = 0.00832$ mol L^{-1}

$$\% \text{ ionisation} = \frac{[NO_2]}{[HNO_2]} = \left(\frac{0.00832}{1.37}\right) \times 100 = 0.607\%$$

Check your understanding 6.6

1 **a** $K_a = \dfrac{\left[H_3O^+\right][OBr^-]}{\left[HOBr\right]}$

b $K_a = \dfrac{\left[H_3O^+\right][CN^-]}{\left[HCN\right]}$

c $K_a = \dfrac{\left[H_3O^+\right]\left[NH_3\right]}{[NH_4^+]}$

2 Water is not included because its concentration is relatively constant, so it does not impact on the values.

3 **a** $pK_a = -\log_{10}K_a$

b The stronger the acid, the larger the value of K_a.

c The stronger the acid, the smaller the value of pK_a .

d pH is a measure hydrogen ion concentration, while K_a gives a measure of the strength of an acid (i.e. the degree of dissociation, as does pK_a). For acids of the same concentration, the stronger the acid, the smaller the pH, larger the K_a and the smaller the value of pK_a.

4 $K_{a1} = \dfrac{[\text{hydrogen malate}]\ H_3O^+}{[\text{malic acid}]}$

$K_{a2} = \dfrac{[\text{malate}]\ H_3O^+}{[\text{hydrogen malate}]}$

The K_a for the first dissociation equilibrium expression would be larger. K_a is the ratio of the concentration of the products divided by the concentration of the reactants. Malic acid is a weak acid, so the majority of the acid would not ionise in water. Since the second expression relies upon products of the first expression, the second K_a must be smaller again.

5

Solution	K_a	pK_a
W	1.7×10^{-5}	4.8
X		3.8
Y		7.4
Z	6.3×10^{-5}	4.2

The smaller the pK_a ,the stronger the acid.

(Strongest) X > Z > W > Y (weakest)

6 pH calculations – concentration of water does not change; ions present due to self-ionisation of water not significant.

K_a calculations – at equilibrium, [HA] is the same as the initial concentration; the weak acid only ionises to a small degree in water.

$[H_3O^+]$ produced by the self-ionisation of water is negligible and has no effect on the calculations.

7 **a** $K_a = 1.05 \times 10^{-10} = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$

$= \frac{[H_3O^+]^2}{3.5\times10^{-3}M}$

$[H_3O^+] = \sqrt{(1.05 \times 10^{-10})(3.5 \times 10^{-3})} = 6.06 \times 10^{-7}$

pH = 6.22

b $[C_6H_5O^-] = 6.06 \times 10^{-7}$ $[C_6H_5OH] = 3.5 \times 10^{-3}$

% ionisation = $\left(\frac{6.06 \times 10^{-7}}{3.5 \times 10^{-3}}\right) \times 100 = 0.0173\%$

8 **a** $CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

b $K_a = 1.74 \times 10^{-5} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

$[H_3O^+]^2 = 1.74 \times 10^{-5} \times [CH_3COOH]$

$[H_3O^+] = \sqrt{(1.74 \times 10^{-5} \times 0.4)} = 0.002638$

pH = 2.58

9 **a** **i** $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

$K_a = \frac{[H_3O^+]\left[CN^-\right]}{\left[HCN\right]}$

pH = 5.15; $[H_3O^+] = 10^{-5.15} = 7.08 \times 10^{-6} = [CN^-]$

[HCN] = 0.10 mol L^{-1}

$K_a = \frac{\left(7.08 \times 10^{-6}\right)^2}{0.10} = 5.01 \times 10^{-10}$

$pK_a = -\log K_a = 9.3$

ii $HS(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^-(aq)$

$$K_a = \frac{[H_3O^+][S^-]}{[HS]}$$

pH = 4.41; $[H_3O^+] = 10^{-4.41} = 3.89 \times 10^{-5} = [S^-]$

$[HS] = 0.017$ mol L^{-1}

$$K_a = \frac{(3.89 \times 10^{-5})^2}{0.017} = 8.9 \times 10^{-8}$$

$pK_a = -\log K_a = 7.1$

b HS is the strongest acid.

10 $pK_a = 4.9$; $K_a = 10^{-4.9} = 1.3 \times 10^{-5}$

$[C_2H_5COOH] = 0.10$ mol L^{-1}

$$K_a = \frac{[C_2H_5COO^-][H_3O^+]}{[C_2H_5COOH]}$$

$$1.3 \times 10^{-5} = \frac{[H_3O^+]^2}{0.10}$$

$[H_3O^+] = \sqrt{(1.3 \times 10^{-5} \times 0.10)} = 1.1 \times 10^{-3}$ mol L^{-1}

Worked example 6.8

1 $HC_6H_6O_6^-(aq) + H_2O(l) \rightleftharpoons H_2C_6H_6O_6(aq) + OH^-(aq)$

$$K_b = \frac{[H_2C_6H_6O_6][OH^-]}{[HC_6H_6O_6^-]}$$

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

$[OH^-] = 10^{-5.15}$

Therefore, $[OH^-] = 7.08 \times 10^{-6}$ mol L^{-1}

$[HC_6H_6O_6^-] = 0.38$ mol L^{-1}

$$K_b = \frac{[OH^-]^2}{[HC_6H_6O_6^-]} \qquad ([OH^-] = [H_2C_6H_6O_6])$$

$$= \frac{(7.08 \times 10^{-6})^2}{0.38}$$

$= 1.32 \times 10^{-10}$

2 $PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$

$$K_b = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]} = 5.9 \times 10^{-3}$$

$$= \frac{[OH^-]^2}{[PO_4^{3-}]}, \text{ as } [OH^-] = [HPO_4^{2-}]$$

$[OH^-]^2 = 5.9 \times 10^{-3} \times [PO_4^{3-}]$

$[OH^-] = \sqrt{}(5.9 \times 10^{-3} \times 0.32) = 0.014 \text{ mol L}^{-1}$

$pOH = -\log[OH^-]$

$= -\log(0.014) = 1.9$

$pH + pOH = 14$

$pH = 14 - pOH = 14 - 1.9 = 12.1$

Check your understanding 6.7

1 K_b is the equilibrium constant for the dissociation of a weak base.

2 a $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

b $$K_b = \frac{[H_2S][OH^-]}{[HS^-]}$$

3 a The stronger a base, the larger the value of K_b.

b The larger the value of K_b, the stronger the base so the smaller the value of pOH.

4 (Weakest) P > R > Q > S (strongest)

5 Assumptions: At equilibrium, [B] is the same as the initial concentration; the weak base only ionises to a small degree in water.

$[OH^-]$ produced by the self-ionisation of water is negligible and has no effect on the calculations.

6 $B^-(aq) + H_2O(l) \rightleftharpoons HB(aq) + OH^-(aq)$

$$K_b = \frac{[HB][OH^-]}{[B^-]}$$

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

$[OH^-] = 10^{-5.61}$

Therefore, $[OH^-] = 2.45 \times 10^{-6}$ mol L^{-1}

$[B^-] = 0.0534$ mol L^{-1}

$$K_b = \frac{[OH^-]^2}{[B^-]} \qquad ([OH^-] = [HB])$$

$$= \frac{(2.45\times10^{-6})^2}{0.0534}$$

$= 1.13 \times 10^{-10}$

7 $Mo(aq) + H_2O(l) \rightleftharpoons HMo^+(aq) + OH^-(aq)$

$$K_b = \frac{\left[HMo^+\right][OH^-]}{\left[Mo\right]} = 1.62 \times 10^{-6}$$

$$= \frac{[OH^-]^2}{\left[Mo\right]}, \text{ since } [OH^-] = [HMo^+]$$

$[OH^-]^2 = 1.62 \times 10^{-6} \times [Mo]$

$[OH^-] = \sqrt{}(1.62 \times 10^{-6} \times 0.300) = 6.97 \times 10^{-4}$ mol L^{-1}

$pOH = -\log[OH^-]$

$= -\log(6.97 \times 10^{-4}) = 3.16$

$pH + pOH = 14$

$pH = 14 - pOH = 14 - 3.16 = 10.8$

Worked example 6.9

1 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$c(NaOH) = 0.1\ mol\ L^{-1}$ $V = 50\ mL = 0.050\ L$ $n = ?$

$n(NaOH) = 0.10 \times 0.050 = 0.005\ mol$ $n(OH^-) = 0.005\ mol$

$c(HCl) = 0.1\ mol\ L^{-1}$ $V = 100\ mL = 0.100\ L$ $n = ?$

$n(HCl) = 0.1 \times 0.100 = 0.0100\ mol$ $n(H_3O^+) = 0.010\ mol$

H_3O^+ is in excess by $0.010 - 0.005 = 0.005 = 5.0 \times 10^{-3}$ mol

$V = 50\ mL + 100\ mL = 0.150\ L$

$$[H_3O^+] = \frac{5.0 \times 10^{-3}}{0.150} = 0.033\ mol\ L^{-1}$$

$pH = -\log 0.033 = 1.5$

2 $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$

$c(HNO_3) = 0.2\ mol\ L^{-1}$ $V = 500\ mL = 0.500\ L$

$n(HNO_3) = c \times V = 0.2 \times 0.500 = 0.1\ mol$

$n(Ba(OH)_2) = \frac{1}{2} \times 0.1 = 0.05\ mol$

$m(Ba(OH)_2) = n \times M = 0.05 \times 171 = 8.6\ g$

3 $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

$c(CH_3COOH) = 0.277\ mol\ L^{-1}$ $V = 100\ mL = 0.100\ L$ $n = ?$

$n(CH_3COOH) = 0.277 \times 0.100 = 0.0277\ mol$

$n(NaOH) = 0.0277\ mol$ $c(NaOH) = 0.1\ mol\ L^{-1}$

$$V(NaOH) = \frac{n}{c} = \frac{0.0277}{0.1} = 0.277\ L = 277\ mL$$

Check your understanding 6.8

1 A solution is neutral when $[H^+] = [OH^-]$ and pH = 7.

2 **a** $2HCl(aq) + Ca(OH)_2(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$

$c(Ca(OH)_2) = 0.1 \text{ mol L}^{-1}$ $\quad V = 75 \text{ mL} = 0.075 \text{ L}$ $\quad n = ?$

$n(Ca(OH)_2) = 0.10 \times 0.075 = 0.0075 \text{ mol}$ $\quad n(OH^-) = 2 \times 0.0075 = 0.015 \text{ mol}$

$c(HCl) = 0.2 \text{ mol L}^{-1}$ $\quad V = 50 \text{ mL} = 0.050 \text{ L}$ $\quad n = ?$

$n(HCl) = 0.2 \times 0.050 = 0.0100 \text{ mol}$ $\quad n(H_3O^+) = 0.010 \text{ mol}$

OH^- is in excess by $0.015 - 0.010 = 0.005 = 5.0 \times 10^{-3}$ mol

$V = 75 \text{ mL} + 50 \text{ mL} = 0.125 \text{ L}$

$$[OH^-] = \frac{5.0\times10^{-3}}{0.125} = 0.04 \text{ mol L}^{-1}$$

$pOH = -\log 0.04 = 1.4$

$pH = 14 - 1.4 = 12.6$

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

$c(KOH) = 0.015 \text{ mol L}^{-1}$ $\quad V = 25 \text{ mL} = 0.025 \text{ L}$ $\quad n = ?$

$n(KOH) = 0.015 \times 0.025 = 3.73 \times 10^{-4} \text{ mol}$ $\quad n(OH^-) = 3.73 \times 10^{-4} \text{ mol}$

$c(HNO_3) = 0.012 \text{ mol L}^{-1}$ $\quad V = 50 \text{ mL} = 0.050 \text{ L}$ $\quad n = ?$

$n(HNO_3) = 0.012 \times 0.050 = 6 \times 10^{-4} \text{ mol}$ $\quad n(H_3O^+) = 6 \times 10^{-4} \text{ mol}$

H_3O^+ is in excess by $6 \times 10^{-4} - 3.73 \times 10^{-4} = 2.27 \times 10^{-4}$ mol

$V = 25 \text{ mL} + 50 \text{ mL} = 0.075 \text{ L}$

$$[H_3O^+] = \frac{2.27\times10^{-4}}{0.0750} = 3.0 \times 10^{-3} \text{ mol L}^{-1}$$

$pH = -\log 3.0 \times 10^{-3} = 2.5$

c $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

$n(NaOH) = n(OH^-) = 3.5 \times 10^{-3} \text{ mol}$

$n(H_2SO_4) = 2.5 \times 10^{-4} \text{ mol}$

$n(H_3O^+) = 2 \times 2.5 \times 10^{-4} = 5 \times 10^{-4}$ mol (H_2SO_4 can donate 2 protons)

OH^- is in excess by $3.5 \times 10^{-3} - 5 \times 10^{-4} = 3.0 \times 10^{-3}$ mol

$pOH = -\log 3.0 \times 10^{-3} = 2.5$

$pH = 14 - 2.5 = 11.5$

3 Amphiprotic means a substance can both donate and accept a proton (H^+), so it can act as both and acid and a base. Salts produced from the neutralisation reaction between a strong acid and strong base do not hydrolyse and the pH of the solution will be neutral.

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

When the salt (NaCl) produced in this reaction is dissolved in water, it produces $Na^+(aq)$ and $Cl^-(aq)$: $NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

Na^+ does not react with water, so it will not affect the pH of the solution. HCl is a strong acid that produces Cl^- as its conjugate base. It is a very weak base, so it will not react to remove a proton from water. The resulting solution will be neutral ($pH = 7$).

When a strong acid and weak base react, the resulting solution will have a $pH < 7$. For example: $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

The ammonium chloride salt produced contains the ammonium cation and chloride anion.

$NH_4Cl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$

The chloride ion, which had come from the strong acid, does not affect the pH of the solution. However, the ammonium cation is the conjugate acid of a weak base. It will react with water (hydrolyse) to produce a hydronium ion according to the reaction:

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

The resulting solution will be acidic ($pH<7$).

4 **a/b**

i $H_2CO_3(aq) + 2KOH(aq) \rightarrow K_2CO_3(aq) + 2H_2O(l)$

Reaction is between a weak acid and a strong base, so $pH>7$.

ii $HNO_3(aq) + NH_3(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$

Reaction is between a strong acid and a weak base, so $pH<7$.

iii $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2\ SO_4(aq) + 2H_2O(l)$

Reaction is between a strong acid and a strong base, so $pH = 7$

5 **a** $HS^-(aq) + H_2O(l) \rightarrow S^-(aq) + H_3O^+(aq)$

b $HS^-(aq) + HCl(aq) \rightarrow H_2S(aq) + Cl^-(aq)$

c $HS^-(aq) + NaOH(aq) \rightarrow NaS(aq) + H_2O(l)$

6 **a** pH would be lower.

b $NaOH(aq) + CH_3OOH(aq) \rightarrow CH_3OONa(aq) + H_2O(l)$

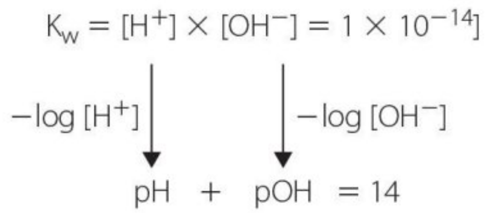
$n(CH_3COOH) = c \times V = 0.83 \times 0.5 \text{ mol} = 0.415 \text{ mol}$

$n(NaOH) = n(CH3OOH) = 0.415 \text{ mol}$

$m = nM = 0.415 \times 40 = 16.6 \text{ g of NaOH}$

Chapter review

1



2 **a** Strength refers to the degree to which an acid or base ionises in water. A strong acid or base ionises completely in water, while only some of the particles of a weak acid or base ionise/dissociate. Concentration is a measure of the number of particles that are present in a given amount of solution. A concentrated solution has many more particles than a dilute solution.

b pH and pOH give a measure of concentration of hydrogen ions and hydronium ions in solution. Solutions need to be of the same concentration and species being measure must be soluble.

K_a and K_b values give a measure of the degree of dissociation of the acid or base and hence can be used to compare strength – only useful for weak acids and bases, more complex for polyprotic acids.

pK_a and pK_b values also useful for comparing strength of weak acids and bases. Not useful acids and bases that dissociate completely.

3 **a** Purple

b Red

c No colour change

4 B

5 C

6 **a** **i** $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

ii $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

b **i** $Na_2O(aq) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$

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

7 **a** Sulfuric acid (H_2SO_4); phosphoric acid (H_3PO_4)

b $H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$ Step 1

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$ Step 2

c Step 1 H_2SO_4/ HSO_4^- H_2O/H_3O^+

Step 2 HSO_4^-/ SO_4^{2-} H_2O/ H_3O^+

8 **a** $pH = -\log[H^+] = -\log(0.050) = 1.30$

$pOH = 14 - pH = 14 - 1.30 = 12.7$

b $\text{pOH} = -\log[\text{OH}^-] = -\log(0.020) = 1.70$

$\text{pH} = 14 - \text{pOH} = 14 - 1.70 = 12.3$

c $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + H_2O\text{(l)}$

$c(\text{HCl}) = 0.2 \text{ mol L}^{-1}$ $V = 40 \text{ mL} = 0.040 \text{ L}$ $n = ?$

$n(\text{HCl}) = 0.2 \times 0.040 = 0.008 \text{ mol}$ $n(H_3O^+) = 0.008 \text{ mol}$

$c(\text{NaOH}) = 0.1 \text{ mol L}^{-1}$ $V = 20 \text{ mL} = 0.020 \text{ L}$ $n = ?$

$n(\text{NaOH}) = 0.10 \times 0.020 = 0.002 \text{ mol}$ $n(\text{OH}^-) = 0.002 \text{ mol}$

H_3O^+ is in excess by $0.008 - 0.002 = 0.006 = 6.0 \times 10^{-3}$ mol

$V = 40 \text{ mL} + 20 \text{ mL} = 0.060 \text{ L}$

$$[H_3O^+] = \frac{6.0 \times 10^{-3}}{0.060} = 0.100 \text{ mol L}^{-1}$$

$\text{pH} = -\log 0.100 = 1.0$ $\text{pOH} = 14 - 1 = 13$

9 **a** $\text{pH} = 0.62$ $[\text{HCl}] = [H^+] = 10^{-0.62} = 0.24 \text{ mol L}^{-1}$

$c_1V_1 = c_2V_2$

$$\boldsymbol{c}_2 = \frac{0.24 \times 50}{500} = 0.024 \text{ mol L}^{-1}$$

$\text{pH} = -\log 0.024 = 1.62$

b $c_1V_1 = c_2V_2$

$$C_2 = \frac{0.152 \times 0.025}{2.0} = 0.0019 \text{ mol L}^{-1}$$

$\text{pH} = -\log 0.0019 = 2.7$

c $c_1V_1 = c_2V_2$

$$c_2 = \frac{0.114 \times 0.010}{0.250} = 0.00456 \text{ mol L}^{-1}$$

$\text{pOH} = -\log 0.00456 = 2.34$

$\text{pH} = 14 - 2.34 = 11.7$

10 $HSO_4^-\text{(aq)} + H_2O\text{(l)} \rightleftharpoons SO_4^{2-}\text{(aq)} + H_3O^+\text{(aq)}$

$\text{pH} = 1.31$, $[H^+] = 10^{-1.31} = 0.0490$

$[SO_4^{2-}] = [H_3O^+]$

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = \frac{[H_3O^+]^2}{[HSO_4^-]} = \frac{0.0490^2}{0.25} = 0.0096$$

11 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

pOH = 14 – 11 = 3

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

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_b = \frac{[OH^-]^2}{[NH_3]} \qquad ([OH^-] = [NH_4^+])$$

$$= \frac{(1 \times 10^{-3})^2}{0.10}$$

$= 1.0 \times 10^{-5}$

12 pH = 13, pOH = 1

$[OH^-] = 1 \times 10^{-1}$ mol L^{-1} = [NaOH] $\qquad V = 705$ mL = 0.750 L

$n = cV = 1 \times 10^{-1} \times 0.750 = 0.0750$ mol

$m = nM = 0.0750 \times 40 = 3$ g

13

Phosphoric acid	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$\frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]}$	7.5×10^{-3}
	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	$\frac{[H^+]\,[HPO_4^{2-}]}{[H_2PO_4^-]}$	6.2×10^{-8}
	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	$\frac{[H^+]\,[PO_4^{3-}]}{[HPO_4^{2-}]}$	2.2×10^{-13}

The equilibrium expression K_a gets smaller for each ionisation for polyprotic acids. It is harder to remove the second and third protons. The conjugate base of phosphoric acid ($H_2PO_4^-$) is weak. $H_2PO_4^-$ ion is amphiprotic and can donate another proton. Because $H_2PO_4^-$ is a weak base, its conjugate acid (HPO_4^{2-}) is a stronger acid and is more likely to donate a proton than accept one. The back reaction is more likely; hence, the concentration of HPO_4^{2-} is going to be less than the concentration of the $H_2PO_4^-$.

14 **a** Let citric acid be represented as HC:

$$K_a = \frac{[C^-][H^+]}{[HC]}$$

b As acid is added, the $[H^+]$ will increase. To partially oppose this increase, the system will favour the back reaction, and therefore partially remove some hydronium ions. Overall there will be a decrease in pH with the addition of acid.

c When the citric acid solution is diluted by a factor of 10, the overall concentration will decrease. The system will partially oppose this by favouring the side with more particles. The ionisation of the citric acid will increase. This could be determined by measuring the pH of citric acid. When this solution is diluted by a factor of 10, a 1-unit change in pH would be expected. By measuring the pH of the diluted solution, it can be experimentally shown that the ionisation increases with dilution because the pH change should not be as dramatic as a 1-unit change.

15 **a** pH = 2.4, $[H^+] = 0.00398$, $[H^+] = [HCOO^-]$ and $[HCOOH]$ is 0.10 mol L^{-1}

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]} = \frac{0.00398^2}{0.1} = 1.6 \times 10^{-4}$$

b pH = 5.3, $[H^+] = 5.1 \times 10^{-6}$, $[H^+] = [OCl^-]$ and $[HOCl]$ is 0.00100 mol L^{-1}

$$K_a = \frac{\left[H^+\right]\left[OCl^-\right]}{\left[HOCl\right]} = \frac{\left(5.1 \times 10^{-6}\right)^2}{0.00100} = 2.5 \times 10^{-8} \text{ mol L}^{-1}$$

16 **a** Basic

b Basic

c Acidic

17 **a** $$K_a = \frac{[OH^-][H_3BO_3]}{[B(OH)_4^-]}$$

b $10^{-pH} = [H^+]$, $[H^+] = 7.76 \times 10^{-12}$ mol L^{-1}

$$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{(7.76 \times 10^{-12})} = 0.0013 \text{ mol L}^{-1}$$

c $[OH^-] = [H_3BO_3] = 0.0013$ mol L^{-1}

d $$K_a = \frac{[OH^-][H_3BO_3]}{[B(OH)_4^-]} = \frac{0.0013^2}{0.1} = 1.7 \times 10^{-5}$$

e $pK_a = -\log K_a = 4.8$

18 **a** $K_a = \dfrac{[CN^-][H_3O^+]}{[HCN]}$

b $K_a = \dfrac{[CN^-][H_3O^+]}{[HCN]} = 6.3 \times 10^{-10}$

$[H_3O^+] = \sqrt{}(6.3 \times 10^{-10} \times 0.00010) = 2.5 \times 10^{-7}$

$pH = 6.6$

c $\dfrac{[CN^-]}{[HCN]} \times 100 = \dfrac{2.5\times10^{-7}}{0.00010} \times 100 = 0.25\%$

d When the solution is above pH 7, the reaction will be driven to the right, minimising the concentration of hydronium ions. This favours the formation of CN^- rather than the HCN. Hydrogen cyanide gas is highly toxic; this reduces the chance of HCN gas being present.

19 **a** $H_2S(aq) + NH_3(aq)\ HS^-(aq) \rightleftharpoons HS^-(aq) + NH_4^+(aq)$

$HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$

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

b $K_a \times K_b = K_w \qquad K_b = K_w / K_a = 1 \times 10^{-14} / 1 \times 10^{-7} = 1 \times 10^{-7}$

c $K_a(NH_4^+) < K_b(HS^-)$ so final solution will be basic

20 **a** $c_1 V_1 = c_2 V_2$

$c_2 = 0.100 \times \dfrac{40}{60} = 0.0667 \text{ mol L}^{-1}$

$[NH_3] = 0.0667 \text{ mol L}^{-1}$

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

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

$K_b = \dfrac{[OH^-]^2}{[NH_3]} \qquad ([OH^-] = [NH_4^+])$

$[OH^-]^2 = 1.77 \times 10^{-5} \times [NH_3]$

$[OH^-] = \sqrt{}(1.77 \times 10^{-5} \times 0.0667) = 1.09 \times 10^{-3} \text{ mol L}^{-1}$

$pOH = -\log[OH^-]$

$= -\log(1.09 \times 10^{-3}) = 2.96$

$pH + pOH = 14$

$pH = 14 - pOH = 14 - 2.96 = 11.0$

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

$c(HCl) = 0.200\ mol\ L^{-1}$ $V = 30.0\ mL = 0.0300\ L$ $n = ?$

$n(HCl) = 0.200 \times 0.0300 = 6.00 \times 10^{-3}\ mol$ $n(H_3O^+) = 6.00 \times 10^{-3}\ mol$

$c(NaOH) = 0.100\ mol\ L^{-1}$ $V = 40.0\ mL = 0.0400\ L$ $n = ?$

$n(NaOH) = 0.100 \times 0.0400 = 4.00 \times 10^{-3}\ mol$ $n(OH^-) = 4.00 \times 10^{-3}\ mol$

H_3O^+ is in excess by $6.00 \times 10^{-3} - 4.00 \times 10^{-3} = 2.00 \times 10^{-3}$ mol

$V = 40.0\ mL + 30.0\ mL = 0.0700\ L$

$$[H_3O^+] = \frac{2.0 \times 10^{-3}}{0.0700} = 0.0286\ mol\ L^{-1}$$

$pH = -\log 0.0286 = 1.54$

Module 6: Acid/base reactions

Chapter 7: Using quantitative analysis

Check your understanding 7.1

1 **a** Volumetric analysis is a quantitative technique for analysing a sample. It involves measuring the volume of a sample solution that reacts with a known volume of another solution of known concentration. Hence, the concentration of the sample solution can be determined.

b Accuracy indicates the number of significant figures to which a measurement is known. A mass balance that can measure to 0.001 g is more accurate than a mass balance that can measure to 0.1 g.

c Parallax error is an error in a measurement due to the relative position of the observer to the measuring scale.

2 Equivalence point is the point when the reactants are present in the mole ratio see in the balanced chemical equation for the reaction, while end point occurs when the indicator changes colour and is the physical sign that that end point has been reached.

3 **a** A pipette is rinsed with the solution that will be placed in the burette during the experiment.

b This ensures the concentration of the solution in the burette remains constant. If rinsed with distilled water, any water remaining in the pipette would dilute the solution.

4

5 Universal indicator is a mixture of several other acid–base indicators, each of which changes colour at a different pH. Hence, universal indicator changes colour at several different pHs.

6 Parallax error can be minimised by ensuring that the observer’s eye level is in line with the measuring scale at the level where the reading will occur.

7 The student did not rinse the burette with the hydrochloric acid solution. This will lead to an error in the concentration of the hydrochloric acid solution, since the water in the burette will dilute the hydrochloric acid that is being used in the experiment. The student did not run some solution through the burette to empty the airlock prior to zeroing the burette for use. This will lead to an error in the volume of hydrochloric acid measured from the burette. The volume measured from the burette will be less than what is delivered from the burette since some of the volume is used to ‘replace’ the airlock.

8 a The sample is basic.

b Phenolphthalein is colourless when the pH is less than 8.5. Methyl orange is yellow when the pH is greater than 4.5. Hence using these two indicators, $4.5 < \text{pH} < 8.5$. Since the bromothymol blue indicator turns blue, the solution must be greater than 7.5, so the pH must be 7.5–8.5.

Check your understanding 7.2

1 A primary standard must have a high molar mass, have high purity and be stable in the presence of air.

2 A primary standard is used to determine the concentration of a solution of unknown concentration.

3 Sodium hydroxide is not appropriate for use as a primary standard since it readily reacts with air.

4 Hydrochloric acid is produced by dissolving hydrogen chloride gas in water. The solubility of hydrogen chloride gas in water changes with temperature. Hence, the concentration of the hydrochloric acid would also change with temperature. It would not be stable over time under standard laboratory conditions.

5 a

$$n_{\text{NaHCO}_3} = C_{\text{NaHCO}_3} \times V_{\text{NaHCO}_3} = 0.135 \times 0.250 = 0.03375 \text{ mol}$$

$$m_{\text{NaHCO}_3} = M_{\text{NaHCO}_3} \times n_{\text{NaHCO}_3} = 84.01 \times 0.03375 = 2.84 \text{ g}$$

b Place a clean and dry 150 mL beaker onto the mass balance and tare the balance. Accurately weigh out 2.84 g of solid $NaHCO_3$ into the beaker. Pour about 80 mL of water into the beaker and stir until all of the $NaHCO_3$ has dissolved. Rinse the spatula with a small volume of water into the beaker. Rinse the 250 mL volumetric flask with water. Use a clean filter funnel to pour the $NaHCO_3$ solution from the beaker into the flask. Rinse the beaker and pour into flask. Rinse the filter funnel and pour into flask. Fill flask with water to the top of the bulb of the flask. Then use a wash bottle to top up the flask until the bottom of the meniscus of the solution is in line with the line on the neck of the flask. Put lid on flask and swirl to mix.

6 A 100 mL measuring cylinder would be a more accurate piece of equipment for this task since it has a scale than can be used to measure to the nearest mL, so could measure 90 mL.

Worked examples 7.1/7.2

1 $\mathrm{(COOH)_2(aq) + 2KOH(aq) \rightarrow (COOK)_2(aq) + 2H_2O(l)}$

$$n_{\mathrm{(COOH)_2 + 2H_2 0}} = \frac{m_{\mathrm{(COOH)_2 + 2H_2 0}}}{M_{\mathrm{(COOH)_2 + 2H_2 0}}} = \frac{0.291}{126.08} = 2.308 \times 10^{-3} \text{ mol}$$

$$n_{\mathrm{KOH}} = 2 \times n_{\mathrm{(COOH)_2}} = 2 \times 2.308 \times 10^{-3} = 4.616 \times 10^{-3} \text{ mol}$$

$$c_{\mathrm{KOH}} = \frac{n_{\mathrm{KOH}}}{V_{\mathrm{KOH}}} = \frac{4.616 \times 10^{-3}}{0.0182} = 0.254 \text{ mol L}^{-1}$$

2 Original sodium carbonate solution:

$$n_{\mathrm{Na_2CO_3}} = \frac{m_{\mathrm{Na_2CO_3}}}{M_{\mathrm{Na_2CO_3}}} = \frac{5.267}{105.99} = 0.04969 \text{ mol}$$

$$c_{\mathrm{Na_2CO_3}} = \frac{n_{\mathrm{Na_2CO_3}}}{V_{\mathrm{Na_2CO_3}}} = \frac{0.04969}{0.250} = 0.1988 \text{ molL}^{-1}$$

Titration between sodium carbonate solution and hydrochloric acid solution:

$\mathrm{Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)}$

$$n_{\mathrm{Na_2CO_3}} = c_{\mathrm{Na_2CO_3}} \times V_{\mathrm{Na_2CO_3}} = 0.1988 \times 0.010 = 1.988 \times 10^{-3} \text{ mol}$$

$$n_{\mathrm{HCl}} = 2 \times n_{\mathrm{Na_2CO_3}} = 2 \times 1.988 \times 10^{-3} = 3.976 \times 10^{-3} \text{ mol}$$

$$c_{\mathrm{HCl}} = \frac{n_{\mathrm{HCl}}}{V_{\mathrm{HCl}}} = \frac{3.976 \times 10^{-3}}{0.0213} = 0.187 \text{ mol L}^{-1}$$

Titration between hydrochloric acid solution and barium hydroxide solution:

$\mathrm{2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)}$

$n_{\mathrm{HCl}} = 0.187 \times 0.0271 = 5.068 \times 10^{-3}$ mol

$$n_{\mathrm{Ba(OH)_2}} = \frac{1}{2} \times n_{\mathrm{HCl}} = \frac{1}{2} \times 5.068 \times 10^{-3} = 2.534 \times 10^{-3} \text{ mol}$$

$$c_{\mathrm{Ba(OH)_2}} = \frac{n_{\mathrm{Ba(OH)_2}}}{V_{\mathrm{Ba(OH)_2}}} = \frac{2.53 \times 10^{-3}}{0.0250} = 0.101 \text{ mol L}^{-1}$$

Changing the concentration of $\mathrm{Ba(OH)_2}$ from molarity to grams per litre:

$$c_{\mathrm{gL^{-1}}} = c_{\mathrm{molL^{-1}}} \times M_{Ba(OH)_2} = 0.101 \times 171.36 = 17.3 \text{ g L}^{-1}$$

Check your understanding 7.3

1 The solution placed in a burette is called the titrant.

2 An analyte can be a titrant. An analyte is the name given to the solution that has the unknown concentration. This solution could be placed in the burette; hence, it could be the titrant.

3 Titrations are repeated to improve the reliability of the results and to identify any results that are outliers and then exclude them. The volumes are averaged to identify the most representative volume that is indicative of the results.

4 **a** Bromothymol blue would be the most appropriate indicator. Since reaction is between a strong acid and a strong base, equivalence would be at a pH of 7. Bromothymol blue changes colour at a neutral end point.

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

$$n_{HCl} = c_{HCl} \times V_{HCl} = 0.0873 \times 0.02500 = 2.18 \times 10^{-3} \text{ mol}$$

$$n_{NaOH} = n_{HCl} = 2.18 \times 10^{-3} \text{ mol}$$

$$c_{NaOH} = \frac{n_{NaOH}}{V_{NaOH}} = \frac{2.18 \times 10^{-3}}{0.03730} = \; = 0.0584 \text{ mol L}^{-1}$$

5 **a** Methyl orange would be an appropriate indicator for this titration (strong acid and weak base).

b The sodium hydrogen carbonate solution would be in the burette, since the volume is slightly different for each titration. The volume of sulfuric acid is the same for each titration, exactly 20.00 mL. This would be delivered via a 20 mL pipette.

c The equivalence point would occur when 1 mol of sulfuric acid reacts with exactly 2 mol of sodium hydrogen carbonate. This would be indicated when the first permanent change in colour of the methyl orange indicator from red to yellow is observed.

d $H_2SO_4(aq) + 2NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + 2H_2O(l)$

e $V_{NaHCO_3} = \frac{(22.35 + 22.40 + 22.35)}{3} = 22.37 \text{ mL}$ (24.35 ml is an outlier)

$$n_{NaHCO_3} = c_{NaHCO_3} \times V_{NaHCO_3} = 0.145 \times 0.02237 = 3.24 \times 10^{-3} \text{ mol}$$

$$n_{H_2SO_4} = \frac{1}{2} \times n_{NaHCO_3} = \frac{1}{2} \times 3.24 \times 10^{-3} = 1.62 \times 10^{-3} \text{ mol}$$

$$c_{H_2SO_4} = \frac{n_{H_2SO_4}}{V_{H_2SO_4}} = \frac{1.62 \times 10^{-3}}{0.02000} = 0.0811 \text{ mol L}^{-1}$$

Worked example 7.3

1 Number of moles of hydrochloric acid added to limestone:

$$n_{\mathrm{HCl}} = c_{\mathrm{HCl}} \times V_{\mathrm{HCl}} = 0.121 \times 0.050 = 6.05 \times 10^{-3} \text{ mol}$$

Reaction between hydrochloric acid and sodium hydroxide:

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

$$n_{\mathrm{NaOH}} = c_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}} = 0.0950 \times 0.0211 = 2.00 \times 10^{-3} \text{ mol}$$

$$n_{\mathrm{HCl}} = n_{\mathrm{NaOH}} = 2.00 \times 10^{-3} \text{ mol}$$

Number of moles of HCl that reacts with $CaCO_3$ = Number of moles of HCl added to limestone – Number of moles of HCl reacted with NaOH

$$n_{\mathrm{HCl\ reacted\ with\ CaCO_3}} = 6.05 \times 10^{-3} - 2.00 \times 10^{-3} = 4.05 \times 10^{-3} \text{ mol}$$

Reaction between hydrochloric acid and calcium carbonate:

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

$$n_{\mathrm{CaCO_3}} = \frac{1}{2} \times n_{\mathrm{HCl}} = \frac{1}{2} \times 4.05 \times 10^{-3} = 2.02 \times 10^{-3} \text{ mol}$$

Calculation of $CaCO_3$ in original limestone sample:

$$m_{\mathrm{CaCO_3}} = n_{\mathrm{CaCO_3}} \times M_{\mathrm{CaCO_3}} = 2.02 \times 10^{-3} \times 100.09 = 0.202 \text{ g}$$

$$\%_{\mathrm{CaCO_3}} = \frac{m_{\mathrm{CaCO_3}}}{m_{\mathrm{limestone}}} = \frac{0.202}{0.552} \times 100 = 36.6\% \times 100 = 36.6\%$$

2 Number of moles of sodium hydroxide added to ammonium sample:

$$n_{\mathrm{NaOH}} = c_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}} = 0.414 \times 0.025 = 0.010 \text{ mol}$$

Reaction between sodium hydroxide and hydrochloric acid:

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

$$n_{\mathrm{HCl}} = c_{\mathrm{HCl}} \times V_{\mathrm{HCl}} = 0.161 \times 0.0212 = 3.41 \times 10^{-3} \text{ mol}$$

$$n_{\mathrm{NaOH}} = n_{\mathrm{HCl}} = 3.41 \times 10^{-3} \text{ mol}$$

Number of moles of NaOH that reacts with NH_4^+ = Number of moles of NaOH added to NH_4^+ – Number of moles of NaOH reacted with HCl

$$n_{\mathrm{NaOH\ reacted\ with\ ammonium}} = 0.010 - 0.00341 = 0.00694 \text{ mol}$$

Reaction between ammonium and sodium hydroxide:

$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$

$$n_{NH_4^+} = n_{NaOH} \times 0.00694 \text{ mol}$$

$$m_{NH_4^+} = n_{NH_4^+} \times M_{NH_4^+} = 0.00694 \times 18.05 = 0.125 \text{ g}$$

$$\%_{NH_4^+} = \frac{m_{NH_4^+}}{m_{sample}} \times 100 = \frac{0.125}{0.375} \times 100 = 33.4\%$$

Check your understanding 7.4

1 A back titration is used if the sample is not soluble in water or if it is difficult to determine a definite end point because the reaction occurs too slowly.

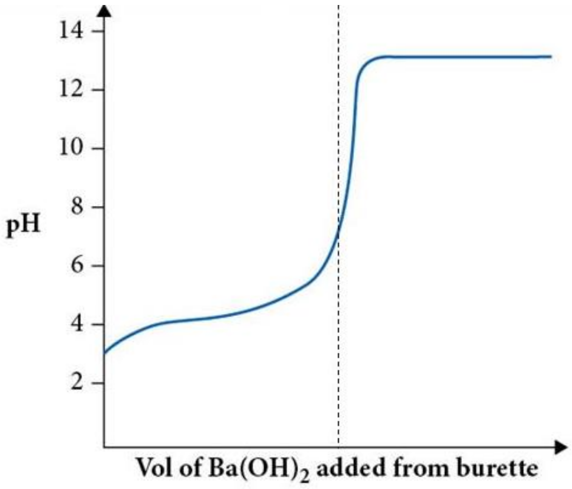
2 a A change in conductivity values

b A conductometric titration can be used:

- with very diluted solutions
- when species being investigated are at trace levels
- with coloured or turbid solutions
- when the system involves relatively incomplete reactions.
- with non-aqueous titrations.

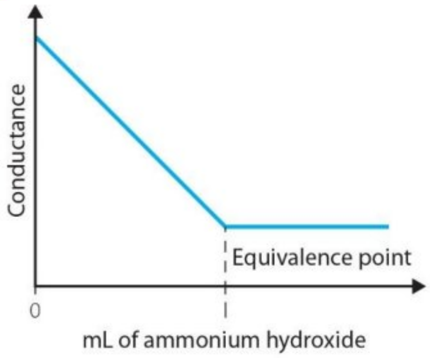
3 Both processes are very similar. The main difference is that one measures changes in pH and the other measures changes in conductivity. Both processes can be used with solutions where the colour of an indicator could not be detected. Both the pH probe and the conductivity meter are placed in the beaker to which the titrant is then added. The data obtained by the instruments is plotted to produce a graphical representation from which the equivalence point can be determined.

4 a



b The equivalence point is where the dotted line crossed the curve.

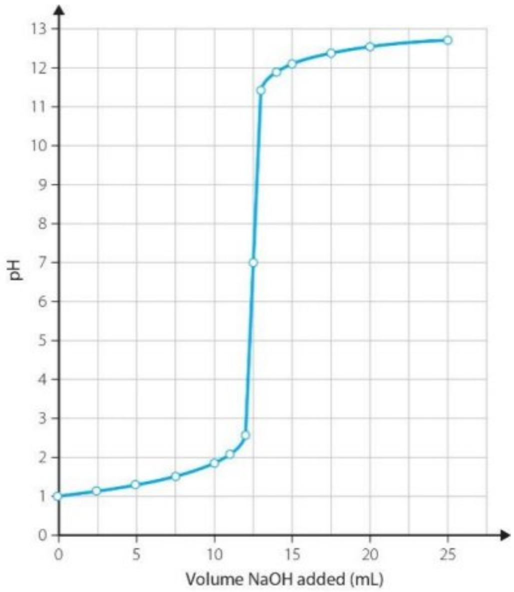
5



6 Some redox titrations do not require the use of an indicator because the different oxidation states of transition metals may have different colours that can be used to determine the end point.

7 Since orange juice has an orange colour, it will mask the colour change of indicators; hence, a pH meter is used.

8 **a**



b 12.5 mL

c Number of moles of hydrochloric acid:

$$n_{HCl} = c_{HCl} \times V_{HCl} = 0.100 \times 0.025 = 2.5 \times 10^{-3} \text{ mol}$$

Reaction between hydrochloric acid and sodium hydroxide:

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

$n_{NaOH} = 2.5 \times 10^{-3}$ mol $V_{NaOH\ added} = 12.5 \text{ mL} = 0.0125 \text{ L}$

$$c_{NaOH} = \frac{2.5 \times 10^{-3}}{0.0125} = 0.2 \text{ mol L}^{-1}$$

9 Number of moles of hydrochloric acid added to sodium sulfite solution:

$$n_{\text{HCl}} = c_{\text{HCl}} \times V_{\text{HCl}} = 0.308 \times 0.050 = 0.0154 \text{ mol}$$

Reaction between excess hydrochloric acid and sodium hydroxide:

$$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$

$$n_{NaOH} = c_{NaOH} \times V_{NaOH} = 0.144 \times 0.0354 = 5.10 \times 10^{-3} \text{ mol}$$

Number of moles of HCl that reacts with Na_2SO_3	=	Number of moles of HCl added to Na_2SO_3	–	Number of moles of HCl reacted with NaOH

$$n_{\text{HCl reacted with sulfite}} = 0.0154 - 0.00510 = 0.0103 \text{ mol}$$

$$2\text{HCl(aq)} + \text{Na}_2\text{SO}_3\text{(aq)} \rightarrow 2\text{NaCl(aq)} + \text{SO}_2\text{(g)} + \text{H}_2\text{O(l)}$$

$$n_{\text{Na}_2\text{SO}_3} = \frac{1}{2} \times n_{\text{HCl}} = \frac{1}{2} \times 0.0103 = 5.15 \times 10^{-3} \text{ mol}$$

$$m_{\text{Na}_2\text{SO}_3} = n_{\text{Na}_2\text{SO}_3} \times M_{\text{Na}_2\text{SO}_3} = 5.15 \times 10^{-3} \times 126 = 0.649 \text{ g}$$

$$\%\text{Na}_2\text{SO}_3 = \frac{m_{\text{Na}_2\text{SO}_3}}{m_{\text{sample}}} \times 100 = \frac{0.649}{0.781} \times 100 = 83.1\%$$

10 **a** The acid was placed in the flask at the beginning of the titration since the pH commenced well below a pH of 7 (hence, in acidic range). A monoprotic acid with a concentration of 0.060 mol L^{-1} would have a pH of 1.22 (i.e. 1–2 on the diagram). However, the pH graph commences with $pH < 1$, which indicates that it is not a monoprotic acid. A diprotic acid with a concentration of 0.060 mol L^{-1} would have a pH of 0.9. This is consistent with the starting pH on the graph. Hence, a diprotic acid is placed in the flask at the beginning of the titration.

b 10 mL since equivalence point is at pH 7

c This is a reaction between a strong acid and a strong base of the same concentration. The acid is diprotic. The volume of base is 10 mL as this is in the burette (titrant). If the reaction stoichiometry was 1:2 (e.g. H_2SO_4 and NaOH) then the volume of acid in the flask would be 5 mL; however, if the base produced $2OH^-$ ions (e.g. $Ba(OH)_2$) then the stoichiometric ratio would be 1:1 and the volume of acid in the flask would also be 10 mL.

Check your understanding 7.5

1 A buffer is a solution of a weak acid and its conjugate base. It maintains a pH within a narrow range, such as ±1 unit. A solution containing sodium hydrogen carbonate and carbonic acid is a buffer.

2 **a** Buffer capacity is the amount of acid or base than can be added to a system without significant change in pH.

b Buffer capacity can be increased by increasing the concentration of the weak acid and conjugate base in a system.

3 **a** A buffer solution is a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. The pH changes very little when a small amount of strong acid or base is added to it. It is used to prevent changes in the pH of a solution.

b **i** When HCl is added, the H^+ ions react with the ethanoate ion forming ethanoic acid. This partially opposes the addition of H^+ ions, maintaining the pH.

ii When the base NaOH is added, the OH^- ions react with the H^+ ions in the solution. This favours the reaction, producing the ethanoate ion and hydrogen ions. This keeps the concentration of H^+ higher and helps to maintain the pH.

4 **a** pH of 8.2 has a $[H_3O^+] = 10^{-8.2}$

pH of 8.1 has a $[H_3O^+] = 10^{-8.1}$

$$\%\text{change} = \frac{(10^{-8.1}) - (10^{-8.2})}{10^{-8.2}} \times 100$$

$$= \frac{(7.9 \times 10^{-9}) - (6.3 \times 10^{-9})}{6.3 \times 10^{-9}} \times 100$$

$$= \frac{(1.6 \times 10^{-9})}{(6.3 \times 10^{-9})} \times 100$$

$$= 25\%$$

b As the concentration of hydronium ion increases in the ocean, carbonate ion (CO_3^{2-}) would react with the hydronium ion to form hydrogen carbonate, partially opposing the acidification or buffering the change.

Calcium carbonate is the main component of shells. If the concentration of the hydronium ion increases too much, shells or carbonate salts will dissolve as the second back reaction is favoured. This reduces the ability of the organism to maintain or build shells.

5 Carbon dioxide will react with water in the blood to form carbonic acid. Carbonic acid is a weak acid and will ionise in accordance to the following equations:

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$; $K_a = 4.5 \times 10^{-7}$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$; $K_a = 4.7 \times 10^{-11}$

The K_a of the first equation is much higher than the second equation. This means that at equilibrium the concentration of hydrogen carbonate (HCO_3^-) is higher than the concentration of the carbonate ion CO_3^{2-}. Addition of hydrogen carbonate will favour the back reaction of the first equation that will reduce the concentration of hydronium ions as carbonic acid forms.

6 Student responses will vary.

Chapter review questions

1 Phenolphthalein is pink in basic solution and clear in neutral and acidic solutions.

2 a The end point of a titration is the point when the indicator changes colour.

b Equivalence point is when the reactants are present in the stoichiometric mole ratio given by the balanced chemical equation, while end point is the physical sign that equivalence point has been reached.

3 The end point of a titration can be determined by using an indicator, which changes colour, observing a sudden change in pH if using a pH meter or a difference change in conductivity.

4 Possible sources of error when using a burette include: parallax error, not rinsing the burette with the solution that is being used and not releasing the airlock before commencing a titration.

5 Rinsing the pipette with water would dilute the sulfuric acid, the solution that was to be placed in the pipette. Therefore, less sodium hydroxide would be used for the titration. Hence, the result would be less than it should be.

6 The number of moles of each of the reactants that are used in the titration are measured accurately from the pipette and the burette. If the reaction vessel was rinsed with one or both of the solutions, then this adds to the number of moles of solution that is reacting. Hence, the moles of reactants are not accurately known since the number of moles of the solution used to rinse the reaction vessel is unable to be measured.

7 The end point of a titration between a strong acid and a weak base involves a sudden change in the pH between pH 8–9 and pH 1–2. The resultant salt is acidic, so it needs an indicator that changes colour in the acidic region (such as methyl orange). The end point of a titration between a weak acid and a strong base involves a sudden change in the pH from 12–13 to about 4. The resultant salt is basic so needs an indicator that changes colour in the basic region (such as phenolphthalein).

8 Anhydrous sodium carbonate can be used as a primary standard since it has a high molar mass, it has a high purity, it does not react with air, it forms a solution and its concentration remains stable over an extended period of time.

9 The concentration of a primary standard solution remains stable over an extended period of time, while a standard solution is one in which the concentration is determined immediately prior to its use.

10 **a** Equivalence point

b When the weak base is added, the highly mobile H^+ ion reacts with the OH^- to form the weakly ionised water molecule. The conductivity of the solution decreases as the H^+ ion is replaced with the larger, less mobile NH_4^+ ions until equivalence point. The graph becomes almost horizontal with continued addition of the weak base because the weak base is not appreciably ionised so few ions are being added to the solution.

11 **a** $Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + H_2O(l)$

b Bromothymol blue would be a suitable indicator for this titration since it is between a strong acid and strong base, so the end point would have a neutral pH. Bromothymol blue changes colour at a pH of 7.

c Using data from the question: $Ba(OH)_2$ was pipetted into the flask and the HCl was in the burette. Hence colour change would be from blue to yellow.

d Number of moles of $Ba(OH)_2$ in original solution:

$$n_{Ba(OH)_2} = \frac{m_{Ba(OH)_2}}{M_{Ba(OH)_2}} = \frac{3.25}{171} = 0.0190 \text{ mol}$$

$$c_{Ba(OH)_2} = \frac{n_{Ba(OH)_2}}{V_{Ba(OH)_2}} = \frac{0.0190}{0.100} = 0.190 \text{ mol L}^{-1}$$

Number of moles of $Ba(OH)_2$ reacted with HCl:

$$n_{Ba(OH)_2} = c_{Ba(OH)_2} \times V_{Ba(OH)_2} = 0.190 \times 0.0200 = 3.80 \times 10^{-3} \text{ mol}$$

$$n_{HCl} = 2 \times n_{Ba(OH)_2} = 2 \times 3.80 \times 10^{-3} = 7.60 \times 10^{-3} \text{mol}$$

$$c_{HCl} = \frac{n_{HCl}}{V_{HCl}} = \frac{7.60 \times 10^{-3}}{0.0178} = 0.427 \text{molL}^{-1}$$

12 **a** Hydrogen peroxide is the reducing agent.

b The different oxidation states of manganese have different colours. Mn^{7+} (in MnO_4^-) is purple, while Mn^{2+} is pale pink. The end point will be determined when the solution turns the first permanent pale pink colour.

c

$$n_{\mathrm{MnO_4^-}} = c_{\mathrm{MnO_4^-}} \times V_{\mathrm{MnO_4^-}} = 0.0200 \times 0.0196 = 3.92 \times 10^{-4}\,\mathrm{mol}$$

$$n_{\mathrm{H_2O_2}} = \frac{5}{2} n_{\mathrm{MnO_4^-}} = \frac{5}{2} \times 3.92 \times 10^{-4} = 9.80 \times 10^{-4}\,\mathrm{mol}$$

$$c_{\mathrm{H_2O_2}} = \frac{n_{\mathrm{H_2O_2}}}{V_{\mathrm{H_2O_2}}} = \frac{9.80 \times 10^{-4}}{0.0200} = 0.0490\ \mathrm{molL^{-1}}$$

Concentration of diluted H_2O_2 solution is 0.0490 mol L^{-1}.

Concentration of original H_2O_2 solution = 10 × concentration of diluted solution of H_2O_2

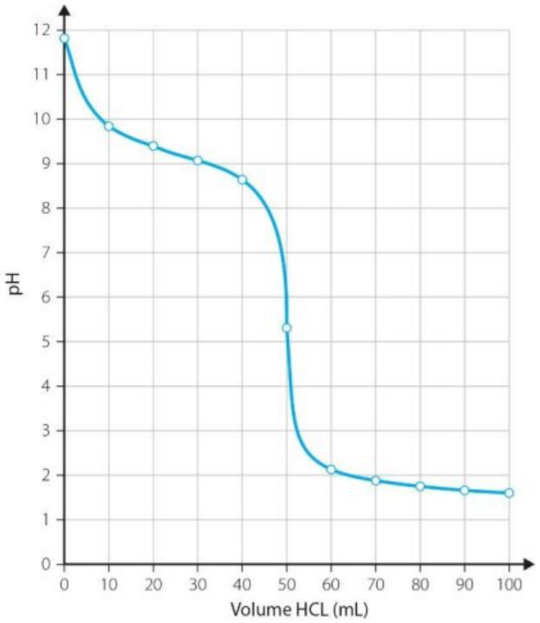
Concentration of original H_2O_2 solution = 10 × 0.0490 = 0.490 mol L^{-1}

13 a A weak acid was pipetted into the reaction vessel.

b Acetic acid is an example of a weak acid.

c The end point for this titration would be pH 8.5.

14 a



b $V_{\mathrm{HCl}} = 50$ mL

c Number of moles of hydrochloric acid:

$n_{\mathrm{HCl}} = c_{\mathrm{HCl}} \times V_{\mathrm{HC}l} = 0.0625 \times 0.050 = 3.125 \times 10^{-3}$ mol

Reaction between hydrochloric acid and ammonium hydroxide:

$HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$

$n_{\mathrm{NH4OH}} = 3.125 \times 10^{-3}$ mol $V_{\mathrm{NaOH}} = 25.0$ mL = 0.025 L

$$c_{\mathrm{NaOH}} = \frac{3.125 \times 10^{-3}}{0.025} = 0.125\ \mathrm{mol\ L^{-1}}$$

15 Number of moles of NaOH added to lawn fertiliser:

$n_{\text{NaOH}} = c_{\text{NaOH}} \times V_{\text{NaOH}} = 1.020 \times 0.02500 = 0.02550$ mol

Reaction between excess sodium hydroxide and hydrochloric acid:

$\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$

$n_{\text{HCl}} = c_{\text{HCl}} \times V_{\text{HCl}} = 0.2154 \times 0.01982 = 4.269 \times 10^{-3}$ mol

$n_{\text{NaOH}} = n_{\text{HCl}} = 4.269 \times 10^{-3}$ mol

Number of moles of NaOH that reacts with NH_4^+ = Number of moles of NaOH added to NH_4^+ – Number of moles of NaOH reacted with HCl

$n_{\text{NaOH reacted with ammonium}} = 0.02550 - 0.004269 = 0.02123$ mol

Reaction between sodium hydroxide and ammonium ion:

$\text{NaOH(aq)} + \text{NH}_4^+\text{(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{NH}_3 + \text{H}_2\text{O(l)}$

$n_{\text{NH}_4^+} = n_{\text{NaOH}} = 0.02123$ mol

$m_{\text{NH}_4^+} = n_{\text{NH}_4^+} \times M_{\text{NH}_4^+} = 0.02123 \times 18.04 = 0.3830$ g

$$\%\text{NH}_4^+ = \frac{m_{\text{NH}_4^+}}{m_{\text{fertiliser}}} \times 100 = \frac{0.3830}{1.432} \times 100 = 26.75\%$$

16 **a** $\text{H}_2\text{PO}_4^-\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HPO}_4^{2-}\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)}$

b $H_2PO_4^-$ is the acid and HPO_4^{2-} is its conjugate base.

c When H^+ ions are added, they react with the HPO_4^{2-} conjugate base, forming the acid $H_2PO_4^-$. This partially opposes the addition of H^+ ions, maintaining the pH. When OH^- ions are added, they react with the H^+ ions in the solution. This favours the forward reaction, producing the hydrogen phosphate and hydronium ions. This keeps the concentration of H^+ higher and helps to maintain the pH.

17 The students recorded different values because one or both students did not use the correct technique for observing the measuring scale on the burette; hence, there is parallax error in one or both of the measurements.

18 Student responses will vary – information provided in section 7.6.

19 Student responses will vary – information provided in section 7.6.

20 Points in discussion could include:

Does not need to be used if only qualitative data is required (e.g. is a particular substance present?)

Useful for when quantitative data is required (e.g. determining concentration of particular heavy metals in water samples; determining if labelling of samples is correct such as distinguishing between orange juice and orange fruit juice drink).

End-of-Module 6 Review

1 C

2 A

3 B

4 B

5 C

6 D

7 C

8 B

9 B

10 C

11 B is diprotic because if it was monoprotic, a 0.1 mol L^{-1} solution would have pH = 1 but

pH = 0.69, so more H^+ then 0.1 mol L^{-1}

12 Beaker I is a strong acid; complete ionisation; species present in solution: H^+, Cl^-.

Beaker II is a weak acid; partial ionisation; species present in solution: CH_3COOH, H^+, CH_3COO^-.

Beaker III is a strong acid; neutral salt; complete dissociation; species present in solution: H^+ , Cl^-, Na^+, Cl^-.

Beaker IV is a strong acid; basic salt; species present in solution: H^+, CH_3COO^-, Cl^-, Na^+.

pH:

Beaker IV – less acidic than 1 and 3, similar to 2

Conductivity:

Beaker IV – lower than 1 and 3 but greater than 2

Explanation:

CH_3COO^- ion is the conjugate base of acetic acid so will react with H^+ ion to reduce acidity of solution to less than HCl. The formation of CH_3COOH molecular species reduces the number of ions so reduces conductivity.

13 **a** Beaker A has pH = 0.44; beaker B has pH = 4.63.

Eva is correct – the pH of the two beakers will be different.

b The pOH of the final solution in both beakers will be the same. Both solutions will have the same number of moles of NaOH since they have the same concentration and volume of NaOH. Both the acids are monoprotic and since they have the same concentration and volume, there will be the same number of moles of acid in both beakers. Therefore, the NaOH will be in excess by the same amount. The NaCl salt produced by the reaction of HCl and NaOH is neutral so it will not affect the final pOH. The $NaCH_3COO$ salt is basic since it is the conjugate salt of a weak acid. However, the K_b value is very small so the degree to which it will hydrolyse water to produce OH^- ions is insignificant compared to the concentration of OH^- present in excess there, so it will also not affect the final pOH.

14 a 54.9 kJ mol^{-1} H_2O produced

b Volume of solution = 101 mL, no heat was produced by dilution of HNO_3, all NaOH reacted, acid was in excess.

c 14.5 mol L^{-1}

15 a Normal blood, $[H^+] = 3.98 \times 10^{-8}$ mol L^{-1}

Patient's blood, $[H^+] = 7.08 \times 10^{-8}$ mol L^{-1}

Patient's $[H^+]$ is higher than normal.

b Since the patient hyperventilated, $[O_2]$ in the blood increased. According to Le Chatelier's principle, in equation 1, equilibrium would move to the right, increasing $[H_3O^+]$ and therefore decreasing pH.

c CO_3^-

d Buffered means that the pH in the blood is maintained despite the addition of small amounts of acid or base.

e According to equation 2: $CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

The addition of HCO_3^- ions would cause the equilibrium to shift to the left. This would reduce $[H^+]$ in the blood, leading to an increase in pH. There would be an increase in $[CO_2(aq)]$, which can be removed through exhalation.

16 a 0.091 mol L^{-1} (based on average titration volume using 2nd, 3rd and 4th titration volumes)

b 0.91 mol L^{-1}

c The titration is between a weak base (NH_3) and a strong acid (HCl). This means the resulting solution would be acid due to the salt produced, which is the conjugate acid (NH_4^+) of NH_3. The pH at equivalence point would be less than 7 so an indicator that changes colour in an acidic range is appropriate. Phenol red changes colour near neutral so using it means the equivalence point would not have been reached when a colour change is seen. It would mean a lesser volume of HCl would need to be added, resulting in a lower concentration of ammonia.

17 **a** $B + H_2O \rightleftharpoons BH^+ + OH^-$

b $K_b = \frac{[BH^+][OH^-]}{[B]}$

c $K_a = 2.3 \times 10^{-11}$

d pH = 11.2

e That the equilibrium concentration of B is the same as the initial concentration of B (0.10 mol L^{-1}). This is valid because B is a weak base so the amount that had reacted to produce BH^+ is very small (6.6×10^{-3}) compared to the initial concentration.

Module 7: Organic chemistry

Chapter 8: Hydrocarbons

Check your understanding 8.1

1 The valence electrons of carbon can share one, two or three pairs of electrons to form single, double or triple bonds. Carbon shares its valence electrons to form chain or ring structures that form the basis of all organic molecules. Valence electrons not involved in carbon–carbon bonding form bonds with atoms like hydrogen, oxygen, nitrogen and the halogens.

2 a Aromatic compounds contain a benzene ring, aliphatic compounds are organic compounds without a benzene ring.

b Saturated compounds only have single carbon–carbon bonds in the molecule. Unsaturated compounds have carbon–carbon double or triple bonds within the molecule.

c Alkanes have all carbon–carbon single bonds, alkenes contain at least one carbon–carbon double bond and alkynes contain at least one carbon–carbon triple bond.

3 Ball and stick models show the bonds between atoms clearly. Space-filling molecules do not show bonds, so will not show the difference between a carbon–carbon single, double or triple bond, but a ball and stick model will show the individual bonds.

4 Four single bonds give a tetrahedral shape around the carbon atom (as seen in row 1 of Table 8.1). A planar shape is seen when a carbon has a double bond and two singles (seen in row 2 of Table 8.1). A carbon with either two double bonds or one triple and one single bond will have a linear shape (row 3 and 4 of Table 8.1).

5 The differences between expanded, condensed and skeletal formulae are seen in Figure 8.5. Expanded formulae show the arrangement of each individual atom. Condensed formulae show the arrangement of the molecule but condenses the hydrogen atoms around each carbon. Skeletal formulae show no atoms, but only the arrangement of the carbon atoms.

Worked example 8.1

1 2,2-dimethylpropane

2 2,3,4,4-tetramethylhexane

Check your understanding 8.2

1 C_nH_{2n+2}

2 1 meth-, 2 eth-, 3 prop-, 4 but-, 5 pent-, 6 hex-, 7 hept-, 8 oct-, 9 non-, 10 dec-

3 Methane CH_4, ethane C_2H_6, propane C_3H_8, butane C_4H_{10}, pentane C_5H_{12}, hexane C_6H_{14}, heptane C_7H_{16}, octane C_8H_{18}, nonane C_9H_{20}, decane $C_{10}H_{22}$

4 **a** 3-methylpentane

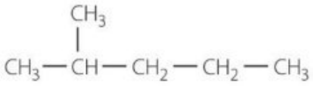
b 3-methylpentane

c 2,2-dimethylbutane

d 3-methylpentane

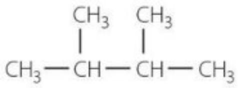
e 3,3,4,4-tetramethylhexane

5 **a**



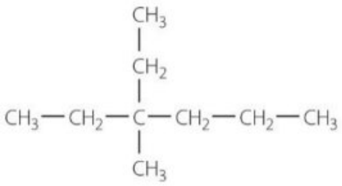
$CH_3-CH(CH_3)-CH_2-CH_2-CH_3$

b



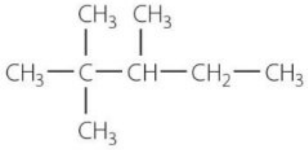
$CH_3-CH(CH_3)-CH(CH_3)-CH_3$

c



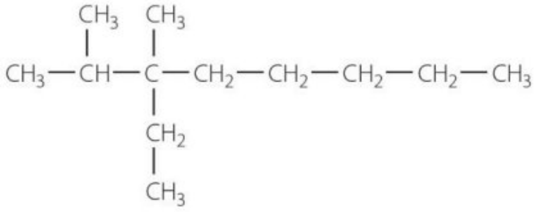
$CH_3-CH_2-C(CH_3)(CH_2CH_3)-CH_2-CH_2-CH_3$

d



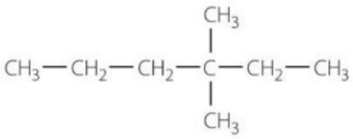
$CH_3-C(CH_3)_2-CH(CH_3)-CH_2-CH_3$

e



$CH_3-CH(CH_3)-C(CH_3)(CH_2CH_3)-CH_2-CH_2-CH_2-CH_2-CH_3$

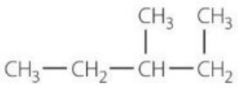
6 **a** Incorrect name, since the branches have not been given the lowest numbers. Correct name: 3,3-dimethylhexane



$$\mathrm{CH_3-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3}$$

b Incorrect, since the longest continuous chain has 5 carbons, not 4.

Correct name: 3-methylpentane



$$\mathrm{CH_3-CH_2-\overset{CH_3}{CH}-\overset{CH_3}{CH_2}}$$

Worked example 8.2

1 2,3-dimethyl-1-butene

2 4-methyl-2-hexene

Check your understanding 8.3

1 C_nH_{2n}

2 Alkanes have no carbon–carbon double bonds, all alkenes have at least one carbon–carbon double bond.

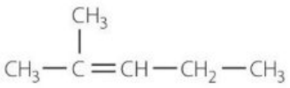
3 **a** 3-methyl-1-butene

b 2,4-dimethyl-2-pentene

c 2,4,4-trimethyl-2-pentene

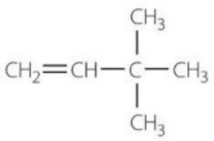
d 2,3-dimethyl-1-butene

4 **a**



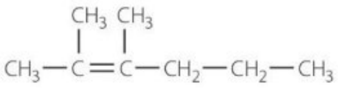
$$\mathrm{CH_3-\overset{CH_3}{C}=CH-CH_2-CH_3}$$

b



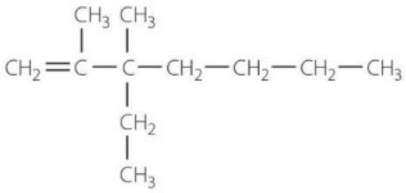
$$\mathrm{CH_2=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3}$$

c



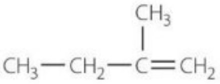
$$\mathrm{CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_2-CH_2-CH_3}$$

d



$$\mathrm{CH_2=\overset{CH_3}{C}-\underset{\underset{CH_3}{CH_2}}{\overset{CH_3}{C}}-CH_2-CH_2-CH_2-CH_3}$$

5 Incorrect, since smallest possible number has not been used for the double bond. Correct name: 2-methyl-1-butene



$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2$

Check your understanding 8.4

1 C_nH_{2n-2}

2 **a** 4-methyl-2-hexyne

b 4-methyl-2-pentyne

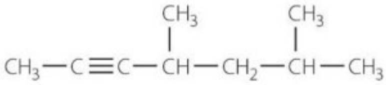
c 3,3-dimethyl-1-pentyne

d 4-methyl-2-pentyne

e 3,3-dimethyl-1-pentyne

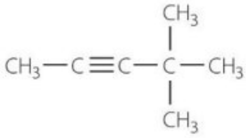
3 **a** $CH_3-CH_2-C\equiv C-CH_2-CH_2-CH_3$

b



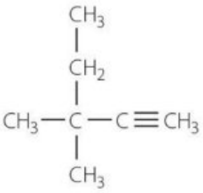
$CH_3-C\equiv C-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$

c



$CH_3-C\equiv C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

4 The longest chain has 5 carbons, not 4. The triple bond was not given the lowest number. Correct name: 3,3-dimethyl-1-pentyne.



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{\overset{CH_3}{|}}{CH_2}}{|}}{C}}-C\equiv CH_3$

Worked example 8.3

1 1-bromo-1,2-dichloro-2-fluoropropane

2 3,4,4,5-tetrachloro-3-methyl-1-pentyne

Check your understanding 8.5

1 **a** 1,2-dichloro-1-butene

b 2,2,3,3-tetrachloro-1-fluorobutane

c 3,4-dichloro-3,4-difluoro-1-pentyne

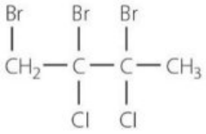
d 3-bromo-1,1,2-trichloro-1-butene

e 1,4,4-trichloro-2-methyl-1-pentene

f 1-bromo-2,2-dimethylbutane

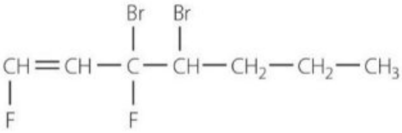
g 4-bromo-2,4-dichloro-3-ethyl-2,3-dimethylhexane

2 **a**



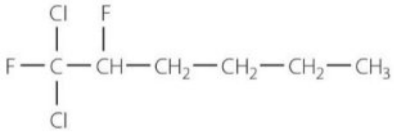
$\overset{Br}{CH_2}-\underset{Cl}{\overset{Br}{C}}-\underset{Cl}{\overset{Br}{C}}-CH_3$

b



$\underset{F}{CH}=CH-\underset{F}{\overset{Br}{C}}-\overset{Br}{CH}-CH_2-CH_2-CH_3$

c



$F-\underset{Cl}{\overset{Cl}{C}}-\overset{F}{CH}-CH_2-CH_2-CH_2-CH_3$

Check your understanding 8.6/8.7

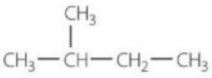
1 Structural isomers have the same molecular formula, but a different structure. For example, butane (C_4H_{10}) has the same molecular formula as 2-methylpropane (also C_4H_{10}), so they are isomers.

2 The two molecules in ‘a’ have the same molecular formula but different names. The top molecule is 2-methylpentane, the bottom molecule is 3-methylpentane. They are isomers. The two molecules in ‘b’ have different numbers of carbon atoms, so they are not isomers.

3 Pentane:

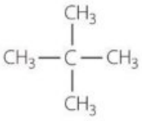
$CH_3-CH_2-CH_2-CH_2-CH_3$

Pentane



$CH_3-\overset{CH_3}{CH}-CH_2-CH_3$

2-methylbutane



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

2,2-dimethylpropane

Butene:

$CH_2=CH-CH_2-CH_3$

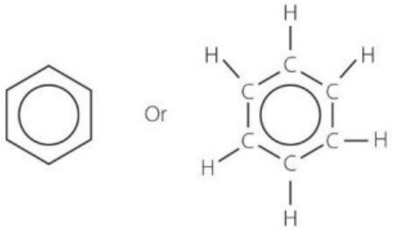
1-butene

$CH_3-CH=CH-CH_3$

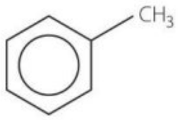
2-butene

4 Aromatic compounds contain the benzene molecule as part of its structure.

5 Parent compound is benzene – C_6H_6



6 The ring structure, including the delocalised electrons, is very stable and does not easily become disrupted to bond with other atoms.

7 

Check your understanding 8.8

1 Fuels, industrial solvents, lubricants

2 Feedstock for production of chemicals and polymers, artificial ripening of fruits, production of synthetic ethanol

3 A feedstock is a chemical used to manufacture other materials and chemicals. For example, ethene is used to make many polymers including polyethene, and is also used to make synthetic ethanol, which is then used as an industrial solvent.

4 Alkanes have only weak dispersion forces between molecules due to the non-polar nature of the molecule. Dispersion forces do not require a lot of energy to break so they have low melting and boiling points.

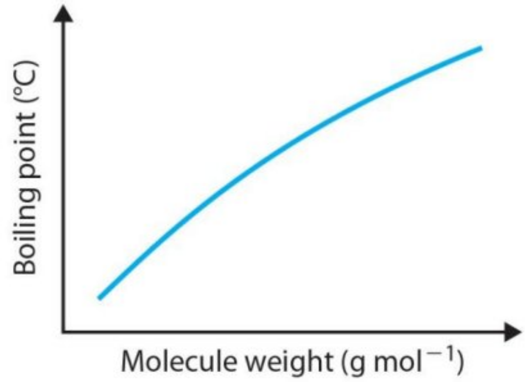
5 As alkanes get larger and there are more atoms per molecule, the overall number of dispersion forces that form between molecules will increase. More dispersion forces will require more energy to break, giving higher boiling points. The first four alkanes have only relatively few dispersion forces between molecules and the temperature required to break them is lower than room temperature, so they are gases. Larger alkanes require a boiling point above room temperature, so they are liquids.

6 a Alkanes are non-polar covalent molecules with no dipole or ionic charges so have no ability to conduct electricity.

b Covalent molecules are unable to form bonds with polar molecules like water so are not soluble in water. They will form dispersion forces with non-polar solvents like cyclohexane so are soluble in non-polar solvents.

7 Alkanes, alkenes and alkynes are all non-polar hydrocarbon molecules with similar shapes and structures. They form the same bonds (dispersion forces) so will have similar physical properties, including melting and boiling points, and solubility.

8

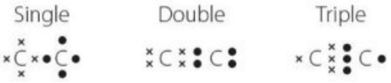


As the molecular weight of an alkane increases, the boiling point will also increase. As an alkane molecule increases in size, it is able to form more dispersion forces due to having more atoms in the molecule. With more dispersion forces between molecules, more energy is required to break these forces, resulting in a higher boiling point.

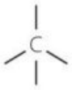
Chapter review questions

1 Carbon bonds readily to other carbon atoms, giving it the ability to form a wide range of structures including chains, rings and branched structures.

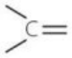
2



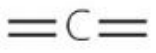
3 **a** Tetrahedral



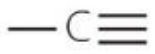
b Planar



c Linear



d Linear



4 Saturated compounds have only carbon–carbon single bonds within the molecule. Alkanes like methane and butane are saturated compounds. Unsaturated compounds have at least one double or triple carbon–carbon bond within the molecule. Alkenes like propene, and alkynes like pentyne, are unsaturated.

5 Aromatic compounds contain the benzene structure within the molecule and include benzene and phenolphthalein. Aliphatic compounds are hydrocarbons without a benzene molecule and include alkanes, alkenes and alkynes.

6

	Alkane	**Alkene**	**Alkyne**
General formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}

Carbon number	Alkane	
1	CH_4	CH_4
2	C_2H_6	$CH_3{-}CH_3$
3	C_3H_8	$CH_3{-}CH_2{-}CH_3$
4	C_4H_{10}	$CH_3{-}CH_2{-}CH_2{-}CH_3$
5	C_5H_{12}	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

Carbon number	Alkene	
2	C_2H_4	$CH_2{=}CH_2$
3	C_3H_6	$CH_2{=}CH{-}CH_3$
4	C_4H_8	$CH_2{=}CH{-}CH_2{-}CH_3$
5	C_5H_{10}	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$
6	C_6H_{12}	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

Carbon number	Alkyne	
2	C_2H_2	$CH{\equiv}CH$
3	C_3H_4	$CH{\equiv}C{-}CH_3$
4	C_4H_6	$CH{\equiv}C{-}CH_2{-}CH_3$
5	C_5H_8	$CH{\equiv}C{-}CH_2{-}CH_2{-}CH_3$
6	C_6H_{10}	$CH{\equiv}C{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

7 **a** 2-methylbutane

b 4-ethyl-2,3,3-trimethylhexane

c 2-pentene

d 2,4,4-trimethyl-2-pentene

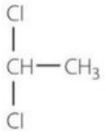
e 3,5-dimethyl-1-hexyne

f 4-methyl-2-hexyne

g 1,2-dichloro-3,3-difluoropentane

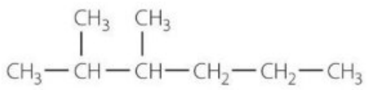
h 1,1,4-trichloro-1,2,4-trifluoro-2-heptene

8 **a**



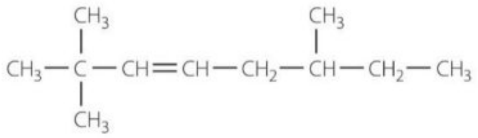
$\overset{Cl}{\underset{Cl}{CH}}-CH_3$

b



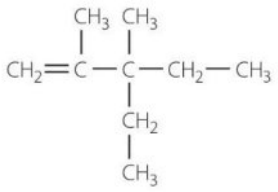
$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2-CH_2-CH_3$

c



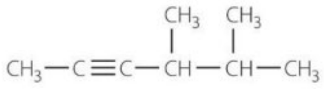
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH-CH_2-\overset{CH_3}{CH}-CH_2-CH_3$

d



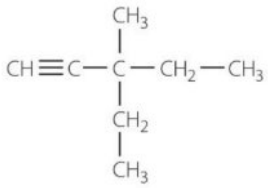
$CH_2=\overset{CH_3}{C}-\overset{CH_3}{\underset{\underset{CH_3}{CH_2}}{C}}-CH_2-CH_3$

e



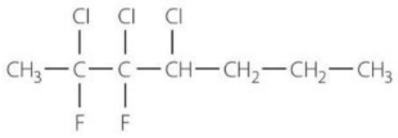
$CH_3-C\equiv C-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$

f



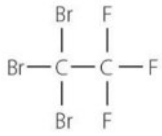
$CH\equiv C-\overset{CH_3}{\underset{\underset{CH_3}{CH_2}}{C}}-CH_2-CH_3$

g



$CH_3-\overset{Cl}{\underset{F}{C}}-\overset{Cl}{\underset{F}{C}}-\overset{Cl}{CH}-CH_2-CH_2-CH_3$

h

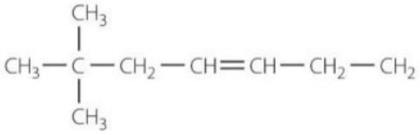


$Br-\overset{Br}{\underset{Br}{C}}-\overset{F}{\underset{F}{C}}-F$

9 **a** The position of the double bond should be indicated with the smallest number possible. Correct name: 1-hexene.

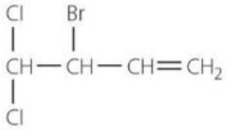
$CH_3-CH_2-CH_2-CH_2-CH=CH_2$

b The position of the double bond should be indicated with the smallest number possible. Correct name: 6,6-dimethyl-3-heptene.



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH=CH-CH_2-CH_2$

c The position of the double bond should be indicated with the smallest number possible. Bromo should come before chloro in the naming of substituents. Correct name: 3-bromo-4,4-dichloro-1-butene.



$\underset{Cl}{\overset{Cl}{CH}}-\overset{Br}{CH}-CH=CH_2$

10 **a** No – same exact molecule (both 2-methylbutane)

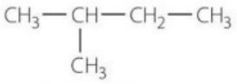
b Yes (2-methylpentane and 3-methylpentane)

c No – same exact molecule (both 3-methylpentane)

d Yes (2,3-dimethylpentane and 2,4-dimethylpentane)

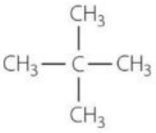
11 **a** $CH_3-CH_2-CH_2-CH_2-CH_3$

Pentane



$CH_3-\underset{CH_3}{CH}-CH_2-CH_3$

2-methyl butane

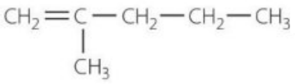


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

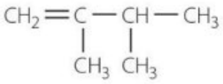
2,2-dimethylpropane

b

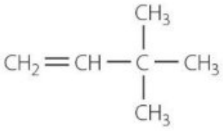
$CH_2=CH-CH_2-CH_2-CH_2-CH_3$ 1-hexene



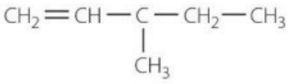
$CH_2=\underset{CH_3}{C}-CH_2-CH_2-CH_3$ 2-methyl-1-pentene



$CH_2=\underset{CH_3}{C}-\underset{CH_3}{CH}-CH_3$ 2,3-dimethyl-1-butene

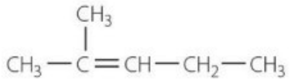


$CH_2=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ 3,3-dimethyl-1-butene

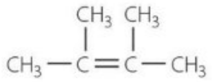


$CH_2=CH-\underset{CH_3}{C}-CH_2-CH_3$ 3-methyl-1-pentene

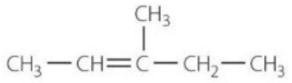
c $CH_3-CH=CH-CH_2-CH_2-CH_3$ 2-hexene



$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3$ 2-methyl-2-pentene



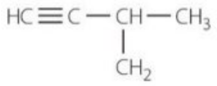
$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$ 2,3-dimethyl-2-butene



$CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$ 3-methyl-2-pentene

d

$HC\equiv C-CH_2-CH_2-CH_3$ 1-pentyne

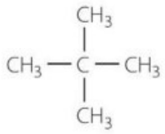


$HC\equiv C-\underset{\underset{CH_2}{|}}{CH}-CH_3$ 3-methyl-1-butyne

12 Position isomers have a functional group like a double bond at different points on the main chain. An example of position isomers is 1-butene and 2-butene. Chain isomers rearrange the carbon skeleton (for example, butane and 2-methylpropane are chain isomers).

13 **a** Chain isomers

b $CH_3-CH_2-CH_2-CH_2-CH_3$



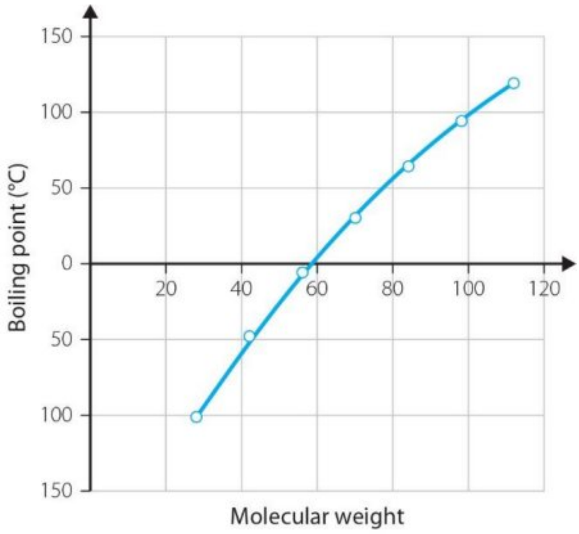
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

c Pentane will have a higher boiling point. Since the molecule is more linear than 2,2-dimethylpropane, it will be able to form more dispersion forces with other molecules. More dispersion forces require more energy to break, resulting in a higher boiling point.

14 **a**

Alkene	Molecular weight
Ethene	28.052
Propene	42.078
1-butene	56.104
1-pentene	70.130
1-hexene	84.156
1-heptene	98.182
1-octene	112.208

b



c As the molecular weight of the alkane increases, the boiling point also increases.

d As the molecular weight of an alkane increases, the boiling point will also increase. As an alkane molecule increases in size, it is able to form more dispersion forces due to having more atoms in the molecule. With more dispersion forces between molecules, more energy is required to break these forces, resulting in a higher boiling point.

15 a Compound Z, Compound X, Compound Y

b If compounds are from the same homologous series, then boiling point will increase with increasing molecular weight due to increased dispersion forces forming between larger molecules. More dispersion forces require more energy to break, resulting in a higher boiling point.

16 No. Hydrocarbons are non-polar molecules that have no dipole charge or ionic charge so are unable to conduct electricity.

Module 7: Organic chemistry

Chapter 9: Functional group compounds

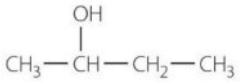
Worked example 9.1

1 3-methyl-3-pentanol

2 3-methyl-2-butanol

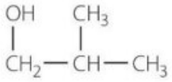
Worked example 9.2

1 Chain isomer – 2-butanol



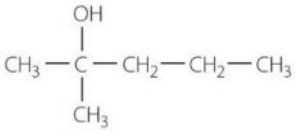
$CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_3$

Position isomer – 2-methyl-1-butanol



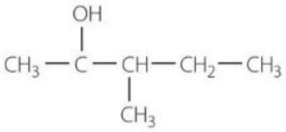
$\overset{\overset{OH}{|}}{CH_2}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

2



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_2-CH_3$

2-methyl-2-pentanol



$CH_3-\overset{\overset{OH}{|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

3-methyl-2-pentanol

Check your understanding 9.1/9.2a

1 A functional group is a group of atoms in a specific arrangement in a molecule. A homologous series contains the same functional group that defines the chemical properties of the group. Examples of functional groups include the alcohol or hydroxyl (—OH) or the carboxylic acid group (—COOH).

2 Alcoholic drinks, additive to petrol, as an industrial solvent

3 The alcohol group is called the hydroxyl group and is represented by —OH.

4 General formula: $C_nH_{2n+1}OH$

3 carbons: C_3H_7OH

6 carbons: $C_6H_{13}OH$

8 carbons: $C_8H_{17}OH$

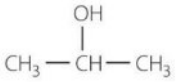
5 **a** 2-butanol

b 2,3-dimethyl-1-butanol

c 2,2-dimethyl-1-butanol

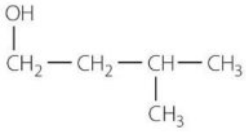
d 3-ethyl-2,3-dimethyl-2-hexanol

6 **a**



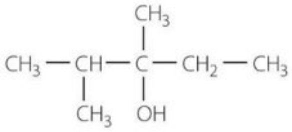
$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$

b



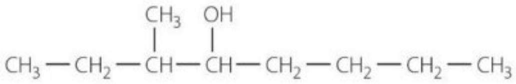
$\overset{\overset{OH}{|}}{CH_2}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

c



$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CH_3$

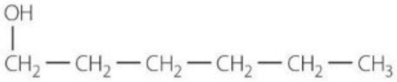
d



$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$

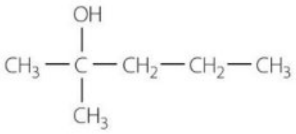
7 **a** Since the only difference is the position of the hydroxyl functional group, they are positional isomers.

b 1-hexanol



$\overset{\overset{OH}{|}}{CH_2}-CH_2-CH_2-CH_2-CH_2-CH_3$

c 2-methyl-2-pentanol



$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-CH_3$

8 A primary alcohol has only one carbon attached to the carbon bearing the hydroxyl functional group. This means the hydroxyl group is attached to the first carbon. 1-propanol and 1-butanol are primary alcohols. Alcohols like 2-butanol and 3 hexanol are secondary alcohols since the hydroxyl carbon is attached to two other carbons. 2-methyl-2-pentanol is a tertiary alcohol since the hydroxyl carbon is attached to three other carbons.

9 **Question 5**: **a** secondary; **b** primary; **c** primary; **d** tertiary

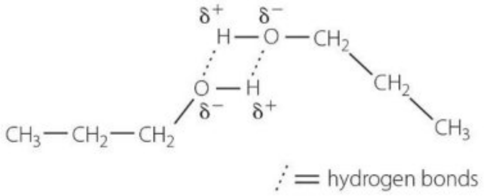
Question 6: **a** secondary; **b** primary; **c** tertiary; **d** secondary

Check your understanding 9.2b

1 Butane (C_4H_{10}) has molecular weight 58.12, while 1-butanol (C_4H_9OH) has molecular weight 74.12. While they both have 4 carbons, the number of electrons and atoms, and the type of atom, differs; this will cause the molecules to have different shapes and ability to form intermolecular bonds. Since physical properties like boiling point and solubility depend on the formation of intermolecular bonds, it is more appropriate to compare molecules with similar molecular weight.

2 The hydroxyl group can form hydrogen bonds between alcohol molecules and with water due to the highly electronegative oxygen causing the formation of very polar bonds. Formation of hydrogen bonds between molecules affects boiling points, while hydrogen bonding to water affects solubility.

3



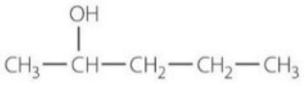
4 Alkenes, alkanes and alkynes can only form dispersion forces between molecules. Alcohols of similar size will form similar dispersion forces between molecules but can also form hydrogen bonds between polar hydroxyl functional groups on different molecules. Hydrogen bonds are significantly stronger than dispersion forces so require more heat energy to weaken or break. Thus, higher temperatures are needed to break the intermolecular forces, so the boiling point is higher for alcohols than simple hydrocarbons.

5 a Solubility of alcohols depends on the balance between the insolubility of the non-polar hydrocarbon chain that cannot form hydrogen bonds with water, and the polar hydroxyl group that forms hydrogen bonds with water. In smaller molecules, the effect of the polar hydroxyl group outweighs the effect of the non-polar hydrocarbon chain, so the molecule overall is water soluble.

b As the chain gets longer, the effect of the non-polar hydrocarbon chain begins to outweigh the effect of the polar hydroxyl group, resulting in decreased solubility. Long chain alcohols are insoluble in water.

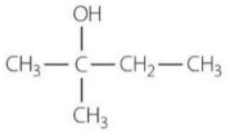
6 Large molecules like glucose can be soluble in water if they have multiple hydroxyl groups, each forming hydrogen bonds with water. The combined effect of the multiple groups can outweigh the effect of a larger hydrocarbon chain, causing the molecule to be water soluble.

7 a



$CH_3-\overset{\displaystyle OH}{\overset{|}{C}}H-CH_2-CH_2-CH_3$

2-pentanol



$CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-CH_2-CH_3$

2-methyl-2-butanol

b 1-pentanol and 2-pentanol would have similar boiling points since they have a similar structure and shape. 2-methyl-2-butanol would have a lower boiling point since its more condensed overall shape would not allow for as many dispersion forces to form between molecules, requiring less heat energy to overcome the secondary forces, lowering the boiling point.

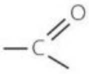
Worked example 9.3

1 2-methylpropanal

2 3,3,4-trimethyl-2-pentanone

Check your understanding 9.3

1 A carbonyl functional group contains an oxygen double-bonded to a carbon. This group can be at the end of a carbon chain (aldehyde) or in the middle of a carbon chain (ketone).



2 Aldehydes have the carbonyl group at the end of a chain, on a terminal carbon. Ketones have the carbonyl group on a non-terminal carbon, in the middle of a chain.

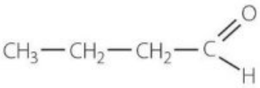
3 **a** 2-methylbutanal

b 4-ethyl-2,5-dimethylhexanal

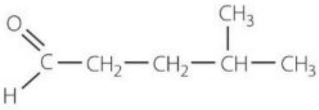
c 3-ethyl-4-methyl-2-pentanone

d 3-methyl-2-butanone

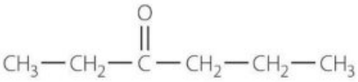
4 **a**



b

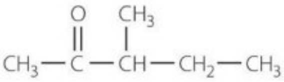


c



$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3$

d



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$

5 The carbonyl group is polar due to the highly electronegative oxygen atom. The carbonyl group forms a negative dipole on the oxygen, allowing for the formation of dipole–dipole bonds between aldehyde and ketone molecules.

6 **a** 1-propanol 60.094 g mol^{-1}, butane 58.12 g mol^{-1}, propanal 58.078 g mol^{-1}. Since the molecular weights are so close, any intermolecular bonding formed will be quite similar due to size and number of electrons, so these molecules can be validly compared.

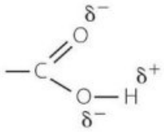
b Butane → propanal → 1-propanol. Butane has only weak dispersion forces between molecules due to the non-polar nature of the hydrocarbon chain. Propanal forms dipole–dipole forces between molecules due to the polar carbonyl group, while 1-propanol forms hydrogen bonds between molecules due to the very polar hydroxyl group. Hydrogen bonds are stronger than dipole–dipole forces, which are stronger than dispersion forces. Stronger bonds require more heat energy to break, so 1-propanol has the highest boiling point, while butane has the lowest.

7 Solubility of aldehydes depends on the balance between the insolubility of the non-polar hydrocarbon chain that cannot form hydrogen bonds with water, and the polar carbonyl group that forms bonds to water. In smaller molecules, the effect of the carbonyl group outweighs the effect of the non-polar hydrocarbon chain, so the molecule overall is water soluble. Larger aldehydes are not soluble since the non-polar hydrocarbon chain has the stronger effect.

8 Alcohols have a hydroxyl group that can form hydrogen bonds to water. Aldehydes do not form hydrogen bonds to water, although they have some attraction to water molecules due to the polar nature of the carbonyl group. Alcohols are thus more soluble in water than aldehydes of similar size due to formation of stronger bonds with water molecules.

Check your understanding 9.4

1



2 **a** The IUPAC name is a systematic name based on its structure that is used by scientists. Each IUPAC organic name is unique and identifies a single molecule.

b One carbon – methanoic acid (IUPAC)/formaldehyde (common)

Two carbons – ethanoic acid (IUPAC)/acetic acid (common)

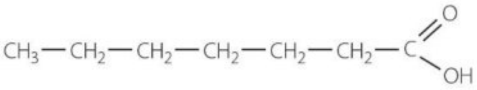
Three carbons – propanoic acid (IUPAC)/propionic acid (common)

3 **a** 2,3-diemthylpentanoic acid

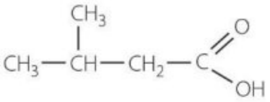
b 2-methylpropanoic acid

c 3-ethyl-4,4-dimethylhexanoic acid

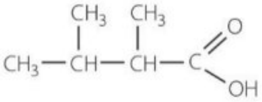
4 **a**



b



c

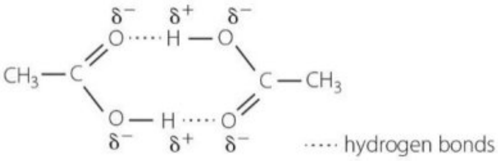


5 As the chain length increases, the number of dispersion forces between molecules increases. More dispersion forces increase the amount of heat energy needed to overcome the secondary forces, resulting in an increased boiling point.

6 **a b c**

Molecule	Homologous series	Functional group name	Intermolecular bonding	Rank boiling point (1 lowest, 5 highest)
1-pentanol	alcohol	hydroxyl	hydrogen bonds	4
Pentanal	aldehyde	carbonyl	dipole–dipole forces	3
Hexane	alkane	NA	dispersion forces	1
Pentanoic acid	carboxylic acids	carboxyl	hydrogen bonds and dipole–dipole forces	5
2-pentanone	ketones	carbonyl	dipole–dipole forces	2

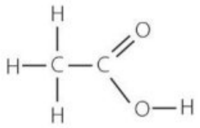
7

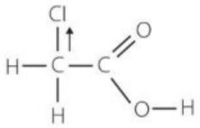


8 The carboxyl group can form hydrogen bonds with water due to its polarity. When the non-polar hydrocarbon chain is small, the carboxyl group outweighs its insoluble effect, so the molecule overall is soluble.

9 Octanoic acid has a much larger hydrocarbon chain than propanoic acid (8 C versus 3 C). In octanoic acid, the non-polar hydrocarbon chain has a much greater effect on the overall solubility than in propanoic acid. Hence, the shorter chain carboxylic acid is more soluble.

10 As seen in the diagram below, chloroethanoic acid has a chlorine substituted for a hydrogen atom in an ethanoic acid molecule. The chlorine atom is more electronegative than the hydrogen atom, so it is a stronger attractor of electrons. This weakens the OH bond and makes it easier to form H^+ ions. A stronger acid will form H^+ ions more easily, so chloroethane is a stronger acid than ethanoic acid.





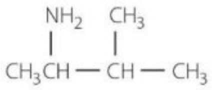
Worked example 9.4

1 Methylpropanamine

2 2,3-dimethyl-2-butanamine

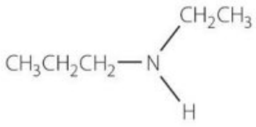
Worked example 9.5

1



$CH_3\overset{NH_2}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$

2



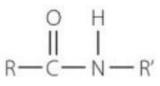
Check your understanding 9.5

1

Amine

$R-NH_2$

Amide



$R-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R'$

2 An amine group (—NH_2) is added to a carboxylic acid to form an amide (—$CONH_2$).

3 a 1-propanamine (primary)

b Triethanamine (tertiary)

c 3-methyl-2-butanamine (primary)

d Ethanamide (primary)

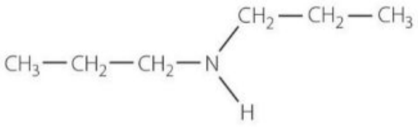
e N-methylethanamide (secondary)

f N-propylpropanamide (secondary)

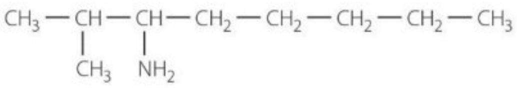
4 **a**

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$

b

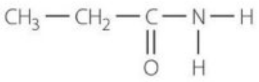


c



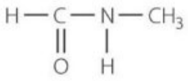
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle NH_2}{|}}{CH}-CH_2-CH_2-CH_2-CH_2-CH_3$

d



$CH_3-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-H$

e



$H-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-CH_3$

5 Both amines and amides have very polar functional groups that can form hydrogen bonds between molecules. Since hydrogen bonds are the strongest intermolecular forces, they require high amounts of heat energy to weaken or break, so amines and amides have relatively high melting and boiling points.

6 **a** Tertiary amines do not have an N—H group so do not form hydrogen bonds with water.

b To form an amide, the N of the amine must have a hydrogen attached that can be removed to attach the amine molecule to the carboxylic acid molecule. Tertiary amines do not have a hydrogen attached to the nitrogen, so they cannot form amides.

c The lack of N—H group reduces its ability to form strong intermolecular bonds compared to primary and secondary amines. Weaker bonds mean less heat energy is needed to weaken or break them, resulting in lower boiling points.

7 As the molecule becomes larger, the effect of the non-polar hydrocarbon chain outweighs the effect of the polar functional group's ability to form hydrogen bonds with water. The non-polar hydrocarbon chain cannot form hydrogen bonds with water, so this makes the larger molecules insoluble.

8 Primary and secondary amides have two polar bonds (C=O and N—H) that can form bonds between amide molecules or form bonds with water. The N—H group in particular can form hydrogen bonds with water, affecting the solubility of the molecule. Tertiary amides only have a C=O group since the nitrogen atom is bound to three carbon atoms. This gives tertiary amides one less polar group, affecting its ability to bond with other amide molecules (boiling point) and no ability to form hydrogen bonds with water (solubility).

Chapter review questions

1 **a** Hydroxyl

b Carboxyl

c Amine

d Ester

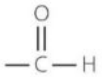
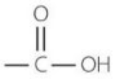
e Carbonyl

f Carbonyl

g Amide

2 The R group represents a generic molecule. The R group can be a hydrogen atom (in some situations only), a carbon chain, carbon ring or aromatic structure.

3

Group	Functional group	Structure	General formula
Alcohol	hydroxyl	—OH	$C_nH_{2n+1}OH$
Aldehyde	carbonyl	 $-\overset{\overset{\displaystyle O}{\Vert}}{C}-H$	$C_nH_{2n}O$
Ketone	carbonyl	 $-\overset{\overset{\displaystyle O}{\Vert}}{C}-$	$C_nH_{2n}O$
Carboxylic acid	carboxyl	 $-\overset{\overset{\displaystyle O}{\Vert}}{C}-OH$	$C_nH_{2n}O_2$

4 Amines contain an $—NH_2$ group, while amides contain the —CONH— functional group and are formed from amides and carboxylic acids. Both primary and secondary amines and amides have higher boiling points and better solubility than tertiary amines and amides due to the lack of N—H bond in tertiary compounds. Amides have a stronger polar functional group than amines, so amides will have higher boiling points and better solubility than amines of similar size.

5 **a** Alcohol: 2-butanol

b Amide: N-methylethanamide

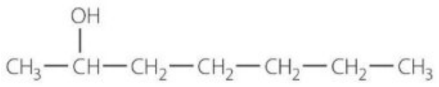
c Carboxylic acid: propanoic acid

d Amine: propanamine

e Ketone: 5-ethyl-3-heptanone

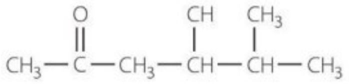
f Alcohol: 3-methyl-3-pentanol

6 **a**



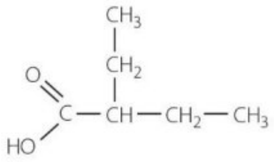
$$\mathrm{CH_3{-}\overset{\displaystyle OH}{\overset{|}{C}}H{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

b

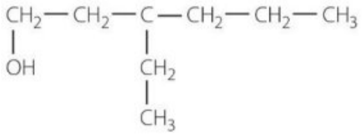


$$\mathrm{CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3{-}\overset{\displaystyle CH}{\overset{|}{C}}H{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}CH_3}$$

c

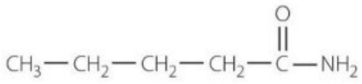


d



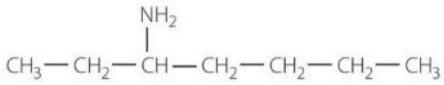
$$\mathrm{\underset{\underset{\displaystyle OH}{|}}{CH_2}{-}CH_2{-}\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{CH_2}}{|}}{C}{-}CH_2{-}CH_2{-}CH_3}$$

e



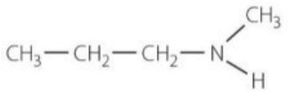
$$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2}$$

f

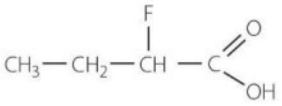


$$\mathrm{CH_3{-}CH_2{-}\overset{\displaystyle NH_2}{\overset{|}{C}}H{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

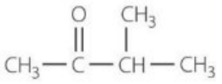
g Please note, this is a structure for methylpropane. The question will be corrected in the textbook at the next reprint.



h This structure is 2-flurobutanoic acid. The question will be correct in the text book at the next reprint.



i

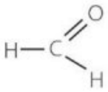


$$\mathrm{CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}CH_3}$$

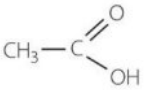
7 Alcohol: ethanol (IUPAC)/ethyl alcohol (common)

$CH_3—CH_2—OH$

Aldehyde: methanal (IUPAC)/formaldehyde (common)



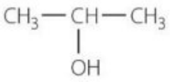
Carboxylic acid: ethanoic acid (IUPAC)/acetic acid (common)



8 **a**

$CH_3—CH_2—CH_2—OH$

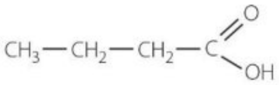
1-propanol



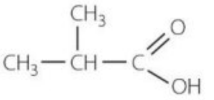
$CH_3—CH(OH)—CH_3$

2-propanol

b



Butanoic acid



2-methyl propanoic acid

9 **a** Alkanes have dispersion forces between molecules, alcohols have hydrogen bonds and dispersion forces between molecules. The hydrogen bonds in alcohols are much stronger than the dispersion forces in alkanes and require more heat energy to weaken or break. Thus, alcohols have higher boiling points than alkanes.

b Carboxylic acids have a carboxyl group with the ability to form hydrogen bonds to other carboxylic acid molecules. These hydrogen bonds are much stronger than the dipole–dipole bonds formed between aldehyde molecules. More heat energy is required to break or weaken hydrogen bonds than dipole–dipole bonds, so carboxylic acids have a higher boiling point than aldehydes.

c Alcohols form hydrogen bonds between molecules. These hydrogen bonds are much stronger than the dipole–dipole bonds formed between aldehyde molecules so require more heat energy to break or weaken. Thus, alcohols have a higher boiling point than aldehydes.

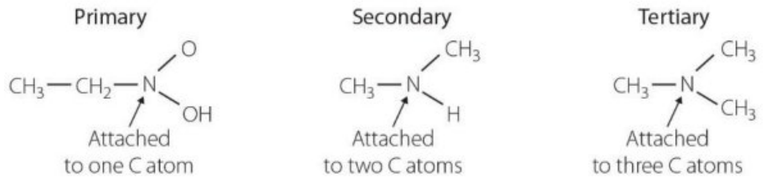
d Amines and amides both form hydrogen bonds between molecules due to the N—H group, but amides also have a C=O group that can form strong intermolecular forces between amide molecules. Thus, more heat energy is required to break or weaken bonds between amide molecules and they have higher boiling points than amides.

10 **a** Chain isomers involve the rearranging of the carbon skeleton. For example, 2-butanol and 2-methyl-2-propanol are chain isomers. Positional isomers change the location of the functional group. Aldehydes and carboxylic acids do not have positional isomers. In ketones, 2-hexanone and 3-hexanone would be examples of positional isomers.

b A functional group isomer is when two different functional groups give the same molecular formula. Aldehydes and ketones are different functional groups but have the same molecular formula for molecules with the same number of carbons.

11 A primary alcohol has only one carbon attached to the carbon bearing the hydroxyl functional group. This means the hydroxyl group is attached to the first carbon. 1-pentanol is a primary alcohol. Alcohols like 2-pentanol are secondary alcohols as the hydroxyl carbon is attached to two other carbons. 2-methyl-2-propanol is a tertiary alcohol since the hydroxyl carbon is attached to three other carbons.

12 **a**



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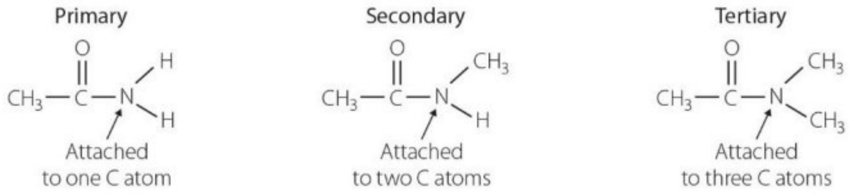
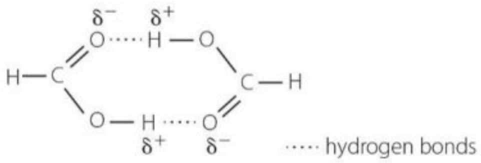


13 Glucose has multiple hydroxyl groups giving the overall molecule more opportunities to form hydrogen bonds with water. Formation of extra hydrogen bonds overcomes the non-polar insoluble effect of the large hydrocarbon structure.

14 As chain length increases, the influence of the non-polar hydrocarbon chain compared to the polar functional group increases. Since the chain cannot form hydrogen bonds to water, it is insoluble. As the chain increases in length, the overall molecule becomes less soluble.

15 As chain length increases, the number of dispersion forces between molecules increases. This increases the strength of the overall intermolecular forces between molecules. More heat energy is required to break these forces, giving a higher boiling point as the chain length increases.

16 Carboxylic acid molecules can form a dimer where the C=O of one molecule bonds to the O—H of a second molecule. The C=O of the second molecule bonds to the O—H of the first molecule.

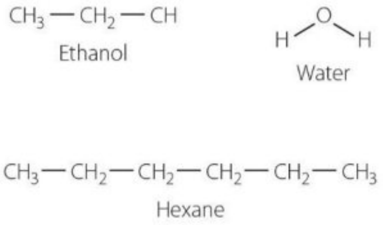


17 Chloroethanoic acid has a chlorine substituted for a hydrogen atom in an ethanoic acid molecule. The chlorine atom is more electronegative than the hydrogen atom so is a stronger attractor of electrons. This weakens the OH bond and makes it easier to form H^+ ions. A stronger acid will form H^+ ions more easily, so chloroethane is a stronger acid than ethanoic acid.

18 Citric acid has a higher ionisation than ethanoic acid so produces more hydrogen ions for the same concentration of acid. Since hydrogen ions are a measure of acidity, citric acid is 'more acidic'.

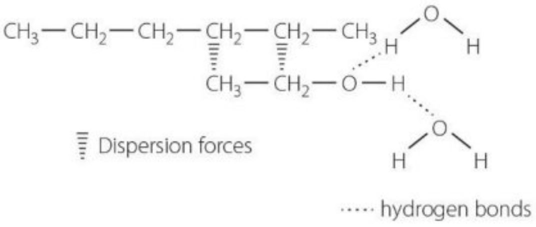
19 Primary and secondary amides have two polar bonds (C=O and N—H) that can form bonds between amide molecules or form bonds with water. The N—H group in particular can form hydrogen bonds with water, affecting solubility of the molecule. Tertiary amides only have a C=O group since the nitrogen atom is bound to three carbon atoms. This gives tertiary amides one less polar group, affecting its ability to bond with other amide molecules (boiling point) and no ability to form hydrogen bonds with water (solubility).

20 a Ethanol has a non-polar component (hydrocarbon chain) and a polar hydroxyl functional group. Water is polar since it has a net dipole. Hexane is a non-polar molecule.



b For substances to dissolve, they need to form the same bonds. Water forms hydrogen bonds; hexane forms dispersion forces. Thus, they do not bond to each other and will not dissolve in each other.

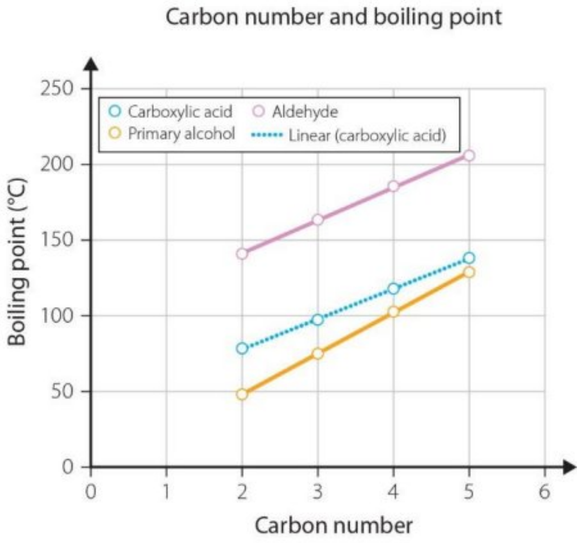
c As seen in the diagram below, the non-polar hydrocarbon chain of ethanol will form dispersion forces with hexane, while the polar hydroxyl group will form hydrogen bonds with water.



d Ethanol very useful in industry since it can dissolve both polar and non-polar substances, removing the need to have two different solvents.

21 Ethanoic acid will have the highest boiling point (118°C) since it has the most polar functional group with both the C=O and —OH parts forming strong intermolecular bonds to other carboxylic acid molecules. 1-propanol will have the middle boiling point (97°C) since it can form hydrogen bonds with its hydroxyl group. Overall, the bonding between alcohol molecules is not as strong as between carboxylic acid molecules. Propanone has the lowest boiling point (56°C) since it only forms dipole–dipole forces between molecules. Stronger bonds require more heat energy to break, so this results in a higher boiling point.

22 **a**



b Carboxylic acids have higher boiling points than primary alcohols, which are higher again than aldehydes. This is due to the increasing strength of the intermolecular forces. Aldehydes have the weakest intermolecular forces, so the lowest boiling point. Carboxylic acids have the strongest intermolecular forces, so the highest boiling point.

All groups increase in boiling point as the carbon number increases. This is due to increased dispersion forces between longer chain molecules increasing the overall strength of intermolecular forces and giving a higher boiling point.

c Ketone – about the same, maybe slightly below the aldehydes. Ketone and amine share the same carbonyl group, so will have very similar strength intermolecular forces.

Amine – around the same as primary alcohol. Both have polar groups that form hydrogen bonds and, thus, their intermolecular forces will be around the same strength.

d Since number of carbons does not equate to molecule size, this is not the most valid comparison. Carboxylic acids have significantly higher molecular weight than other compounds with the same number of carbons. This affects the formation of dispersion forces, giving two ways to change the physical properties between groups. It is, thus, not valid to say that carbon number alone is the determining factor.

Module 7: Organic chemistry

Chapter 10: Hydrocarbon reactions

Check your understanding 10.1

1 Ethanal (IUPAC)/acetaldehyde (common); benzene (IUPAC)/coal naptha (common); propanone (IUPAC)/acetone (common)

2 Chemical labels should include the chemical name, concentration (if a solution) and possible hazards of use.

3 **a** A SDS records the correct IUPAC name of the chemical as well as common names, so even if labelled with common names people know what they are using and handling.

b A SDS contains steps for safe use, as well as possible harmful consequences of contact or ingestion of the chemicals. It also outlines first aid treatment for the chemical in question.

4 Volatility – ease with which a vapour will form. Vapours are easily ingested and can cause medical issues. Flashpoint – lowest temperature at which a liquid forms an ignitable mixture in air near the surface of the liquid. Since many organic chemicals have a very low flashpoint, they are easily ignited and very flammable. Highly reactive – most organic compounds are highly reactive, so will react with substances in the air, water or other chemicals, potentially causing a dangerous product to form.

5 Contact effects – occur through absorption via the skin – the solvent dissolves fat in the tissue, allowing the chemicals to enter the bloodstream and travel to the organs. Symptoms include burning or tingling skin, welts and rashes, or chemical burns.

Acute poisoning – occurs immediately or a few hours after contact. Commonly due to exposure to organic vapours. Symptoms include headaches, nausea, dizziness, poor coordination and loss of consciousness.

Chronic poisoning – occurs after repeated exposure, usually over years or decades. Symptoms include chronic fatigue, physical weakness, mood changes, organ damage and nervous system damage.

6 Elimination or substitution of harmful chemicals. Industries have replaced harmful chemicals with less harmful options that do the same job.

Isolation from chemical contact. This can be done with physical barriers, or use of lab coat, glasses and gloves to prevent chemical contact.

Ventilation to remove harmful vapours. This can be done with fume cupboards or extractor fans.

7 **a** Inhalation of vapours. Skin contact. Chemicals igniting near a heat source.

b Inhalation – use a fume cupboard where possible, otherwise open windows and use fans if possible.

Skin contact – use gloves, lab coats and glasses.

Chemicals igniting – keep chemicals contained and covered with lids on containers. Keep chemicals away from heat sources unless necessary.

8 Organic chemicals should never be washed down a sink since they will end up in local waterways and poison animals and plants. Organic waste is collected and treated then disposed of by commercial operators.

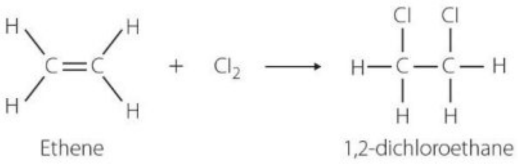
9 **a** 1-butanol has a higher flashpoint (above room temperature) than ethanol (below room temperature). Hence, ethanol will easily form an ignitable mixture at room temperature, while 1-butanol will be less likely to form an ignitable mixture and is thus safer to use.

b Ethanoic acid has a high flashpoint and is less likely to evaporate at room temperature than hexane. Hexane is easily evaporated and will form vapours that could be inhaled and cause illness.

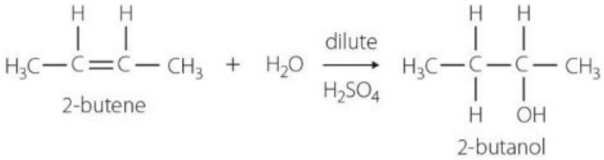
Check your understanding 10.2

1 **a** $C_5H_8(l) + 7O_2(g) \rightarrow 5CO_2(g) + 4H_2O(l)$

b



c



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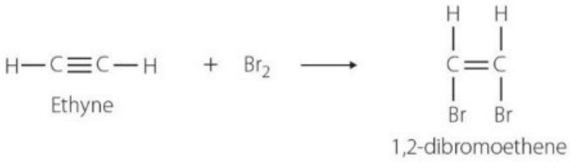


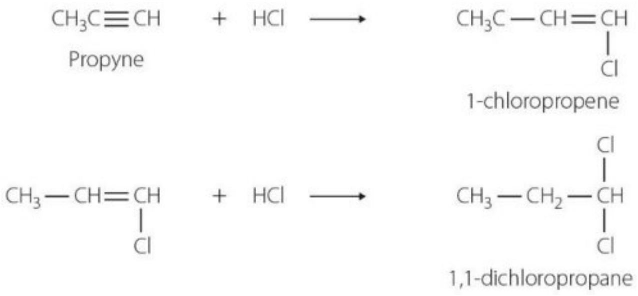
2 A metal catalyst works in the following steps.

- The metal catalyst breaks the bonds within the hydrogen molecule, forming weak metal–hydrogen bonds
- The alkene reacts with the metal catalyst, breaking the C=C double bond, forming weak metal–carbon bonds
- The metal catalyst causes the carbon and hydrogen atoms to join leaving the metal the same as initially

3 **a** Liquid oils have multiple double bonds in their hydrocarbon chains. Hydrogen gas is added with a nickel catalyst and heated. Sufficient hydrogen is added to add across some but not all of the double bonds. The final result is more saturated than the initial molecule and is known as margarine (a solid fat).

b Ethanol is an important industrial chemical, used as a solvent and in the manufacture of many products. Traditionally ethanol is produced by fermentation, but this process cannot produce the quantities required in industry. Production of ethanol from ethene is used to increase the quantities of ethanol that can be produced.

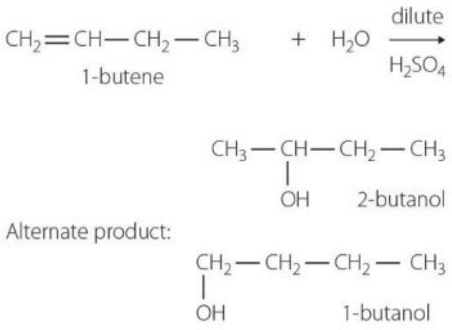
4 When a hydrogen halide (HCl) is added to an alkyne (propyne), the first step involves the triple bond being changed to a double bond as the H and Cl atoms add across the triple bond. In the second step, the chloroalkene (1-chloropropene) formed is added to more HCl to form a haloalkane (1,1-dichloropropane).



$$CH_3C{\equiv}CH + HCl \longrightarrow CH_3C{-}CH{=}CH(Cl)$$

$$CH_3{-}CH{=}CH(Cl) + HCl \longrightarrow CH_3{-}CH_2{-}CHCl_2$$

5



$$CH_2{=}CH{-}CH_2{-}CH_3 + H_2O \xrightarrow[H_2SO_4]{dilute} CH_3{-}CH(OH){-}CH_2{-}CH_3$$

Alternate product: $CH_2(OH){-}CH_2{-}CH_2{-}CH_3$

Water is an asymmetrical reagent (will add a H atom and an OH group across each side of the double bond). Markovnikov's rule states that the H atom will bond to the carbon that is already bonded to the largest number of carbon atoms (in this case the terminal carbon). This is the preferred option and gives a major product (2-butanol). A smaller amount of an alternate product (1-butanol) will also form.

6 Addition of water to an alkene forms an alcohol, while addition of water to an alkyne forms a ketone (except ethyne, which forms ethanal). Addition of water to an alkene requires the use of dilute sulfuric acid as a catalyst, while addition of water to an alkyne requires a catalyst of a mercury(II) compound and sulfuric acid.

Check your understanding 10.3

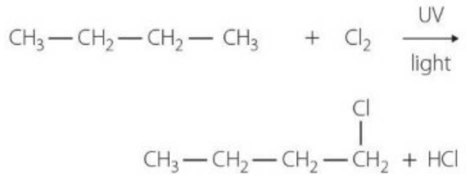
1 Halogens will add to alkanes without any extra conditions being required due to the reactivity of the double bond. Halogens will only add to alkanes under UV light due to the relative lack of reactivity of alkanes.

2 Addition reactions occur, so the two reactants add, and no atoms are left over. In a substitution reaction, one atom (usually hydrogen) in the organic molecule is replaced with another atom. There are atoms left over after a substitution reaction.

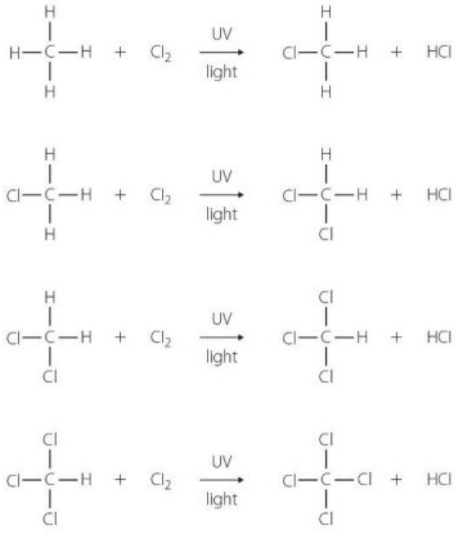
3 Complete combustion produces carbon dioxide and water and the maximum possible energy. Incomplete combustion produces carbon monoxide and/or carbon (soot) as well as water. The amount of energy released decreases as less oxygen is available.

4 **a** $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

b



c



5 Complete: $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

Incomplete: $C_4H_{10}(g) + \frac{9}{2}O_2(g) \rightarrow 4CO(g) + 5H_2O(l)$ OR

Incomplete: $C_4H_{10}(g) + \frac{5}{2}O_2(g) \rightarrow 4C(g) + 5H_2O(l)$

6 Carbon monoxide and carbon/soot both cause negative health consequences if inhaled/ingested. Carbon monoxide at low levels causes impaired judgement, dizziness and headaches. At higher levels, it can cause loss of consciousness and death. Soot particles can coat the lungs, preventing oxygen absorption. Soot particles can also carry molecules of fuel and other toxins into the body.

7 If the bromine is not decolourised, then the hydrocarbon does not have double bonds to react with the bromine; thus, it must be an alkane.

Check your understanding 10.4

1 Automobile fuels, plastic packaging, clothes fibres

2 a Crude oil is a mixture of hydrocarbons that is separated by fractional distillation. The property used is the different boiling points of the hydrocarbons in the mixture. The crude oil is heated to a gas then it rises up the fractionating tower, condensing at different levels that are set at different temperatures.

b Heavier fractions condense at higher temperatures, which are lower down in the tower. Kerosene will condense lower down than petrol.

3 Both catalytic and thermal cracking are used to convert less useful long chain hydrocarbons into more useful smaller molecules. Catalytic cracking uses a zeolite (aluminosilicate) catalyst, moderate temperatures and low pressure to convert the hydrocarbons while thermal cracking uses higher temperatures and pressures, but no catalyst to achieve the same outcome.

4 Environmental: issues arise from release of carbon dioxide (the enhanced greenhouse effect and associated problems) and from oil spills. Oil spills cause animal death, and destruction of plant life and ecosystems for years after the spills. The enhanced greenhouse effect has caused loss of sea ice, rising sea levels and increased ocean acidification, which is destroying corals and affecting the breeding of other sea life.

Economic: oil spills result in loss of tourism, fishing and other businesses in areas where the oil spills have occurred. There are economic consequences from the enhanced greenhouse effect as temperatures rise and there are more frequent severe weather effects.

Social: oil spills cause psychological stress to residents through loss of income and negative economic consequences. The enhanced greenhouse effect will cause refugees through loss of land as sea levels rise. There is also significant stress associated with more frequent severe weather effects.

5 A greenhouse gas is an atmospheric gas that absorbs and traps infrared radiation in the atmosphere. Greenhouse gases include carbon dioxide and methane.

6 The increased emission of carbon dioxide correlates with increases in global temperatures. Levels of carbon dioxide are currently the highest on record, and recent times has also seen the hottest years in recorded history.

7 Loss of sea ice and resulting increase in sea levels. This has reduced hunting grounds for some species of animals like polar bears and they are currently facing extinction. Rising sea levels will see a loss of land in highly populated areas including the Asian subcontinent.

Increased ocean acidification is seeing a decline in the health of coral reefs.

Increased carbon dioxide levels is resulting in a rise in global temperatures, affecting weather patterns and creating more frequent and severe weather events.

8 Emitted gases from power station is captured and passed through a liquid amine that absorbs the carbon dioxide. The rest of the gases pass through and are released with up to 80% less carbon dioxide than the initial gas. The carbon dioxide is stored underground in geological features in a process called sequestration.

9 a The increased convenience, availability and cheap nature of polymers is causing large amounts to be used by society. Much of this is not recycled and goes into landfill where it takes hundreds of years to break down, and when it does it releases toxic chemicals into the environment. Much of our plastic waste ends up in the ocean where it does not break down easily and is eaten by aquatic life.

b Recycling uses less energy than making new polymers, so local councils and governments encourage householders to recycle polymers. Polymers are labelled with their composition to help people sort recyclable polymers from non-recyclable ones.

Chapter review questions

1 A SDS contains information about IUPAC naming and common names for clear identification of a chemical. It outlines properties, hazards, precautions for safe handling and first aid steps to be taken if an issue occurs.

2 Many organic substances have a variety of common names. Due to the possible hazards of dealing with all organic chemicals, it is important that people know exactly what they are working with and how to use the chemical safely.

3 Volatile – ease with which an organic substance will evaporate and form a vapour.
Flashpoint – temperature at which an organic liquid will form an ignitable mixture in air near the surface of the liquid.

Volatility (evaporation) does not necessarily create an ignitable mixture.

4 More volatile chemicals will form vapours, often at room temperature. When using volatile chemicals, a fume cupboard should be used if available, otherwise use in a well-ventilated area and keep containers covered where possible. Organic chemicals with a low flashpoint could ignite if placed near a heat source. All organic chemicals should be kept away from

any heat sources unless they are directly being heated. Use of heat with organic chemicals should be closely monitored.

5 Inhalation involves breathing in vapours. When the vapours hit the lungs, they dissolve through the walls and enter the bloodstream, travelling to the organs where they can deposit and build-up over time.

Ingestion involves swallowing chemicals that pass through the stomach wall and into the bloodstream.

Absorption occurs through skin contact where the organic chemicals dissolve through the skin and enter the bloodstream.

6 Acute poisoning – occurs immediately or a few hours after contact. Commonly due to exposure to organic vapours and subsequent inhalation. Symptoms include headaches, nausea, dizziness, poor coordination and loss of consciousness.

Chronic poisoning – occurs after repeated contact and inhalation exposure, usually over years or decades. Symptoms include chronic fatigue, physical weakness, mood changes, organ damage and nervous system damage.

7 If a fume cupboard is available, then experiments with organic chemicals should be conducted in a fume cupboard to avoid possible inhalation of volatile chemicals. Students should always wear gloves, safety glasses and lab coat to avoid any skin contact. Hands should be washed afterwards to remove any chemicals so as to avoid ingestion. Small volumes should be used to avoid a build-up of organic waste.

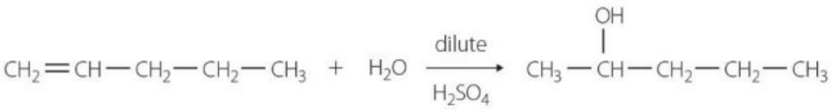
8 **a** Hydration

b Combustion

c Halogenation

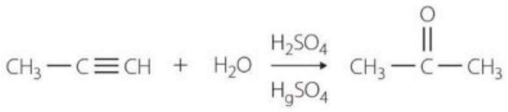
d Substitution

9 **a**



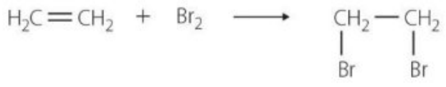
$$CH_2{=}CH-CH_2-CH_2-CH_3 + H_2O \xrightarrow[H_2SO_4]{\text{dilute}} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_2-CH_3$$

b



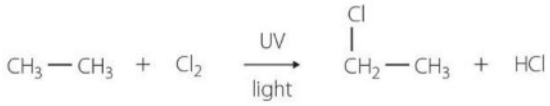
$$CH_3-C\equiv CH + H_2O \xrightarrow[H_gSO_4]{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

10 a



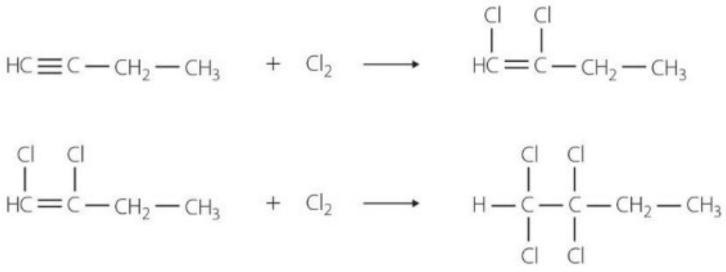
$$H_2C{=}CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}{-}\underset{Br}{CH_2}$$

b



$$CH_3{-}CH_3 + Cl_2 \xrightarrow[\text{light}]{\text{UV}} \overset{Cl}{CH_2}{-}CH_3 + HCl$$

c



$$HC{\equiv}C{-}CH_2{-}CH_3 + Cl_2 \longrightarrow \overset{Cl}{HC}{=}\overset{Cl}{C}{-}CH_2{-}CH_3$$

$$\overset{Cl}{HC}{=}\overset{Cl}{C}{-}CH_2{-}CH_3 + Cl_2 \longrightarrow H{-}\underset{Cl}{\overset{Cl}{C}}{-}\underset{Cl}{\overset{Cl}{C}}{-}CH_2{-}CH_3$$

d

$$H_2C{=}CH{-}CH_3 + HCl \longrightarrow CH_3{-}\overset{Cl}{CH}{-}CH_2$$

11 a $C_7H_{14}(l) + \frac{21}{2}O_2(g) \rightarrow 7CO_2(g) + 7H_2O(l)$

b $C_3H_4(l) + 4O_2(g) \rightarrow 3CO_2(g) + 2H_2O(l)$

c $C_5H_{14}(l) + \frac{17}{2}O_2(g) \rightarrow 5CO_2(g) + 7H_2O(l)$

12 $C_4H_{10}(l) + \frac{9}{2}O_2(g) \rightarrow 4CO(g) + 5H_2O(l)$

$C_4H_{10}(l) + \frac{5}{2}O_2(g) \rightarrow 4C(g) + 5H_2O(l)$

13 Carbon monoxide and carbon/soot both cause negative health consequences if inhaled/ingested. Carbon monoxide at low levels causes impaired judgement, dizziness and headaches. At higher levels, it can cause loss of consciousness and death. Soot particles can coat the lungs, preventing oxygen absorption. Soot particles can also carry molecules of fuel and other toxins into the body.

14 **a** Addition of hydrogen to an alkene requires a metal catalyst like nickel, platinum, palladium or rhodium.

b Production of margarine involves a nickel metal catalyst.

c A Lindlar catalyst (palladium deposited on calcium carbonate) acts as an inhibitor, preventing the alkene reacting to form an alkane.

d Adding water to an alkene requires the presence of dilute sulfuric acid.

e Adding water to an alkyne requires mercury(II) compounds and sulfuric acid.

15 Crude oil is heated to approximately 400°C where most of its fractions are turned into gases, then fed into a fractionating tower that decreases in temperature towards the top. The hot gases rise up the tower and condense at different levels depending on their boiling points. The fractions are collected in trays at the different levels and removed from the tower.

16 Environmental: issues arise from release of carbon dioxide (the enhanced greenhouse effect and associated problems) and from oil spills. Oil spills cause animal death, and destruction of plant life and ecosystems for years after the spills. The enhanced greenhouse effect has caused loss of sea ice, rising sea levels and increased ocean acidification, which is destroying corals and affecting the breeding of other sea life.

17 Extra carbon dioxide in the atmosphere affects the equilibrium between gaseous CO_2 (atmosphere) and aqueous CO_2 (ocean). The equilibrium shown below is shifted to the right, increasing the amount of CO_2 in the oceans.

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

Increased CO_2 sees both equilibria below to also shift to the right, firstly increasing the amount of carbonic acid (HCO_3) and then the amount of H_3O^+, thus increasing acidity.

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

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

18 **a** Carbon dioxide absorbs infrared radiation, trapping heat in the atmosphere.

b When fuel, like octane, combusts, it produces carbon dioxide as seen below. With increased combustion of fuel for vehicle transport and electricity generation, levels of carbon dioxide are rising, trapping extra heat in the atmosphere.

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$$

c Carbon dioxide measurements have been constantly taken for over 50 years and have increased significantly in that time. Carbon dioxide measurements from ice cores have also been compared, constantly showing current levels of CO_2 are the highest they have been.

19 Loss of sea ice and resulting increase in sea levels. This has reduced hunting grounds for some species of animals like polar bears and they are currently facing extinction. Rising sea levels will see a loss of land in highly populated areas including the Asian subcontinent.

Increased ocean acidification is seeing a decline in the health of coral reefs.

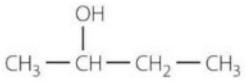
Increased carbon dioxide levels is resulting in a rise in global temperatures affecting weather patterns, creating more frequent and severe weather events.

20 a The increased convenience, availability and cheap nature of polymers is causing large amounts to be used by society. Much of this is not recycled and goes into landfill where it takes hundreds of years to break down, and when it does it releases toxic chemicals into the environment. Much of our plastic waste ends up in the ocean where it does not break down easily and is eaten by aquatic life.

b Recycling uses less energy than making new polymers, so local councils and governments encourage householders to recycle polymers. This makes recycling polymers more economically viable than producing new polymers from scratch. Polymers are labelled with their composition to help people sort recyclable polymers from non-recyclable ones.

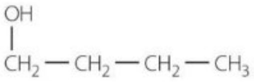
21 a

①



$CH_3-CH(OH)-CH_2-CH_3$

②



$CH_2(OH)-CH_2-CH_2-CH_3$

b Product (1) is more likely to form. Markovnikov's rule states that when an asymmetrical reactant like water is added, then the hydrogen from the reactant will add to the carbon that has the most hydrogens already attached. In this case, the hydrogen will prefer to add to the terminal carbon, leaving the hydroxyl group to attach to carbon 2.

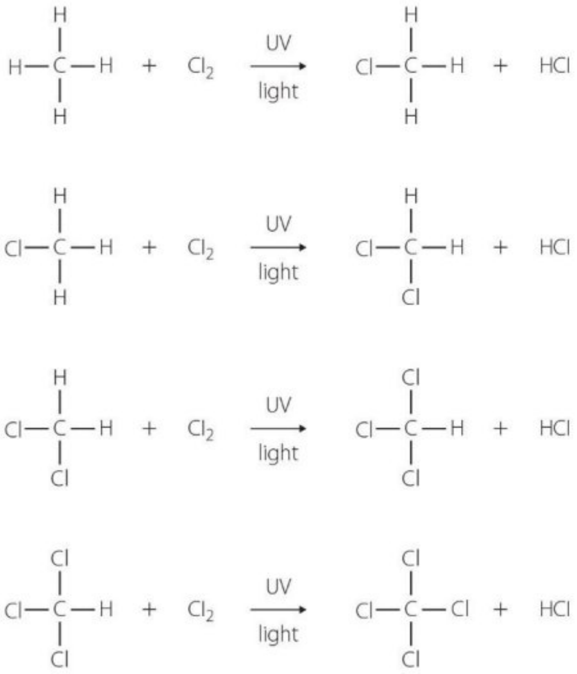
22 a When the reactant is symmetrical, like Br_2 or H_2 then one atom will add to each side of a double/triple bond, and the product will be the same no matter which atom attaches where. For example, when Br_2 is added to 1-propene, the product will only be 1,2-dibromopropane.

b When the reactant is asymmetrical, like HBr or H_2O, then the hydrogen atom will prefer to attach to the carbon that already has the most hydrogens on it due to Markovnikov's rule. The rest of the reactant will attach to the other carbon. However, the alternate product can occur, but will only form in small amounts. An example is when water is added to 1-butene. The preferred product is 2-butanol; however, small amounts of 1-butanol will also form.

23 **a** Alkanes like methane will only undergo substitution reactions when UV light is present.

b If bromine water (orange-yellow) is added to samples of alkane and alkene under normal light, the bromine will add to the alkene, causing the mixture to decolourise as the bromine adds into the organic molecule. The mixture containing the alkane will stay orange-yellow since the bromine does not add to the organic molecule.

c



24 **a** In a fume cupboard, place 3 mL of heptane into one test tube and place in a test-tube rack. Place 2 mL of 2-heptene in a second test tube and place into the rack.

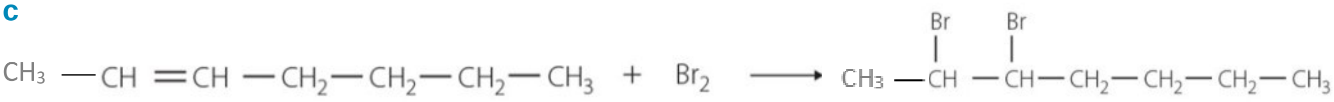
Add 1 mL of bromine (Br_2) to each test tube, stopper and gently shake. Observe any colour changes.

The test tube containing heptane should stay orange-yellow.

The test tube containing 2-heptene should decolourise.

b Both the bromine and the organic samples emit vapours that could be harmful. Where possible, this experiment should be done in a fume cupboard, or in a well-ventilated area. Lids should be kept on all containers and stoppers used with the test tubes.

c



$$CH_3-CH=CH-CH_2-CH_2-CH_2-CH_3 + Br_2 \longrightarrow CH_3-\overset{\overset{Br}{|}}{CH}-\overset{\overset{Br}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$$

25 a A is soluble in water, so it can only be water or ethanol. Since it does not combust, it must be water.

B is not soluble in water, so it must be 1-hexene or pentane. Since it decolourises bromine in the absence of UV light, it must have a double bond, so it is 1-hexene.

C is not soluble in water, and does not decolourise bromine, so it is pentane

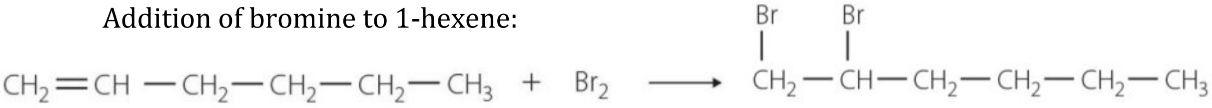
D is, thus, ethanol. It is soluble in water and undergoes combustion.

b Combustion of ethanol: $C_2H_5OH(l) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Combustion of pentane: $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

Combustion of 1-hexene: $C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

Addition of bromine to 1-hexene:



$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + Br_2 \longrightarrow \underset{\substack{|\\ Br}}{CH_2}{-}\underset{\substack{|\\ Br}}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

Student book answers

Module 7: Organic chemistry

Chapter 11: Alcohols

Worked example 11.1

1 $q = m \times c \times \Delta T = 100 \times 4.18 \times (45.1 - 14.5) = 12791\ \text{J} = 12.791\ \text{kJ}$

$MM\,(C_3H_8O) = (12.01 \times 3) + (1.008 \times 8) + 16.00 = 60.094\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{0.372}{60.094} = 6.19 \times 10^{-3}\ \text{mol}$$

$$\Delta H = \frac{12.791}{6.19 \times 10^{-3}} = -2066 = -2.07 \times 10^{3}\ \text{kJ mol}^{-1}$$

2 $MM(C_2H_5OH) = (12.01 \times 2) + (1.008 \times 6) + 16.00 = 46.068\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{0.843}{46.068} = 0.0183\ \text{mol}$$

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

$$1360 = \frac{q}{0.0183}$$

$q = 24.89\ \text{kJ} = 24.89 \times 10^{3}\ \text{J}$

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

$24.89 \times 10^{3} = 175 \times 4.18 \times \Delta T$

$\Delta T = 34.0°\text{C}$

Worked example 11.2

1 $MM(C_4H_{10}O) = (4 \times 12.01) + (10 \times 1.008) + 16.00 = 74.12\ \text{g mol}^{-1}$

$$\text{Heat released} = \frac{\Delta H}{MM} = \frac{2670}{74.12} = 36.02\ \text{kJ g}^{-1}$$

2 $0.81\ \text{g mL}^{-1} = 810\ \text{g L}^{-1}$

$$\text{Heat released} = \frac{(\Delta H \times density)}{MM} = \frac{(2670 \times 810)}{74.12} = 2.9 \times 10^{4}\ \text{kJ L}^{-1}$$

Check your understanding 11.1

1 Enthalpy of combustion is the heat energy released when 1.00 mole of fuel is combusted in excess oxygen at standard atmospheric pressure.

2 **a** $C_5H_{11}OH(l) + \frac{15}{2}O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

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

3 $C_2H_5OH(l) + 3O_2 \rightarrow 2CO_2(g) + 3H_2O(l)$

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

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

The first equation shows the complete combustion of ethanol producing carbon dioxide. The second two equations show examples of incomplete combustion producing carbon monoxide (CO) and carbon/soot (C). The most heat would be released by complete combustion, with incomplete combustion giving progressively less heat released as the amount of oxygen available reduces.

4 This should be based on how you designed Investigation 11.1. Be sure to include all measurements taken including mass of fuel, temperature of water and mass of water heated.

5 $q = m \times c \times \Delta T = 120 \times 4.18 \times 11.3 = 5668\ \text{J} = 5.68\ \text{kJ}$

$MM(C_6H_{14}O) = (12.01 \times 6) + (1.008 \times 14) + 16.00 = 102.172\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{1.26}{102.172} = 0.012\ \text{mol}$$

$$\Delta H = \frac{5.68}{0.012} = -473\ \text{kJ mol}^{-1}$$

6 **a** $q = m \times c \times \Delta T = 150 \times 4.18 \times (39.6 - 16.3) = 14609\ \text{J} = 14.609\ \text{kJ}$

$MM(C_4H_{10}O) = (12.01 \times 4) + (1.008 \times 10) + 16.00 = 74.12\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{0.48}{74.12} = 6.48 \times 10^{-3}\ \text{mol}$$

$$\Delta H = \frac{14.609}{6.48 \times 10^{-3}} = -2256 = -2.3 \times 10^{3}\ \text{kJ mol}^{-1}$$

b $MM(C_4H_{10}O) = (4 \times 12.01) + (10 \times 1.008) + 16.00 = 74.12\ \text{g mol}^{-1}$

$$\text{Heat released} = \frac{\Delta H}{MM} = \frac{2256}{74.12} = 30.4\ \text{kJ g}^{-1}$$

Since this is less than the theoretical value by about 15%, it can be said that the accuracy of this experiment is poor.

7 **a** $MM(C_4H_{10}) = (12.01 \times 4) + (1.008 \times 10) = 58.12 \text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{1.00}{58.12} = 0.0172 \text{ mol}$$

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

$$2874 = \frac{q}{0.0172}$$

$$q = 49.43 \text{ kJ} = 49.43 \times 10^3 \text{ J}$$

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

$$49.43 \times 10^3 = 750 \times 4.18 \times \Delta T$$

$$\Delta T = 15.8°\text{C}$$

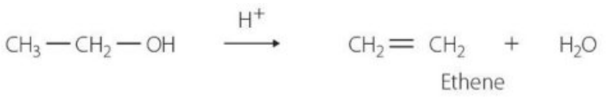
b Loss of heat to surroundings including equipment and the air. Incomplete combustion resulting in less heat than the theoretical maximum being released from the fuel. Both of these would result in less heat than maximum possible being transferred to the water, so the temperature rise would be less than expected.

8 Placing the flame as close to the calorimeter (container holding the water) as possible so more heat would be transferred to the water. Creating a heat shield to prevent heat dissipating in the air rather than being transferred to the water. Having a lid on the calorimeter to prevent heat escaping from the surface of the water. All of these would have a higher temperature change of the water occur as more heat would be transferred or retained by the water. A higher change in temperature would result in a higher enthalpy value, closer to the theoretical value and, thus, be more accurate.

Check your understanding 11.2/11.3/11.4

1 Alcohols need to be heated with concentrated sulfuric or phosphoric acid to dehydrate into alkenes.

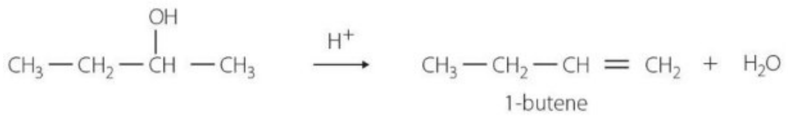
2 **a**



$$CH_3-CH_2-OH \xrightarrow{H^+} CH_2=CH_2 + H_2O$$

Ethene

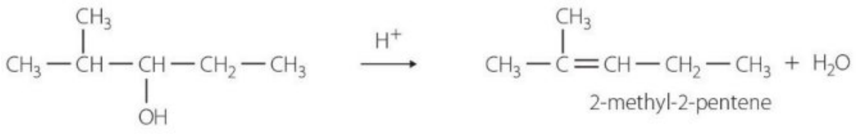
b



$$CH_3-CH_2-CH(OH)-CH_3 \xrightarrow{H^+} CH_3-CH_2-CH=CH_2 + H_2O$$

1-butene

c



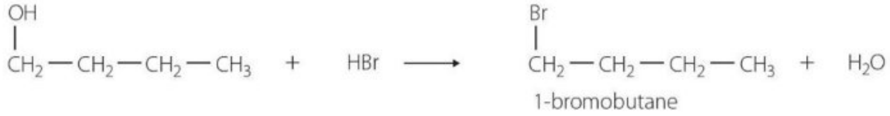
$$CH_3-CH(CH_3)-CH(OH)-CH_2-CH_3 \xrightarrow{H^+} CH_3-C(CH_3)=CH-CH_2-CH_3 + H_2O$$

2-methyl-2-pentene

3 **a**

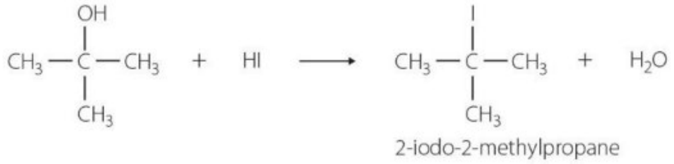
$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 + HCl \longrightarrow CH_3-\overset{Cl}{\overset{|}{C}H}-CH_3 + H_2O$$

b



$$\overset{OH}{\overset{|}{C}H_2}-CH_2-CH_2-CH_3 + HBr \longrightarrow \overset{Br}{\overset{|}{C}H_2}-CH_2-CH_2-CH_3 + H_2O$$

c



$$CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3 + HI \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{I}{\overset{|}{C}}}}-CH_3 + H_2O$$

4 2-methyl-2-propanol would react most readily since it is a tertiary alcohol. Tertiary alcohols react most readily with hydrogen halides, then secondary, and then primary least readily.

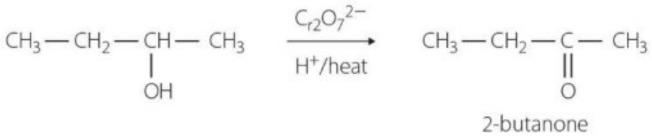
5 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Colour change from purple to colourless (note: in the lab MnO_2 often forms, which is brown)

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

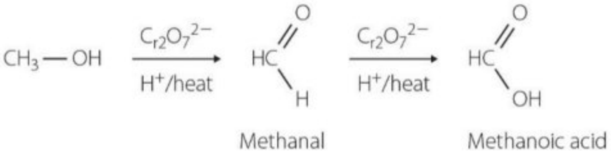
Colour change from orange to green

6 **a**



$$CH_3-CH_2-\underset{OH}{\underset{|}{C}H}-CH_3 \xrightarrow[H^+/heat]{Cr_2O_7^{2-}} CH_3-CH_2-\underset{O}{\underset{||}{C}}-CH_3$$

b



c 2-methyl-2-hexanol is a tertiary alcohol so will not oxidise.

7 **a** 1-propanol to propanal half equations:

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

$C_3H_8O(l) \rightarrow C_3H_6O(l) + 2H^+ + 2e^-$

1-propanol to propanal full balanced equation:

$2MnO_4^-(aq) + 6H^+(aq) + 5C_3H_8O(l) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5C_3H_6O(l)$

Propanal to propanoic acid half equations:

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

$C_3H_6O(l) + H_2O(l) \rightarrow C_3H_6O_2(l) + 2H^+ + 2e^-$

Propanal to propaoic acid full balanced equation:

$2MnO_4^-(aq) + 6H^+(aq) + 5C_3H_6O(l) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5C_3H_6O_2(l)$

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

$C_5H_{12}O(l) \rightarrow C_5H_9O(l) + 3H^+(aq) + 3e^-$

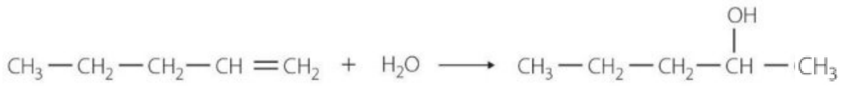
Full equation:

$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 2C_5H_{12}O(l) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 2C_5H_9O(l)$

8 This should be based on Investigation 11.2. Essentially, you would use either dichromate ions or permanganate ions added to each alcohol. Since ethanol is primary, it will oxidise, causing a colour change, while 2-methyl-2-propanol is tertiary, so the mixture will not change colour.

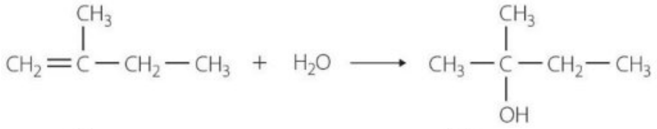
Check your understanding 11.5

1 **a**



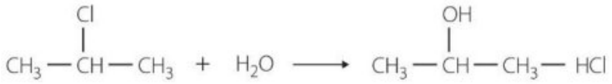
$CH_3—CH_2—CH_2—CH{=}CH_2 + H_2O \longrightarrow CH_3—CH_2—CH_2—\overset{\mathrm{OH}}{\overset{|}{CH}}—CH_3$

b



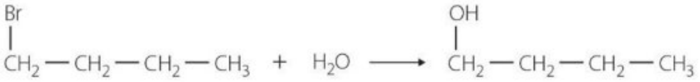
$CH_2{=}\overset{\mathrm{CH_3}}{\overset{|}{C}}—CH_2—CH_3 + H_2O \longrightarrow CH_3—\overset{\mathrm{CH_3}}{\overset{|}{\underset{\underset{\mathrm{OH}}{|}}{C}}}—CH_2—CH_3$

c



$CH_3—\overset{\mathrm{Cl}}{\overset{|}{CH}}—CH_3 + H_2O \longrightarrow CH_3—\overset{\mathrm{OH}}{\overset{|}{CH}}—CH_3— HCl$

d

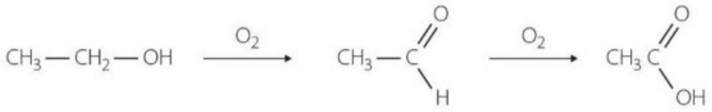


$\overset{\mathrm{Br}}{\overset{|}{CH_2}}—CH_2—CH_2—CH_3 + H_2O \longrightarrow \overset{\mathrm{OH}}{\overset{|}{CH_2}}—CH_2—CH_2—CH_3$ + HBr

e $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g) + HBr$

f $(C_6H_{10}O_5)_n(aq) + nH_2O(l) \rightarrow nC_6H_{12}O_6(aq)$

g



2 The C—X bond of a haloalkane is much easier to break than a C—H or C—C bond since all C—X bond energies are much lower than the C—H bond that breaks in a non-halogenated alkane.

3 The bond energy for C—F is higher than both the C—H and C—C bond, so fluoroalkanes will not undergo substitution reactions.

4 1-chloropropane is a primary haloalkane, so it will react only very slowly. 2-methyl-2-chloropentane is a tertiary alcohol so will be highly reactive, much more than 1-chloropropane.

5 Yeast intake glucose from the fermentation solution and convert it to energy through normal metabolic pathways. Ethanol is a by-product of this reaction when it occurs under anaerobic (no oxygen) conditions. The ethanol is excreted as a waste product into the fermentation mixture.

6 Anaerobic conditions (no oxygen). Oxygen will cause the ethanol to oxidise into ethanoic acid giving an unpleasant taste. Low temperatures are also required as the yeast and the enzymes involved are very sensitive to temperature and will stop working at higher temperatures. You could also give slightly acidic and dilute conditions as answers to this question.

Check your understanding 11.6

1 Fuels are used for heating and cooking (natural gas), vehicle fuel (petrol and diesel – primarily alkanes) and electricity production (natural gas and coal).

2 Fossil fuels are becoming increasingly harder to extract since they are running out. They are rising in cost, and are associated with significant environmental issues like mining, the enhanced greenhouse effect and other forms of pollution.

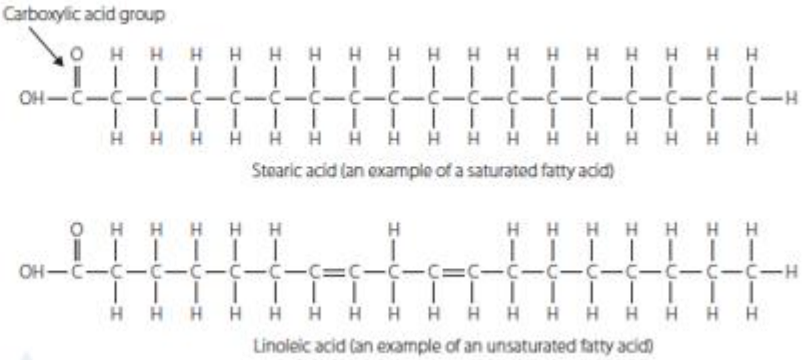
3 Biofuels are produced from recently living organic sources like crops and animal waste.

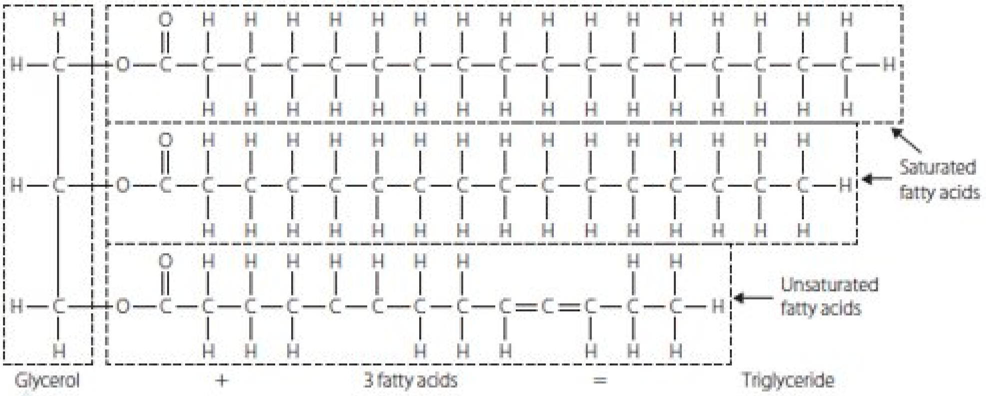
4 Bioethanol is produced from crops like corn, sorghum, wheat and sugar cane. It is fermented in the same way that drinking alcohol is produced using yeast and anaerobic conditions. The final mixture is distilled to purify the ethanol produced.

5 Advantages: use of bioethanol releases significantly less carbon dioxide than petrol when combusted; bioethanol is cheaper than fossil fuels; bioethanol carbon dioxide technically is a zero net release since the carbon dioxide used to grow the crops through photosynthesis was only recently removed from the atmosphere so its return is not adding extra carbon dioxide.

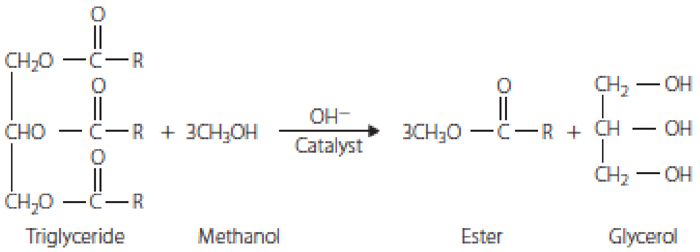
Disadvantages: bioethanol has slightly lower fuel economy than petrol since it has approximately 34% less energy per volume.

6





7 To produce biodiesel, triglycerides (fats and oils) are reacted with short chain alcohols like methanol or ethanol producing an ester (the biodiesel) and glycerol as a by-product. The process is called transesterification



8 Advantages: produces significantly less carbon dioxide than fossil fuel diesel, and technically has zero net addition to atmospheric carbon dioxide during use. Can be used in concentrations up to around 20% without vehicle modification.

Disadvantages: produces slightly less energy (around 9%) than fossil fuel diesel and requires significant vehicle modification to use at high percentages in the fuel mix.

Chapter review questions

1 **a** A biofuel is produced from recently living organic sources like crops and animal wastes. Fossil fuels also come from living organisms, but those that have been dead for millions of years.

b Bioethanol and biodiesel

2 Describe an experiment based on your available equipment and your experimental design in Investigation 11.1. Identify risks that may include flammability of organic fuels, hot equipment and contact with organic chemicals. Ensure you have measured the mass and temperature of the water and mass of fuel used.

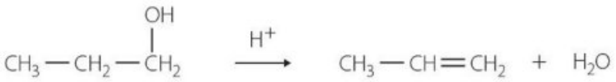
3 **a** Incomplete combustion of fuel; loss of heat to equipment and surrounding air

b Both errors result in less heat than the maximum theoretical amount being transferred to the water. A lower temperature change will lead to a lower enthalpy value calculated than the theoretical.

c Placing the flame as close to the calorimeter (container holding the water) as possible so more heat would be transferred to the water. Creating a heat shield to prevent heat dissipating in the air rather than being transferred to the water. Having a lid on the calorimeter to prevent heat escaping from the surface of the water. All of these would have a higher temperature change of the water occur as more heat would be transferred or retained by the water. A higher change in temperature would result in a higher enthalpy value, closer to the theoretical value and, thus, be more accurate.

4 **a/ b**

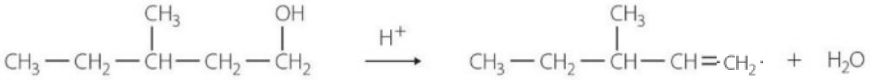
i



$$CH_3-CH_2-\overset{OH}{CH_2} \xrightarrow{H^+} CH_3-CH=CH_2 + H_2O$$

1-propene

ii



$$CH_3-CH_2-\overset{CH_3}{CH}-CH_2-\overset{OH}{CH_2} \xrightarrow{H^+} CH_3-CH_2-\overset{CH_3}{CH}-CH=CH_2 + H_2O$$

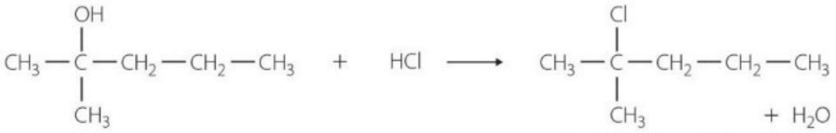
3-methyl-1-pentene

iii

$$CH_3-\overset{OH}{CH}-CH_2-CH_3 + HBr \longrightarrow CH_3-\overset{Br}{CH}-CH_2-CH_3 + H_2O$$

2-bromobutane

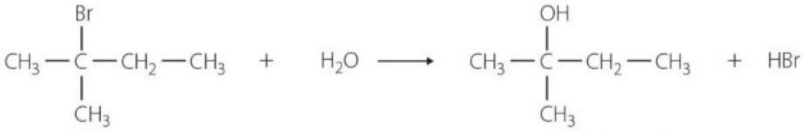
iv



$$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3 + HCl \longrightarrow CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3 + H_2O$$

2-chloro-2-methylpentane

v



$$CH_3-\overset{Br}{\underset{CH_3}{C}}-CH_2-CH_3 + H_2O \longrightarrow CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3 + HBr$$

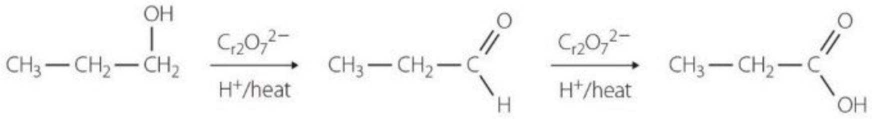
2-methyl-2-butanol

vi

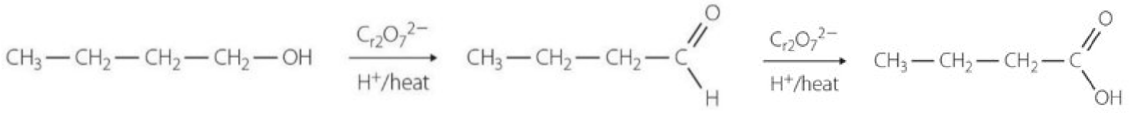
$$\overset{Cl}{CH_2}-CH_3 + H_2O \longrightarrow \overset{OH}{CH_2}-CH_3 + HCl$$

Ethanol

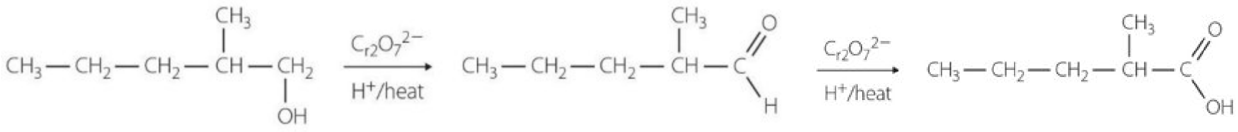
5 **a**



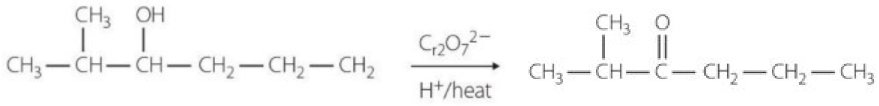
b



c



d



6 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Colour change from purple to colourless (note: in the lab MnO_2 often forms, which is brown)

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Colour change from orange to green

When added to alcohols, if the alcohol oxidises then as the dichromate or permanganate ions reduce they will change colour, showing that the alcohol has oxidised.

7 **a** This should be based on Investigation 11.2. Essentially, you would use either dichromate ions or permanganate ions added to each alcohol. Prepare the permanganate and dichromate ions as described in Investigation 11.2

b Assume acidified dichromate ions are used. The test tube containing 1-pentanol would see the mixture change colour from orange to green. The test tube containing 2-methyl-2-pentanol would stay orange.

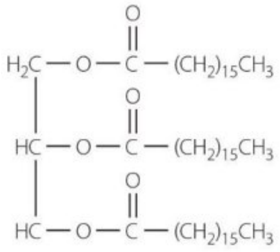
c The orange to green colour change is from the reduction of dichromate ions. This occurs as the alcohol oxidises. Since 1-pentanol is a primary alcohol it will oxidise, so a colour change is seen. 2-methyl-2-pentanol is a tertiary alcohol, so it will not oxidise and the dichromate ions will not reduce nor change colour.

8 **a** Fermentation: $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$

b Fermentation requires anaerobic conditions, low temperatures, and a dilute and slightly acidic solution. No special conditions are required for hydration of haloalkanes.

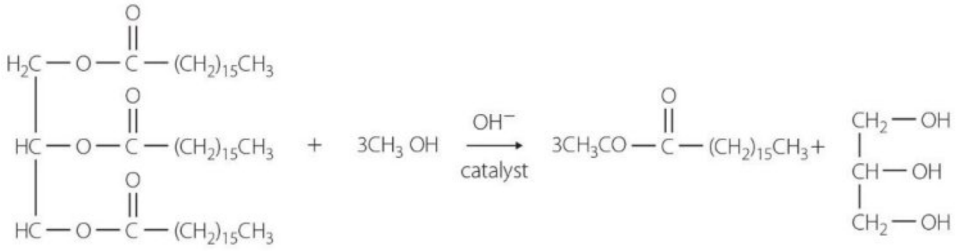
c Biofuel is produced by fermentation since it is produced from the glucose found in crops. Living sources are required for production of a biofuel.

9 **a**



b As there are no carbon–carbon double or single bonds this is a saturated triglyceride.

c



d Transesterification

10 **a** **i** $MM(H_2) = (2 \times 1.008) = 2.016\ \text{g mol}^{-1}$

$$\text{Heat released} = \frac{\Delta H}{MM} = \frac{285}{2.016} = 141\ \text{kJ g}^{-1}$$

ii $MM(C_2H_6O) = (2 \times 12.01) + (6 \times 1.008) + 16.00 = 46.068\ \text{g mol}^{-1}$

$$\text{Heat released} = \frac{\Delta H}{MM} = \frac{1360}{46.068} = 29.52\ \text{kJ g}^{-1}$$

iii $MM(C_8H_{18}) = (8 \times 12.01) + (18 \times 1.008) = 114.224\ \text{g mol}^{-1}$

$$\text{Heat released} = \frac{\Delta H}{MM} = \frac{5460}{114.224} = 47.8\ \text{kJ g}^{-1}$$

iv $MM(C_{12}H_{22}O_{11}) = (12 \times 12.01) + (22 \times 1.008) + (11 \times 16.00) = 342.296\ \text{g mol}^{-1}$

$$\text{Heat released} = \frac{\Delta H}{MM} = \frac{5650}{342.296} = 16.5\ \text{kJ g}^{-1}$$

b Fuels are usually bought by mass or volume, so this compares the way people buy fuel.

c **i** Hydrogen → ethanol → octane → sucrose

ii Sucrose → ethanol → octane → hydrogen

d The relative size of the molecules influences the energy per mass. One mole of different substances varies a lot in terms of mass so results for heat released vary as well.

11 $q = m \times c \times \Delta T = 500 \times 4.18 \times (29.0 - 15.9) = 27379\ \text{J} = 27.379\ \text{kJ}$

$MM(C_4H_{10}O) = (12.01 \times 4) + (1.008 \times 10) + 16.00 = 74.12\ \text{g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{0.72}{74.12} = 0.00971\ \text{mol}$$

$$\Delta H = \frac{27.379}{0.00971} = -2820 = -2.82 \times 10^3\ \text{kJ mol}^{-1}$$

12 $q = m \times c \times \Delta T$

$q = 350 \times 4.18 \times 77 = 112\,651\ \text{J} = 112.7\ \text{kJ}$

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

$$(1360 \times 0.45) = \frac{112.7}{n}$$

$n = 0.184\ \text{mol}$

$MM(C_2H_5OH) = (12.01 \times 2) + (1.008 \times 6) + 16.00 = 46.068\ \text{g mol}^{-1}$

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

$0.184 = \frac{m}{46.068}$

$m = 8.48$ g

13 **a** 1.00 L petrol = 0.70 g mL^{-1} = 700 g L^{-1}

$m(C_8H_{18}) = 700$ g

$MM(C_8H_{18}) = (8 \times 12.01) + (18 \times 1.008) = 114.224$ g mol^{-1}

$n = \frac{m}{MM} = \frac{700}{114.224} = 6.13$ mol

Heat released = 5460 × 6.13 = 33 461 kJ

b Heat released = $\Delta H \times n$

$33\,461 = 2200 \times n$

$n = 15.21$ mol

$MM(C_3H_8) = (3 \times 12.01) + (8 \times 1.008) = 44.094$ g mol^{-1}

$m = nMM = 15.21 \times 44.094 = 670.7$ g

Density = mass/volume so volume = mass/density = $\frac{670.7}{0.49}$ = 1369 = 1.4 L

c $1.00/\$1.45 = \frac{1.40}{x}$

x = $2.03

14 The C—Cl bond is harder to break than the C—Br bond, so in terms of the halogen present, 2-methyl-2-bromopropane will be more reactive. Since 2-methyl-2-bromopropane is a tertiary haloalkane, it will be more reactive than the primary haloalkane 1-chloropropane. Hence, 2-methyl-2-bromopropane will be more reactive with water.

15 **a** The C—X bond of a haloalkane is much easier to break than a C—H or C—C bond since all C—X bond energies are much lower than the C—H bond that breaks in a non-halogenated alkane.

b The bond energy for C—F is higher than both the C—H and C—C bond so fluoroalkanes will not undergo substitution reactions.

16 Grapes contain simple monosaccharide sugars, like glucose, that can be fermented by yeast, as seen in the equation:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g).$$

Carbohydrates contain complex polysaccharide sugars that cannot be fermented until they are broken down into simple monosaccharides, as in the equation:

$$(C_6H_{10}O_5)_n(aq) + nH_2O(l) \rightarrow nC_6H_{12}O_6(aq).$$

17 Advantages: use of bioethanol and biodiesel releases significantly less carbon dioxide than petrol when combusted. Biodiesel and bioethanol are grown from crops through photosynthesis, where the carbon dioxide was only recently removed from the atmosphere. So, technically combustion of biofuels is a zero-net release since the carbon dioxide was recently used to grow the crops so its return is not adding extra carbon dioxide to the atmosphere. Both bioethanol and biodiesel are cheaper than comparable fossil fuels.

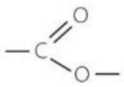
Disadvantages: both bioethanol and biodiesel have slightly lower fuel economy than petrol and diesel when in pure form. Biofuels also use land that could otherwise be used to grow food crops. There is potential for the need to clear extra land to accommodate extra crops for biofuels.

Module 7: Organic chemistry

Chapter 12: Reactions of organic acids and bases

Check your understanding 12.1/12.2

1



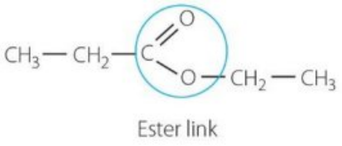
2 **a** Propyl ethanoate

b Butyl methanoate

c Propyl pentanoate

3 **a/b/c**

i



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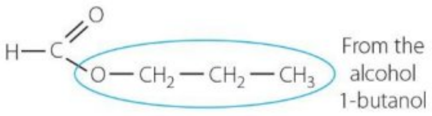
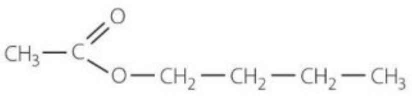


iii



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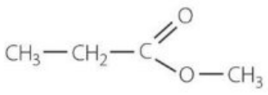
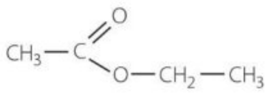
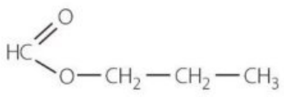


Methyl propanoate



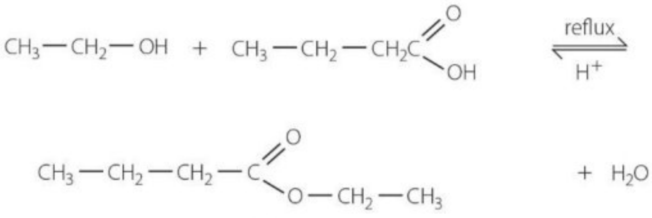
Ethyl ethanoate



Propyl methanoate

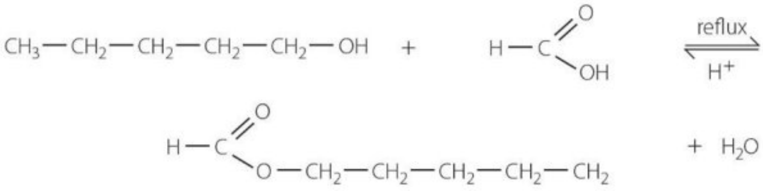
5 a/b

i



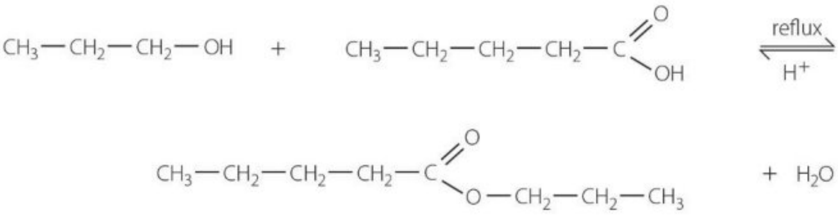
Ethyl butanoate

ii



Pentyl methanoate

iii



Propyl pentanoate

6 a Ester reactions are slow and can take years for an ester to form naturally. In a laboratory, sulfuric acid is used as a catalyst to increase the rate of reaction and form an ester in a much shorter period of time.

b Reflux is extended heating where the volatile mixture is heated above boiling point then passed into a vertical condenser where the mixture is cooled, condensed and returned to the reaction vessel. This is necessary so there is no loss of reactants and products during the extended heating, which is needed to ensure a good yield of ester forms.

7 a The ester formed is non-polar, so washing with water will allow for separation from any polar components in the mixture like the sulfuric acid catalyst and any short chain alcohols or carboxylic acids. These substances dissolve in water, so a separating funnel is used to separate the two liquid layers from each other. The non-polar layer and the polar layer have different densities, so they will separate.

b Addition of sodium carbonate will cause long chain carboxylic acid molecules (insoluble in water) to become soluble carboxylate ions (soluble in water) by the equation:

$RCOOH(l) + CO_3^{2-}(aq) \rightarrow RCOO^-(aq) + CO_2(g) + H_2O(l)$

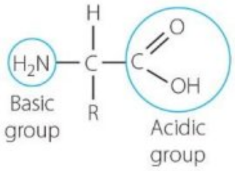
The carboxylate ion forms ion–dipole bonds with water, so it comes out of the non-polar layer and dissolves in the polar layer. This process separates the carboxylic acid from the ester.

Check your understanding 12.3

1 **a** Both organic and inorganic acids donate protons and ionise in the same manner. They also react with bases, metals and carbonates in the same way. Both inorganic and organic bases accept protons and react with acids in the same way.

b Organic acids and bases are all weak acids and bases. Inorganic acids can be either strong or weak.

2



3 **a** $CH_3CH_2CH_2NH_2(aq) + HCl(aq) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + Cl^-(aq)$

b $2HCOOH(aq) + Na_2CO_3(aq) \rightleftharpoons 2HCOO^-(aq) + 2Na^+(aq) + H_2O(l) + CO_2(g)$

c $2CH_3COOH(aq) + Ca(s) \rightleftharpoons 2CH_3COO^-(aq) + Ca^{2+}(aq) + H_2(g)$

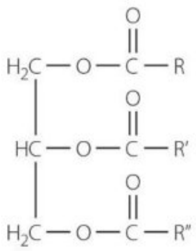
4 Organic acids ionise to different extents since they are weak acids. Thus, they produce different amounts of hydrogen ions for one mole of acid that ionises. Since pH is directly related to concentration of hydrogen ions, this gives different organic acids different pH values related to their ability to ionise. From Table 12.3, oxalic acid has the lowest pH, so it produces the greatest amount of hydrogen ions per mole, so is the strongest acid in that table. Ethanoic acid with the highest pH produces the least amount of hydrogen ions, so it is the weakest acid in that table.

Check your understanding 12.4

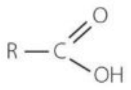
1 **a** Surfactant molecules (soap and detergent molecules) break the hydrogen bonding between water molecules and spread the water out onto a surface, increasing its ability to wet a surface.

b Emulsifiers cause mixing of polar and non-polar substances. The polar/ionic section of the surfactant molecule bonds to the polar component, while the non-polar hydrocarbon tail bonds to the non-polar component. This allows the two components to mix.

2 **a**

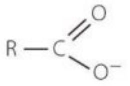


b



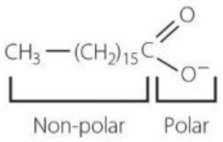
R = long chain (10–20 C)

c



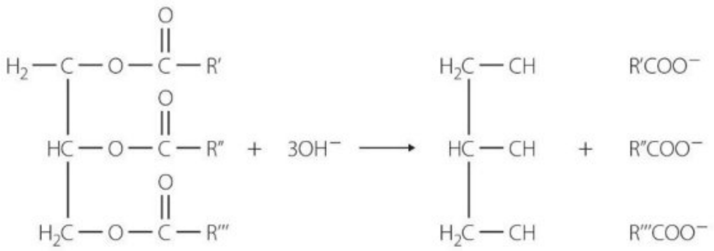
R = long chain (10–20 C)

3 As seen in the diagram below, a soap ion (similar to detergent ions) has a polar head region that can form ion–dipole bonds to water. It also has a non-polar hydrocarbon tail that can form dispersion forces to non-polar substances like grease and oil. Thus, soap and detergent ions can bond to both polar and non-polar substances.



4 Both soaps and detergents have a long non-polar hydrocarbon tail that can bond to non-polar substances. Both also have a polar or ionic head region that can bond to polar substances. However, soaps have a carboxylate ion head that is always negatively charged. Detergents can have an anionic (negatively charged), cationic (positively charged) or non-ionic (polar functional group) head. They all still bond to polar substances but using different methods. Anionic and cationic can form ion–dipole bonds, but non-ionic will only form hydrogen bonds.

5 **a**



b $2RCOO^{-}(aq) + Ca^{2+}(aq) \rightarrow Ca(RCOO)_2(s)$

6 The addition of sodium hydroxide to a fat/oil requires extended heating for the reaction to occur. Once the soap ions have curdled, they can be scraped off and dried to form solid soap. Remaining soap ions in the mixture can be precipitated by adding concentrated sodium chloride (salting out).

7 Add 3 mL of the soap to a test tube. Add 3 mL of the detergent to another test tube. Add 5 mL deionised water to each test tube. Shake and record height of the lather.

Repeat process but this time add 5 mL of 0.1 mol L^{-1} calcium chloride solution instead of water (hard water). Shake and record height of lather.

The detergent should show little difference. The soap will likely precipitate out upon addition of calcium chloride and the lather height should decrease significantly.

8 Using diagrams similar to Figure 12.17 describe the following points.

Surfactant molecules bind the non-polar end into the grease, while also bonding with water molecules through the ionic head region.

Agitation of the mixture will cause the grease to lift off the surface, where it becomes surrounded by surfactant molecules.

A circular structure of a grease droplet surrounded by surfactant molecules forms.

The micelle is soluble in water due to the ion–dipole bonds formed by the ionic head and surrounding water molecules.

Micelles are all negatively charged so they repel each other, remain suspended in the water and are washed away with the dirty water.

Check your understanding 12.5

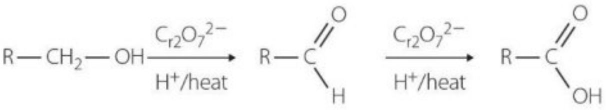
1 a Adding carbonate ions to form a gas (carbon dioxide) only occurs in carboxylic acids, so this is a distinctive test.

b Adding acidified dichromate ions to see an orange to green colour change is a positive test for primary and secondary alcohols and aldehydes, so it is not a distinctive test.

2 Flow charts show each step in the production of a chemical and how chemicals move through a chemical plant or process. It shows raw materials, waste products and by-products, movement of chemicals from one step to another, where heat is used or produced, and where catalysts or pressure or other special conditions are required.

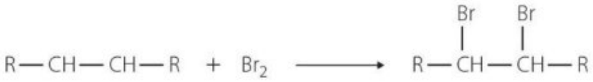
3 Raw materials are found in nature and need little to no preparation before use in a chemical process. Seawater, air, mineral deposits and sand are raw materials.

4 **a** Reagent: acidified dichromate ions. Add 4–5 drops of acidified dichromate ions to separate 3 mL samples of each alcohol. Stopper, shake and place in a water bath to provide heat. The test tube containing the primary alcohol will change colour from orange to green, while the test tube containing the tertiary alcohol will stay orange.



$$R-CH_2-OH \xrightarrow[H^+/heat]{C_{r2}O_7^{2-}} R-CHO \xrightarrow[H^+/heat]{C_{r2}O_7^{2-}} R-COOH$$

b To identify the alkene, add 1 mL bromine water to 3 mL of each substance in a different test tube. The test tube containing the alkene will decolourise; the other two test tubes will stay orange-yellow.

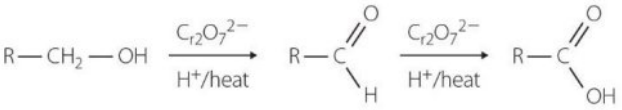


$$R-CH-CH-R + Br_2 \longrightarrow R-\underset{}{\overset{Br}{\overset{|}{C}H}}-\overset{Br}{\overset{|}{C}H}-R$$

To identify the carboxylic acid, add 1 mL sodium carbonate solution to 3 mL of each substance in a different test tube. The test tube containing the carboxylic acid will form gas bubbles; the other two test tubes will not form bubbles.

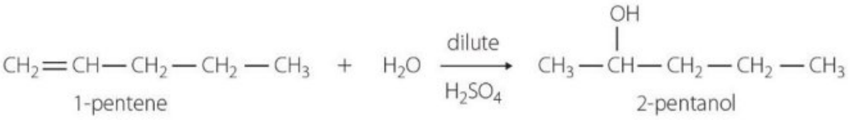
$RCOOH(l) + CO_3^{2-}(aq) \rightarrow RCOO^-(aq) + CO_2(g) + H_2O(l)$

To identify the primary alcohol, add 4–5 drops of acidified dichromate ions to separate 3 mL samples of each substance. Stopper, shake and place in a water bath to provide heat. The test tube containing the primary alcohol will change colour from orange to green; the other test tubes will stay orange.

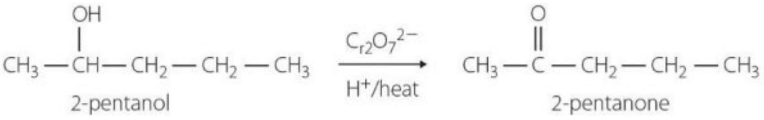


$$R-CH_2-OH \xrightarrow[H^+/heat]{C_{r2}O_7^{2-}} R-CHO \xrightarrow[H^+/heat]{C_{r2}O_7^{2-}} R-COOH$$

5

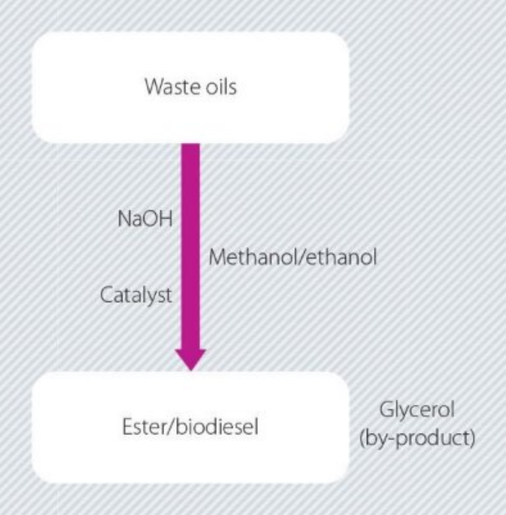


$$\underset{\text{1-pentene}}{CH_2=CH-CH_2-CH_2-CH_3} + H_2O \xrightarrow[H_2SO_4]{dilute} \underset{\text{2-pentanol}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CH_2-CH_3}$$



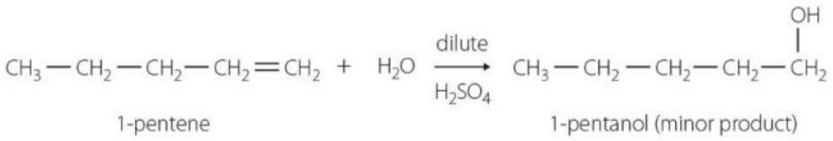
$$\underset{\text{2-pentanol}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CH_2-CH_3} \xrightarrow[H^+/heat]{C_{r2}O_7^{2-}} \underset{\text{2-pentanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3}$$

6

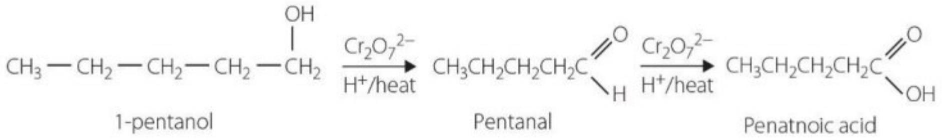


7 To create the ester, pentanoic acid and ethanol are required.

To produce pentanoic acid, 1-pentene is added to water with a dilute sulfuric acid catalyst to produce the minor product 1-pentanol. The 1-pentanol is then added to acidified dichromate ions where it oxidises first to pentanal then to pentanoic acid.

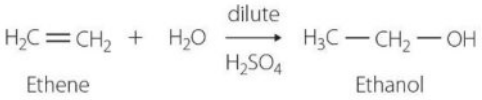


$$CH_3-CH_2-CH_2-CH_2=CH_2 + H_2O \xrightarrow[H_2SO_4]{dilute} CH_3-CH_2-CH_2-CH_2-\overset{OH}{\overset{|}{CH_2}}$$



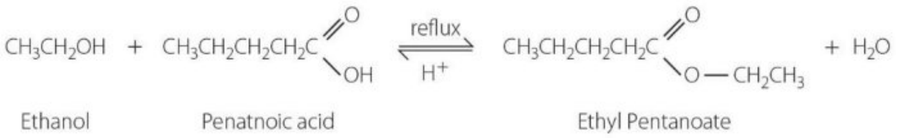
$$CH_3-CH_2-CH_2-CH_2-\overset{OH}{\overset{|}{CH_2}} \xrightarrow[H^+/heat]{Cr_2O_7{}^{2-}} CH_3CH_2CH_2CH_2C\genfrac{}{}{0pt}{}{/\!\!/O}{\diagdown H} \xrightarrow[H^+/heat]{Cr_2O_7{}^{2-}} CH_3CH_2CH_2CH_2C\genfrac{}{}{0pt}{}{/\!\!/O}{\diagdown OH}$$

To produce ethanol, ethene is added to water with a dilute sulfuric acid catalyst.



$$H_2C=CH_2 + H_2O \xrightarrow[H_2SO_4]{dilute} H_3C-CH_2-OH$$

The two products are then reacted with a concentrated sulfuric acid catalyst and refluxed to produce ethyl pentanoate.



$$CH_3CH_2OH + CH_3CH_2CH_2CH_2C\genfrac{}{}{0pt}{}{/\!\!/O}{\diagdown OH} \underset{H^+}{\overset{reflux}{\rightleftharpoons}} CH_3CH_2CH_2CH_2C\genfrac{}{}{0pt}{}{/\!\!/O}{\diagdown O-CH_2CH_3} + H_2O$$

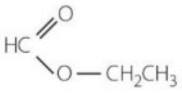
Chapter review questions

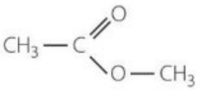
1 **a** Ethyl propanoate

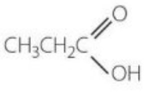
b Propyl propanoate

c Methyl butanoate

2


Ethyl methanoate


Methyly ethanoate


Propanoic acid

3 The two esters are chain isomers; the ester/carboxylic acid is an example of functional group isomerism.

4 **a** Both soaps and detergents have a long non-polar hydrocarbon tail that can bond to non-polar substances. Both also have a polar or ionic head region that can bond to polar substances. However, soaps have a carboxylate ion head that is always negatively charged. Detergents can have an anionic (negatively charged), cationic (positively charged) or non-ionic (polar functional group) head. They all still bond to polar substances but using different methods. Anionic and cationic can form ion–dipole bonds, but non-ionic will only form hydrogen bonds. The use of soaps and detergents as emulsifiers and cleaners is almost identical.

b Detergents can have an anionic (negatively charged), cationic (positively charged) or non-ionic (polar functional group) head. Anionic detergents are used in household cleaners and laundry detergents since they create a good lather and have a harsh action. Cationic detergents are used as fabric softeners, disinfectants and hair conditioners due to their biocidal (bacteria killing) nature and ability to reduce friction and tangling. Non-ionic detergents are used in dishwashers and since glass cleaners as they do not lather easily.

5 Surfactant molecules bind the non-polar end into the grease, while also bonding with water molecules through the ionic head region.

Agitation of the mixture will cause the grease to lift off the surface, where it becomes surrounded by surfactant molecules.

A circular structure of a grease droplet surrounded by surfactant molecules forms.

The micelle is soluble in water due to the ion–dipole bonds formed by the ionic head and surrounding water molecules.

Micelles are all negatively charged so repel each other, remain suspended in the water and are washed away with the dirty water.

6 Soaps do not function well in hard water since they form a solid precipitate with the calcium and magnesium ions in the water: $2RCOO^-(aq) + Ca^{2+}(aq) \rightarrow Ca(RCOO)_2(s)$.

The precipitate formed settles on clothes and reduces the cleaning ability of the soap. Detergents do not form a solid precipitate with the calcium and magnesium ions in hard water so are better cleaners than soaps in hard water.

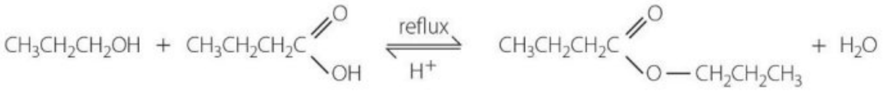
7 **a** Esters only form dipole–dipole bonds between molecules, which are weaker than the hydrogen bonds formed between carboxylic acid molecules so require less heat energy to break so have lower boiling points.

b Carboxylic acids can form hydrogen bonds with water, while esters cannot. Esters do have some attraction to water molecules through the polar functional group, but not as strong as hydrogen bonds; thus, esters are less soluble in water than carboxylic acids of the same size.

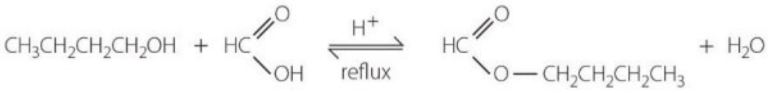
8 Organic acids contain carbon in an organic structure form; inorganic acids do not. However, both have hydrogen atoms that are relatively easily removed. Both organic and inorganic acids donate protons and ionise in the same manner. They also react with bases, metals and carbonates in the same way. Both inorganic and organic bases accept protons and react with acids in the same way. Organic acids are all weak acids, while inorganic acids can be either strong or weak.

9 Organic acids ionise to different extents since they are weak acids. Thus, they produce different amounts of hydrogen ions for one mole of acid that ionises. Since pH is directly related to concentration of hydrogen ions, this gives different organic acids different pH values related to their ability to ionise. Oxalic acid has the lowest pH, so produces the greatest amount of hydrogen ions per mole, so is a stronger acid. Ethanoic acid with the highest pH produces the least amount of hydrogen ions so is a weaker acid.

10 **a**



b



c $2CH_3CH_2CH_2COOH(aq) + 2Li(s) \rightleftharpoons 2CH_3CH_2CH_2COO^-(aq) + 2Li^+(aq) + H_2(g)$

d $HCOOH(aq) + NaOH(aq) \rightleftharpoons HCOO^-(aq) + Na^+(aq) + H_2O(l)$

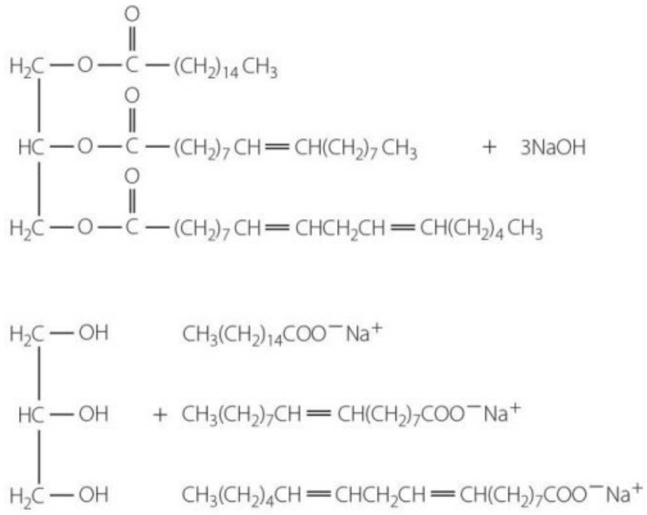
e $2CH_3CH_2(CH_3)CH_2CH_2COOH(aq) + Na_2CO_3(aq) \rightleftharpoons 2CH_3CH_2(CH_3)CH_2CH_2COO^-(aq) + 2Na^+(aq) + H_2O(l) + CO_2(g)$

f $CH_3CH_2CH_2NH_2(aq) + HCl(aq) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + Cl^-(aq)$

11 **a** Since it has multiple carbon–carbon double bonds, it is unsaturated and more likely to be an oil.

b Three soap ions. Each fatty acid chain will separate and become a fatty acid ion (soap ion). Since there are three fatty acid chains on the molecule, three soap ions will form.

c



12 **a** Either:

Addition of 4–5 drops of acidified dichromate ions to 3 mL of each substance. Stopper, shake and place in a water bath to heat. The test tube containing the 1-butanol will change from orange to green; the test tube with butanoic acid will stay orange.

Or:

Addition of 1 mL sodium carbonate solution to 3 mL of each substance. Do not stopper to avoid gas build-up. The test tube containing butanoic acid will generate gas bubbles; the test tube with 1-butanol will not.

b Addition of 4–5 drops of acidified dichromate ions to 3 mL of each substance. Stopper, shake and place in a water bath to heat. The test tube containing the 2-propanol will change from orange to green; the test tube with 2-methyl-2-propanol will stay orange.

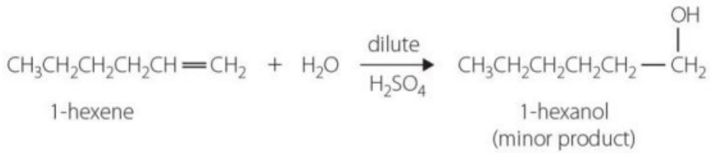
c Addition of 1 mL bromine to 3 mL of each substance. The test tube with heptane will stay orange-yellow; the test tube with 2-heptene will decolourise.

d Addition of 1 mL bromine to 3 mL of each substance. The test tube with ethyne will stay orange-yellow; the test tube with ethyl ethanoate will decolourise.

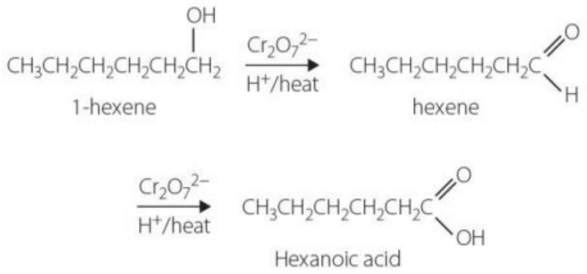
13 **a** Flow charts provide an easy visual representation of the process in order rather than large paragraphs of text. Flow charts allow identification of a range of processes, chemicals and other conditions to be easily represented (heat, catalysts, waste products, etc.).

b Flow charts do not often show equations that clearly show the reactions occurring. Flow charts are not necessarily representative of the scale of the process, or the time in which a process occurs.

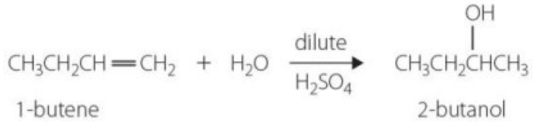
14 **a** 1-hexene is added to water with a dilute sulfuric acid catalyst to produce the minor product 1-hexanol.



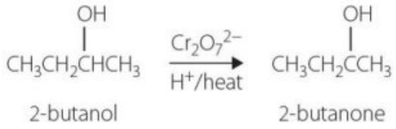
This is then oxidised with acidified dichromate ions and a concentrated sulfuric acid catalyst and heated to produce hexanal, which is then further oxidised to hexanoic acid.



b 1-butene is added to water with a dilute sulfuric acid catalyst to produce 2-butanol.



2-butanol is then oxidised with acidified dichromate ions and a concentrated sulfuric acid catalyst and heated to produce 2-butanone



15 **a** Reflux is extended heating where the volatile mixture is heated above boiling point then passed into a vertical condenser where the mixture is cooled, condensed and returned to the reaction vessel. This is necessary so there is no loss of reactants and products during the extended heating, which is needed to ensure a good yield of ester forms.

b The ester formed is non-polar, so washing with water will allow for separation from any polar components in the mixture like the sulfuric acid catalyst and any short chain alcohols or carboxylic acids. These substances dissolve in water, so a separating funnel is used to separate the two liquid layers from each other. The non-polar layer and the polar layer have different densities, so they will separate.

c Addition of sodium carbonate will cause long chain carboxylic acid molecules (insoluble in water) to become soluble carboxylate ions (soluble in water) by the equation:

$RCOOH(l) + CO_3^{2-}(aq) \rightarrow RCOO^-(aq) + CO_2(g) + H_2O(l)$

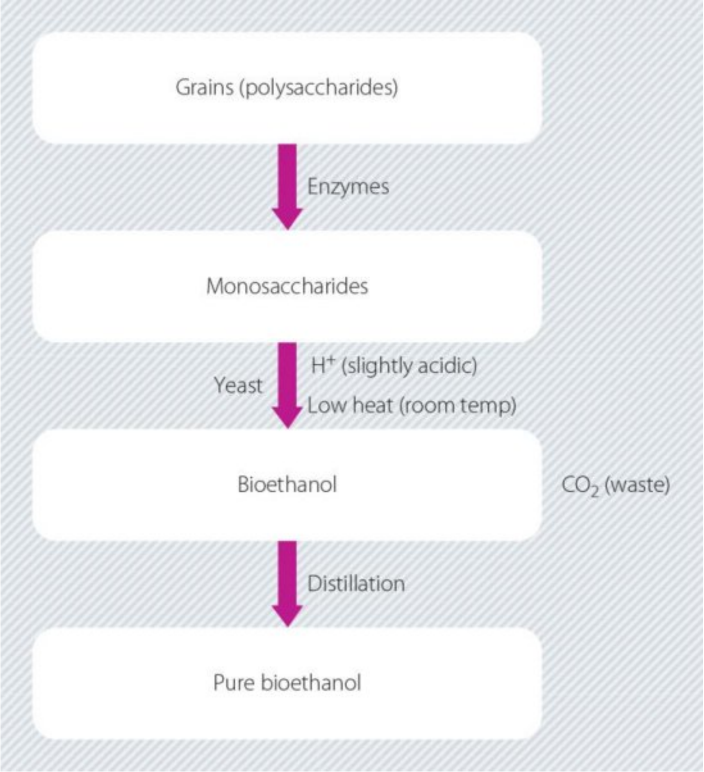
The carboxylate ion forms ion–dipole bonds with water, so it comes out of the non-polar layer and dissolves in the polar layer. This process separates the carboxylic acid from the ester.

16 Risk 1: flammable organic chemicals. Containers should be stoppered if not in use and kept away from heat sources. When refluxing, use a heating mantle instead of a Bunsen burner, if possible. Ensure all joins in glassware are tight and no gas escapes the reflux set-up.

Risk 2: build-up of gas when adding sodium carbonate while purifying. Do not stopper separating funnel until all gas has formed and escaped.

17 Describe the experiment you performed, based on Investigation 12.3. Include risks involving use of concentrated sodium hydroxide and heating oils. Ethanol used is flammable and could be a risk.

18



Module 7: Organic chemistry

Chapter 13: Polymers

Check your understanding 13.1

1 Monomers are small molecules that join in polymerisation reactions to form polymers. Polymers are made up of many monomers joined together.

2 Natural polymers are manufactured by living organisms and include silk, wool and hair. Synthetic polymers are manufactured in laboratories or in factories.

3 Thermoplastic polymers soften on heating and can be easily recycled by melting and remoulding. Thermosetting polymers do not become soft or change shape when heated so they are not suitable for recycling. Thermosetting polymers are usually stronger, more chemically resistant and more durable than thermoplastic polymers.

4 During a polymerisation reaction, monomers link together to form long chains called polymers. Monomers can add together with no excess atoms or molecules left over; this is an addition reaction. Monomers can also add together with the formation of a small molecule like water; this is a condensation reaction.

5 a $C_{14}H_{30}(s) \rightarrow C_8H_{18}(l) + C_6H_{12}(l)$

b $C_6H_{12}(l) \rightarrow 2C_3H_6(g)$

6 A catalyst allows for a reaction to occur at a faster rate but without the need for high temperatures. This makes it a safer and more efficient reaction.

Check your understanding 13.2

1 a Monomers used in addition polymerisation must have a carbon–carbon double bond.

b Monomers with a carbon–carbon double bond add together. The carbon–carbon double bond breaks, leaving free electrons that bond to other monomers, creating a chain of carbon atoms and the final polymer.

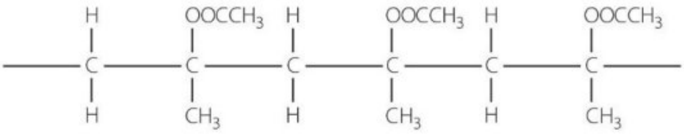
2 Monomer: ethane; polymer: polyethene

3 a Crystalline polymers are very ordered with chains usually lining up and packing closely together. Amorphous polymers are very disordered and contain a lot of branched chains in a random arrangement.

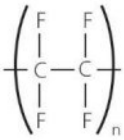
b Crystalline polymers have stronger bonding between chains since they are packed more closely together. Materials that are made from crystalline polymers are strong, dense, tough and rigid with high melting points. Amorphous polymers have much weaker bonds between chains due to the disordered structure. Materials are soft, flexible, have low tensile strength with low melting points.

4 Copolymers are polymers with chains built from more than one monomer. Copolymers are designed for specific purposes with each monomer providing specific properties for the overall polymer.

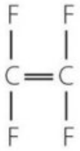
5



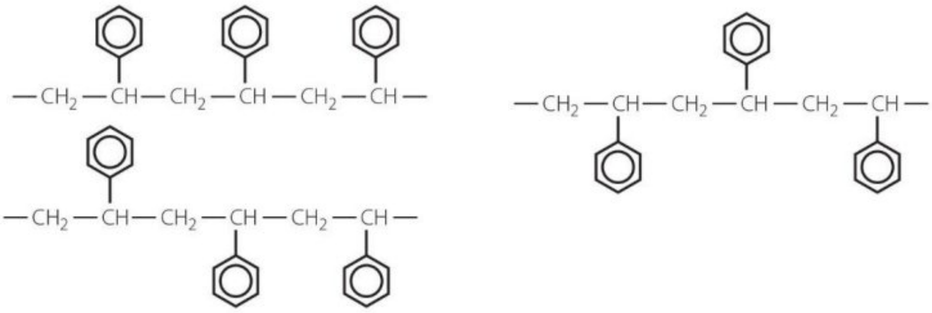
6 **a**



b

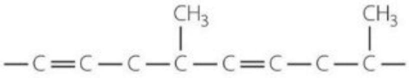


7 **a**

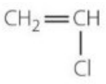


b Since the arrangement of the benzene group is random along the chain, each chain would pack together differently. This would change the strength of bonds between the chains with more closely packed chains having stronger bonds, and weaker bonds when chains are less tightly packed. The bonding between chains determines properties like strength, melting point, flexibility and density.

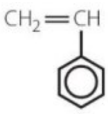
8 **a**



b



Chloroethene



Styrene (ethylnylbenzene)

9 Poly(vinyl chloride) contains a C—Cl bond with a highly electronegative chlorine. This makes the C—Cl bond very polar, allowing it to form dipole–dipole bonds between chains. Polystyrene forms only dispersion forces between the non-polar chains. The dispersion forces are weaker than the dipole–dipole bonds in PVC and make polystyrene more flexible and less strong and rigid than PVC.

10 Addition polymerisation is addition of the same type of monomer. Copolymerisation involves the addition of two different monomers to create a polymer with completely different properties than the polymers that would form from each monomer alone.

Check your understanding 13.3

1 In crystalline regions, chains are packed closely together and have strong intermolecular bonding. Stronger bonding gives polymers that are rigid, strong and have high melting points. In amorphous regions, chains are not packed closely and the chains are disordered with weak intermolecular bonds between chains. This makes amorphous polymers flexible with lower melting points.

2 Cross-linking occurs when covalent or ionic bonds form between chains. This increases the strength of bonding between chains and makes cross-linked polymers more rigid and strong with high melting points.

3 Chains with little to no branching pack very closely together, giving crystalline polymers. When chains have high branching, they cannot pack closely together, giving amorphous polymers.

4 **a** Larger side groups will have more atoms; thus, more electrons and will be able to form stronger dispersion forces between chains. Stronger bonding between chains gives more rigid and less flexible polymers.

b Longer chains have more intermolecular bonding between chains. Higher viscosity occurs when molecules have stronger/more intermolecular bonds between chains, making it harder for the chains to slide across each other.

5 Recycling usually involves heating to soften and remould the polymer. With ionic and covalent cross-links, which will not break unless very high temperatures exist, they are not suitable for recycling since the chains will be unable to rearrange themselves into new shapes.

6 **a** Biodegradable, transparent, rigid, recyclable

b High melting point, flexible, transparent, non-toxic

c Transparent, rigid, high melting point, water resistant

d Water resistant, flexible, tough, chemical resistant

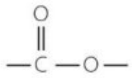
e Flexible, water resistant, tough, strong

Check your understanding 13.4

1 Polyesters and polyamides

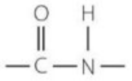
2 In an addition polymer, there are no leftover atoms or molecules when the monomers join. In a condensation polymer, a small molecule like water is eliminated when two monomers join.

3 **a**



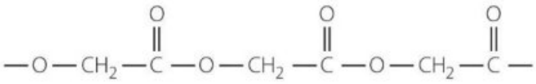
$-\overset{O}{\overset{\|}{C}}-O-$

b



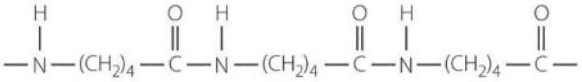
$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-$

4 **a** **i**



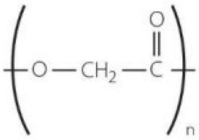
$-O-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{O}{\overset{\|}{C}}-$

ii



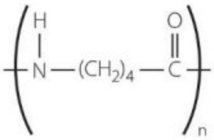
$-\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$

b **i**



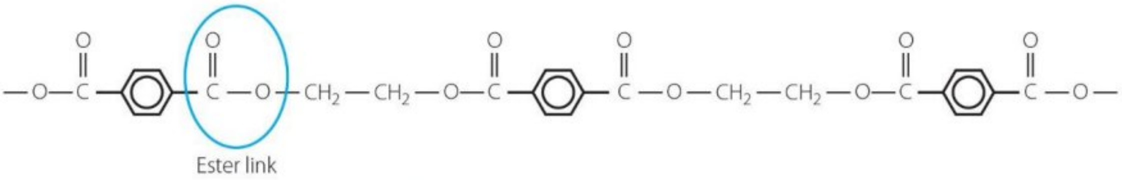
$\left(-O-CH_2-\overset{O}{\overset{\|}{C}}-\right)_n$

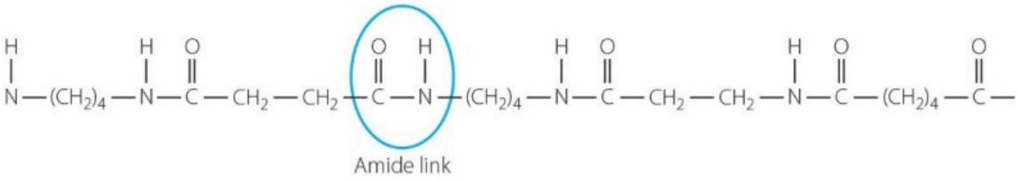
ii



$\left(-\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right)_n$

5





$\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_4-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$

6 **a** Polymer 1: polyester

Polymer 2: polyamide

b (see question **5**)

c Polymer 1: ester

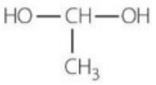
Polymer 2: amide

7 **a** **i** Polyamide

ii Polyester

b **i** $H_2N-(CH_2)_5-NH_2$ $HOOC-(CH_2)_7-COOH$

ii



$HO-\underset{CH_3}{\underset{|}{CH}}-OH$

$HOOC-CH_2-CH_2-COOH$

c Polymer 1: amine and carboxylic acid

Polymer 2: alcohol and carboxylic acid

d Polymer 1: 1,5-pentandiamine and heptandioic acid

Polymer 2: 1,1-ethandiol and ethandioic acid

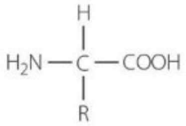
8 Polymer 1: hydrogen bonding and dipole–dipole forces. The N—H and C=O groups are both very polar so will form relatively strong intermolecular forces between chains.

Polymer 2: dipole–dipole and dispersion forces. The polar C=O bond will form dipole–dipole bonds between chains, while the non-polar methyl group will form dispersion forces.

Check your understanding 13.5

1 Natural polymers are manufactured by living organisms and include silk, wool and hair. Synthetic polymers are manufactured in laboratories or in factories.

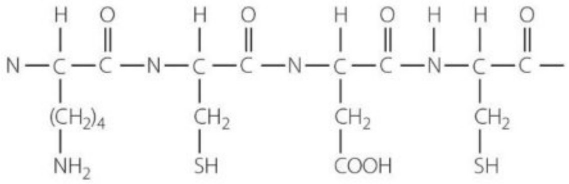
2



$H_2N-CH(R)-COOH$

3 Alanine and serine both have an amine group and a carboxylic acid group attached to the main carbon atom. Serine has a $-CH_2OH$ as the R group, while alanine has only a CH_3 methyl group.

4



5 Alpha and beta glucose have identical molecular formula and very similar structure. The difference is in the hydroxyl (OH) group on carbon 1. In alpha glucose it lies below the ring, while in beta glucose it lies above the ring.

6 Starch and cellulose are both composed of glucose monomers joined together with a glycosidic link. Starch is made up of alpha glucose monomers, while cellulose is made up of beta glucose monomers.

Chapter review questions

1 Both types of polymerisation involve the joining of monomer molecules to form long chains called polymers. Addition polymerisation involves the joining of monomers with no loss of atoms or molecules. Condensation polymerisation involves the joining of monomers with the elimination of a small molecule like water. Addition monomers must have a double bond, condensation monomers must have groups like alcohol, amine and carboxylic acid to undergo condensation reactions.

2 Isotactic arrangements allow for close packing of chains, with maximising dispersion forces between them and have giving properties like rigidity, strength and high melting points. Atactic arrangements have chains that are not closely packed so have only weak forces of attraction between chains. This gives properties like flexibility and low melting points. Syndiotactic arrangements have methyl groups alternating above and below the chain so they can stack together very closely, giving relatively strong bonding between chains. This bonding is not as strong as isotactic bonding, but stronger than atactic bonding. This gives properties like toughness, transparency but not the rigid of other polymers.

3 a Cross-linking is the formation of ionic or covalent bonds between chains. These bonds are very strong, so the polymer will be strong, rigid and have a high melting point.

b Branched chains do not stack closely so will have weak intermolecular bonds. Weak bonds between chains give flexibility and low melting points.

c Side groups attached to the carbon backbone can have a variety of effects depending on size and structure. Side groups can increase the intermolecular bonding between chains, giving more rigidity, or weaken the intermolecular bonds by separating the chains, giving flexibility.

4 A

5 A – increasing chain length increases intermolecular bonds between chains.

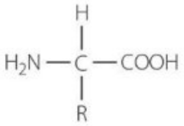
6 C – the monomer for an addition polymer should have a carbon–carbon double or triple bond.

7 A – a small molecule is eliminated each time a link is made, so the final mass of the polymer will be less.

8 B

9 Ester links, amide links and peptide links are all found in condensation polymers and formed when functional groups join and there is elimination of a small molecule. Ester links involve the ester functional group and are formed between an alcohol and carboxylic acid functional group, while both amide and peptide links have the amide group formed between an amide and carboxylic acid functional group. Amide and peptide links are structurally identical; however, the amide link in a polypeptide (used to make proteins) are called peptide links since they join peptide monomer units.

10



$H_2N-CH(R)-COOH$

The R group can be non-polar, consisting of a methyl group or other length hydrocarbon chain or benzene ring. These groups form weak dispersion forces between chains. The R group can be polar and will form stronger hydrogen bonds between chains. Other R groups are capable of forming ions through acid–base reactions so can form ion–dipole or ionic bonds between chains. Some R groups contain atoms like sulfur that can form a primary covalent bond between chains. The strength of bonding between chains influences properties like strength, rigidity and melting point.

11 a HDPE chains pack closely due to lack of side chains, while LDPE chains are more spread out, leading to less chains per volume and giving a less dense material than HDPE.

b HDPE, due to stronger intermolecular bonding between chains. Since the chains are more tightly bound, they will give the polymer greater strength and rigidity.

c **i** HDPE, since it is more rigid

ii LDPE could be suitable if rigid enough to hold liquid. LDPE are often more easily recycled so are suitable for disposable bottles.

d Polyethylene is very difficult to break down since it has strong a C—C backbone that needs extreme conditions to break. Paper is made of natural polymers like cellulose and starch, which contain glycosidic links that are much easier to break down without extreme conditions.

12 D – the monomer has a double bond so it is an addition reaction that does not produce any extra molecules.

13 D – with an amine and carboxylic acid group, it can form an amide group between two monomers.

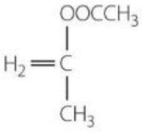
14 a Dispersion forces

b Dipole–dipole forces (C—Cl) and dispersion forces (hydrocarbon chain)

c Hydrogen bonds (N—H), dipole–dipole forces (C=O) and dispersion forces (hydrocarbon chain)

d Dipole–dipole forces (C=O) and dispersion forces (hydrocarbon chain)

15 a **i**



$H_2{=}C(OOCCH_3)(CH_3)$

ii Addition

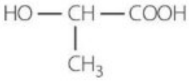
b **i** $H_2N—(CH_2)_6—NH_2$ $HOOC—(CH_2)_8—COOH$

ii Condensation

c **i** $H_2N—(CH_2)_{10}—COOH$

ii Condensation

d **i**



$HO—CH(CH_3)—COOH$

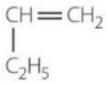
ii Condensation

e **i**

$HO—CH_2—CH_2—CH_2—OH$

ii Condensation

f **i**



$\underset{C_2H_5}{\underset{|}{CH}}=CH_2$

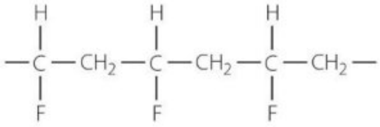
ii Addition

g **i**

$\underset{Cl}{\underset{|}{CH}}=CH_2$ $CH_2=CH_2$

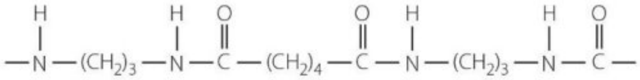
ii Addition

16 **a**



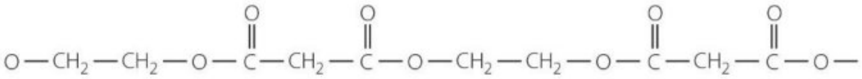
$-\underset{F}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_2-\underset{F}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_2-\underset{F}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_2-$

b



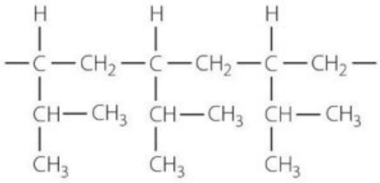
$-\overset{H}{\overset{|}{N}}-(CH_2)_3-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_3-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-$

c

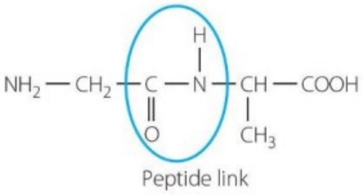


$O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-$

d

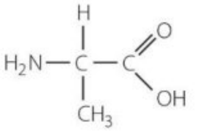


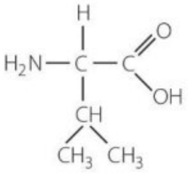
17



$NH_2-CH_2-\underset{O}{\underset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{CH_3}{\underset{|}{CH}}-COOH$

18





19 The polymer in question **15 a** would form both dispersion forces due to the methyl groups and also dipole–dipole forces due to the ester groups on the side chains.

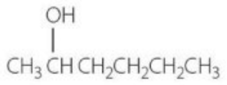
The polymer in question **15 b** would form hydrogen bonds between the N—H group and dipole–dipole forces between the C=O groups. The long hydrocarbon chain could also form dispersion forces between chains.

20 Biochemistry involves work with enzymes and many other molecules that are based on proteins. Proteins are formed from the condensation reactions of amino acids to form polypeptide chains. These chains then fold to form proteins that are a key part of all biochemistry.

21 Cellulose is composed of long chains of beta glucose molecules joined by glycosidic links. The unbranched chains form hydrogen bonds with each other to form a cross-linked structure. These bonds are strong, which gives cellulose strength and rigidity. This makes it ideal for plant cell walls to provide the plant with the rigidity and strength to stay upright.

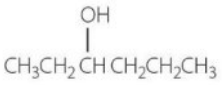
End-of-module 7 review

1 **a**



$CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2CH_3$

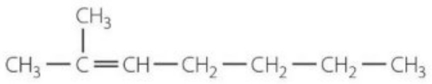
2-hexanol



$CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_3$

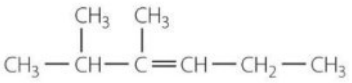
3-hexanol

b



$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-CH_2-CH_3$

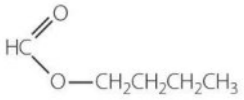
2-methyl-2-heptene



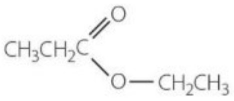
$CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3$

2,3-dimethyl-3-hexene

c



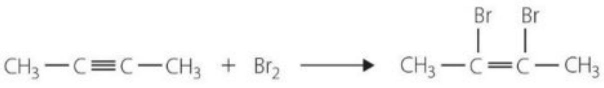
Butyl methanoate



Ethyl propanoate

2 **a** $CH_2{=}CHCH_3 + H_2 \xrightarrow[\text{catalyst}]{\text{metal}} CH_3CH_2CH_3$ Propane

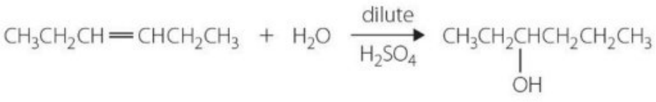
b



$CH_3-C\equiv C-CH_3 + Br_2 \longrightarrow CH_3-\overset{\overset{Br}{|}}{C}=\overset{\overset{Br}{|}}{C}-CH_3$

2,3-dibromo-2-butene

c

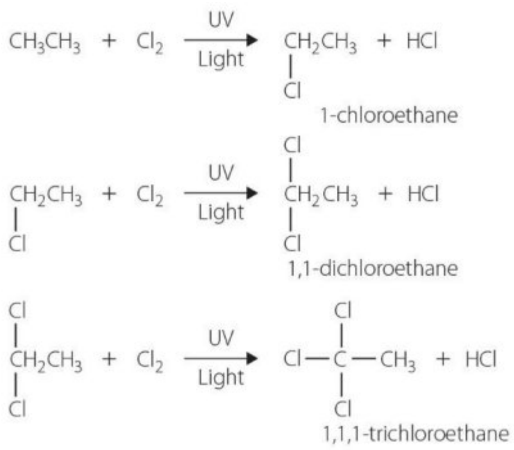


$CH_3CH_2CH{=}CHCH_2CH_3 + H_2O \xrightarrow[H_2SO_4]{\text{dilute}} CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_2CH_3$

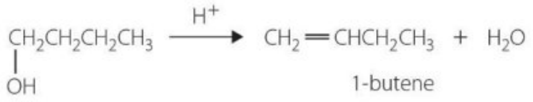
3-hexanol

d $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

e

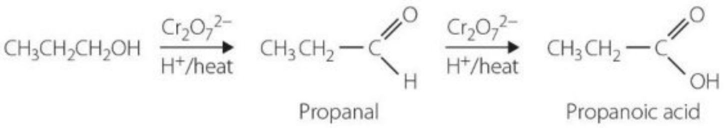


f



g

h

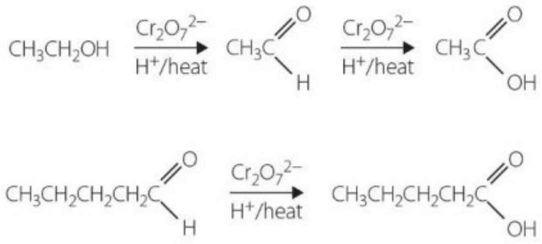


i $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$

j $2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2CH_3COO^-(aq) + 2Na^+(aq) + CO_2(g) + H_2O(l)$

k

3 Since R did not react with acidified dichromate ions it must be butanoic acid. Both ethanol (primary alcohol) and pentanal (aldehyde) will react with acidified dichromate ions. As the primary alcohol and aldehyde oxidise, the dichromate ions (orange) reduce to chromium(III) ions (green).



The addition of sodium carbonate to R with the production of gas bubbles confirms it is butanoic acid since carboxylic acids react with carbonate ions to form carbon dioxide gas.

$2CH_3CH_2CH_2COOH(aq) + CO_3^{2-}(aq) \rightarrow 2CH_3CH_2CH_2COO^- + CO_2(g) + H_2O(l)$

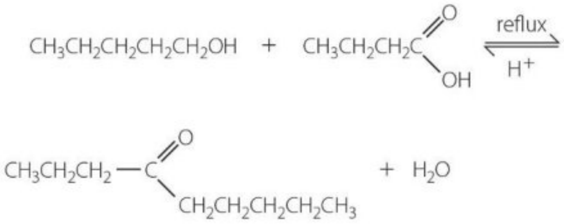
When samples of P and Q were put into water, only P was fully soluble. P must be ethanol since it is a short chain alcohol, while pentanal has a longer carbon chain and will not be very soluble in water.

4 **a** As the length of the hydrocarbon chain increases, more dispersion forces form between the larger molecules. More dispersion forces require more heat energy to break or weaken, which increases the melting and boiling points of the compounds as they increase in size.

b Solubility in organic molecules is about a balance between the polar functional groups, which can form hydrogen bonds to water, and the non-polar hydrocarbon chain that only forms dispersion forces and does not dissolve in water. Short chain alcohols and carboxylic acids have the polar functional groups (hydroxyl and carboxyl) outweighing the effect of the non-polar non-soluble hydrocarbon chain. As the hydrocarbon chain gets longer, its insolubility begins to outweigh the smaller polar functional group. Thus, as the molecule gets larger, it gets less soluble, eventually becoming insoluble.

c Tertiary amides have three hydrocarbon chains attached to the nitrogen so has no N—H bond, where primary and secondary amides both have an N—H bond. The N—H bond is very polar and allows for hydrogen bonding to occur between amide molecules and also to water. This gives primary and secondary amides much higher melting and boiling points and better solubility than tertiary amides.

5 **a** Alcohol: 1-pentanol; carboxylic acid: butanoic acid



Other chemicals: concentrated sulfuric acid catalyst

b See Figure 12.7, page 345. The reaction mixture (alcohol, sulfuric acid and carboxylic acid) is heated with the heating mantle to above boiling point of the components. The reactants evaporate and rise up the condenser where they cool, condense and return to the round bottom flask. This way, extended heating can occur without any loss of reactants and products.

c Production of an ester is an equilibrium reaction so once equilibrium has been reached there will be both reactants and products present in the final mixture.

d Wash with water to remove water soluble substances including short chain alcohols and carboxylic acids, sulfuric acid. This is done in a separating funnel where a polar and a non-polar layer will form. The polar layer is discarded.

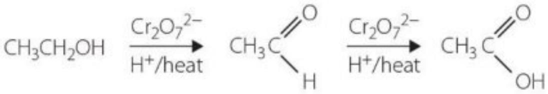
Add carbonate ions to react with non-polar carboxylic acid molecules, which will then convert to infinitely soluble carboxylate ions that will dissolve in the polar layer.

Wash mixture again with water to remove the carboxylate ions and leave behind the non-polar ester.

Distillation can be done to purify the ester further if required.

e SDS would be used to identify each reactant and product and ensure correct steps are taken to prevent risks like inhalation, skin contact or other exposure. Should anything occur, a SDS also has steps for first aid.

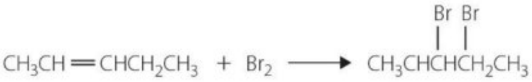
6 **a** Ethanol is a primary alcohol and 2-methyl-2-propanol is a tertiary alcohol. Addition of acidified dichromation ions (4–5 drops) to 3 mL of each substance in a test tube. Test tubes are added to a water bath to heat. The test tube containing ethanol would change from orange to green, the test tube with 2-methyl-2-propanol would stay orange.



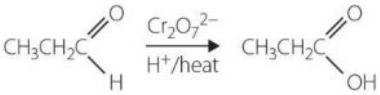
b Addition of sodium carbonate to each substance would see gas bubbles form in the pentanoic acid solution, but not in the 2-pentanone solution.

$2CH_3CH_2CH_2CH_2COOH(aq) + Na_2CO_3(aq) \rightarrow 2CH_3CH_2CH_2CH_2COO^-(aq) + 2Na^+(aq) + CO_2(g) + H_2O(l)$

c Addition of bromine to each substance would see the mixture containing 2-pentene decolourise as the bromine adds across the double bond, while the mixture with pentane would stay orange-yellow.



d Addition of acidified dichromate ions to each substance will see an orange to green colour change in the test tube with propanal in it, but the test tube with propanone will stay orange.



7 **a** Methanol:

$q = m \times c \times \Delta T = 300 \times 4.18 \times (42.8 - 21.4) = 26\,836 \text{ J} = 26.84 \text{ kJ}$

$MM(\text{CH}_4\text{O}) = 12.01 + (1.008 \times 4) + 16.00 = 32.042 \text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{3.6}{32.042} = 0.112 \text{ mol}$$

$$\Delta H = \frac{26.84}{0.112} = -2066 = -239 \text{ kJ mol}^{-1}$$

1-propanol:

$q = m \times c \times \Delta T = 300 \times 4.18 \times (37.5 - 18.3) = 24\,077 \text{ J} = 24.08 \text{ kJ}$

$MM(\text{C}_3\text{H}_8\text{O}) = (12.01 \times 3) + (1.008 \times 8) + 16.00 = 60.094 \text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{2.3}{60.094} = 0.0383 \text{ mol}$$

$$\Delta H = \frac{24.08}{0.0383} = -629 \text{ kJ mol}^{-1}$$

2-propanol:

$q = m \times c \times \Delta T = 300 \times 4.18 \times (39.9 - 20.1) = 24\,829 \text{ J} = 24.83 \text{ kJ}$

$MM(\text{C}_3\text{H}_8\text{O}) = (12.01 \times 3) + (1.008 \times 8) + 16.00 = 60.094 \text{ g mol}^{-1}$

$$n = \frac{m}{MM} = \frac{2.6}{60.094} = 0.0433 \text{ mol}$$

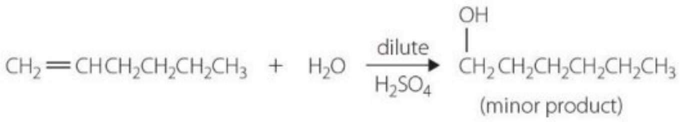
$$\Delta H = \frac{24.83}{0.0433} = -573 \text{ kJ mol}^{-1}$$

b kJ g^{-1} (kilojoules per gram) – since fuels are usually sold by mass rather than by moles, so it would be better to compare in kJ g^{-1}.

c Energy values would be significantly below theoretical values. Heat loss to the surroundings, including the container, tripod and surrounding air would decrease the heat transferred to the water, thus decreasing the accuracy of the results. Since the combustion reaction takes time, heat can be lost from the surface of the water, thus decreasing the theoretical maximum temperature of the water, reducing the enthalpy value calculated.

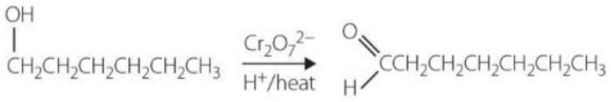
d Carbon monoxide and carbon/soot both cause negative health consequences if inhaled/ingested. Carbon monoxide at low levels causes impaired judgement, dizziness and headaches. At higher levels it can cause loss of consciousness and death. Soot particles can coat the lungs, preventing oxygen absorption. Soot particles can also carry molecules of fuel and other toxins in to the body.

8 **a** 1-hexene would be added to water with a dilute sulfuric acid catalyst to produce the minor product 1-hexanol.

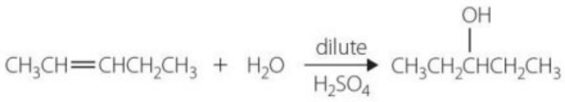


$$CH_2{=}CHCH_2CH_2CH_2CH_3 + H_2O \xrightarrow[H_2SO_4]{\text{dilute}} \overset{\overset{OH}{|}}{CH_2}CH_2CH_2CH_2CH_2CH_3 \text{ (minor product)}$$

1-hexanol is added to acidified dichromate ions and heated to form hexanal. This reaction is completed in a distillation set-up where the 1-hexanol is heated before the acidified dichromate ions are added, so the hexanal evaporates as soon as it forms. This prevents further exposure to the dichromate ions, so it does not oxidise any further.

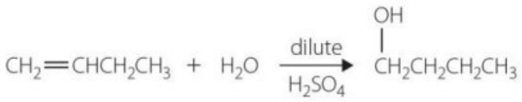


b 2-pentene is added to water with a dilute sulfuric acid catalyst to produce 3-hexanol.



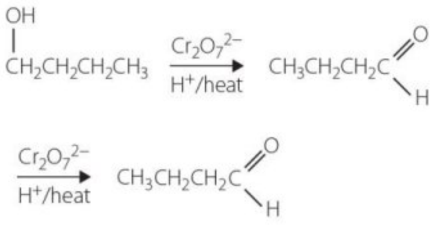
$$CH_3CH{=}CHCH_2CH_3 + H_2O \xrightarrow[H_2SO_4]{\text{dilute}} CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_2CH_3$$

c 1-butene is added to water with a dilute sulfuric acid catalyst to produce the minor product 1-butanol.

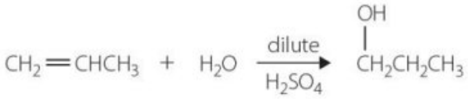


$$CH_2{=}CHCH_2CH_3 + H_2O \xrightarrow[H_2SO_4]{\text{dilute}} \overset{\overset{OH}{|}}{CH_2}CH_2CH_2CH_3$$

1-butanol is added to acidified dichromate ions and heated to produce butanal, which is then oxidised further to butanoic acid.

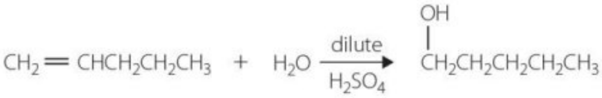


d Propene is added to water with a dilute sulfuric acid catalyst to produce the minor product 1-propanol.



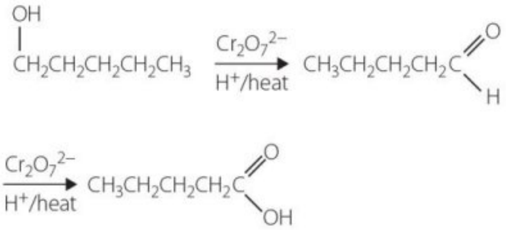
$$CH_2{=}CHCH_3 + H_2O \xrightarrow[H_2SO_4]{\text{dilute}} \overset{OH}{\overset{|}{CH_2}}CH_2CH_3$$

1-pentene is added to water with a dilute sulfuric acid catalyst to poduce the minor product 1-pentanol.

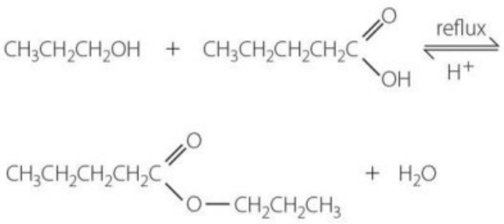


$$CH_2{=}CHCH_2CH_2CH_3 + H_2O \xrightarrow[H_2SO_4]{\text{dilute}} \overset{OH}{\overset{|}{CH_2}}CH_2CH_2CH_2CH_3$$

1-pentanol is added to acidified dichromate and heated to produce pentanal and then pentanoic acid.



The 1-propanol and pentanoic acid are added with concentrated sulfuric acid and refluxed to create the ester propyl pentanoate.



9 **a** Bioethanol and biodiesel are both produced from recent living sources like crops, grains, and animal waste. Bioethanol is produced via fermentation of simple sugars from crops, while biodiesel is produced via transesterification of waste oils from food manufacturers and restaurants.

b Both products are produced from recently living organic sources. Thus, the carbon dioxide that is emitted upon combustion is only retuning recently removed carbon dioxide that was removed via photosynthesis of crops. Technically the combustion alone is a zero net addition of carbon dioxide to the atmosphere (excluding production and transport costs). Fossil fuel combustion adds extra carbon dioxide to the atmosphere since the original carbon dioxide was removed millions of years ago; it is not considered to be a zero net return.

c Environmental: issues arise from release of carbon dioxide (the enhanced greenhouse effect and associated problems) and from oil spills. Oil spills cause animal death, and destruction of plant life and ecosystems for years after the spills. The enhanced greenhouse effect has caused loss of sea ice, rising sea levels and increased ocean acidification, which is destroying corals and affecting the breeding of other sea life.

Economic: oil spills result in loss of tourism, fishing and other businesses in areas where the oil spills have occurred. There are economic consequences from the enhanced greenhouse effect as temperatures rise and there are more frequent severe weather effects.

Social: oil spills cause psychological stress to residents through loss of income and negative economic consequences. The enhanced greenhouse effect will cause refugees through loss of land as sea levels rise. There is also significant stress associated with more frequent severe weather effects.

10 **a** Both types of polymers involve the joining of monomer molecules to form long chains called polymers. Addition polymerisation involve the joining of monomers with no loss of atoms or molecules. Condensation polymerisation involves the joining of monomers with the elimination of a small molecule like water. Addition monomers must have a double bond, while condensation monomers must have groups like alcohol, amine and carboxylic acid to undergo condensation reactions.

b Catalytic cracking or thermal cracking is used to convert long chain alkanes to smaller chain alkanes and alkenes that are more useful:

$C_{14}H_{30}(s) \rightarrow C_8H_{18}(l) + C_6H_{12}(l)$

Catalytic cracking uses temperatures of around 500°C, pressures of 4–20 atmospheres and a zeolite catalyst. Thermal cracking uses higher temperatures and pressures (700°C and around 70 atmospheres).

c Crystalline polymers like HDPE have stronger bonding between chains since they are packed more closely together. Materials that are made from crystalline polymers are strong, dense, tough and rigid with high melting points. Amorphous polymers like LDPE have much weaker bonds between chains due to the disordered structure. Materials made from LDPE are soft, flexible, have low tensile strength with low melting points.

d **i**

ii $H_2N-(CH_2)_5-COOH$

The monomers for Kevlar are diamines and dicarboxylic acids, so two monomers are needed since each monomer contains one required functional group. The single monomer of nylon-6,6 contains both necessary functional groups with an amine on one end and a carboxylic acid on the other end.

Module 8: Applying chemical ideas

Chapter 14: Analysis of inorganic substances

Check your understanding 14.1

1 Student responses should include – manage and control pollution for safety and health of the population; identify pollutants; check for toxic substances; monitor air, water and soil quality.

2 For example: fertilisers – eutrophication, chemical spills – pollute waterways and soil affecting plants and animals

3 Water quality guidelines provides indicators of acceptable levels on substances in water, thus helping to ensure drinking water is uncontaminated and that water sources are monitored to address problems and maintain safety and health of organisms.

4 Naturally occurring substances can become pollutants if their concentrations are above health guidelines and acceptable levels for a particular purpose. For example, salt occurs naturally in water; however, it should not be present in drinking water above guideline levels.

Check your understanding 14.2

1 A precipitation reaction is one where following the mixing of two clear solutions a solid is formed.

2 A sparingly soluble salt may not be detected if its concentration in solution less than

$1–10 \text{ g L}^{-1}$.

3 a Soluble

b Insoluble

c Soluble

d Insoluble

e Soluble

4 a $NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

b $CuSO_4(aq) + 2KOH(aq) \rightarrow Cu(OH)_2(s) + K_2SO_4(aq)$

c $NiCl_2(aq) + K_2SO_4(aq) \rightarrow 2KCl(aq) + NiSO_4(s)$

d $Na_2CO_3(aq) + FeSO_4(aq) \rightarrow FeCO_3(s) + Na_2SO_4(aq)$

e $Zn(NO_3)_2(aq) + (NH_4)_2S(aq) \rightarrow 2NH_4NO_3(aq) + ZnS(s)$

f $K_2CO_3(aq) + CaCl_2(aq) \rightarrow 2KCl(aq) + CaCO_3(s)$

Check your understanding 14.3

1 Ground state is when all the electrons are in the lowest possible energy level. Excited state is when there is a gap in the lower energy levels since one or more electrons have moved to higher energy levels.

2 The wavelengths of light emitted results from differences between the high energy shells and the lower energy shells. The energy differences for all the shells and subshells depend upon the size of the atom, the attraction of the electrons to the nucleus and the size of the electron clouds. Since each atom has the same number of protons, size of nucleus and electron pulling power, the energy levels between the shells and subshells have to be the same for all atoms of an element. This is why sodium always emits the same wavelengths of light when heated.

3 Each element has a unique set of energy levels, so when the electrons move between the energy levels, it will involve absorption and emission of energy particular to that element. This means that every element will emit light with a different set of wavelengths to every other element.

4 **a** Sparingly solubility salts have a higher solubility compared to insoluble salts, so they will only precipitate when they are present in higher concentrations than those of insoluble salts.

b Concentrating the solution by evaporating some of the solvent should result in precipitation of the salt.

5 **a** The solution would contain barium chloride. While both compounds produce a white precipitate with the SO_4^{2-} ion, the pale green colour of the flame tests confirms the presence of the Ba^{2+} ion.

b Add a solution containing I^-. If Pb^{2+} is present, a yellow precipitate will form, while no precipitate would result if Ca^{2+} is present. A red-brick colour in a flame test would verify the presence or absence of Ca^{2+}.

6 **a** A confirmation test would verify the presence of the cation and eliminate the possibility of a contaminant.

b **i** If Ag^+ is present, addition of Cl^- forms a white precipitate that dissolves in ammonia solution.

ii If Fe^{3+} is present, addition of thiocyanate (SCN^-) forms a deep red solution.

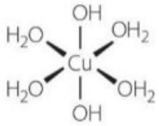
iii If Ba^{2+} is present, a flame test would produce a pale green flame colour.

7 **a** A complex ion is one in which a central metal ion is attached to a number of small molecules or ions called ligands.

b A ligand is a molecule or ion that binds to a central metal ion to form a complex ion.

8 **a** The formula represents that of a complex compound in which a copper(II) ion is the central ion, which has 4 water and 2 hydroxide ions attached to it.

b



9 Silver chloride dissolves in ammonia solution because the chloride ions attached to the silver ion are replaced by ammonia molecules to produce the ion diamine silver, $[Ag(NH_3)_2]^+$.

$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

10 List possible ions then highlight the common one to all three reagents.

Reagent added	A	B	C	D
KI	Pb^{2+}	Ba^{2+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}	Ba^{2+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}	Ba^{2+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}
H_2SO_4	Pb^{2+}, Ba^{2+}, Ca^{2+}	Cu^{2+}, Fe^{2+}, Fe^{3+}	Pb^{2+}, Ba^{2+}, Ca^{2+}	Pb^{2+}, Ba^{2+}, Ca^{2+}
NaOH	Pb^{2+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}	Fe^{2+}, Fe^{3+}	Ba^{2+}	Pb^{2+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}

A is Pb^{2+}.

B is most likely Fe^{3+} due to the brown precipitate; however, it could also be Fe^{2+} if solution is left. Check by adding thiocyanate (SCN^-), which forms a deep red solution with Fe^{3+}.

C is Ba^{2+}; it could possibly be Ca^{2+} but this is unlikely since D is Ca^{2+}. Check using a flame test, which would give a pale green flame if Ba^{2+} is present.

D is Ca^{2+}.

Check your understanding 14.4

1 Using K^+ would not be effective since all K^+ salts are soluble.

2 Sodium carbonate. If sodium chloride was present, then addition of silver nitrate would cause a precipitation of AgCl. If the carbonate was present, then the addition of the acid would cause the bubbles. Nitric acid would react with carbonate to form salt, carbon dioxide and water. The bubble of gas could be due to the carbon dioxide gas being produced.

3 **a** Using litmus paper would not distinguish between the two ions since both are basic.

b Test for the presence of hydroxide ion using either of the cations Pb^{2+} or Cu^{2+}, where a precipitate would be produced.

4 **a** Silver halide precipitates have similar colours so it may not be easy to distinguish between them.

b Test using a dilute or concentrated solution of ammonia. Silver chloride precipitate dissolves in a dilute ammonia solution, silver bromide dissolved in a concentrated ammonia solution, while silver iodide does not dissolve in either.

5 When the solution has a pH < 2, phosphate ions will not precipitate with Ba^{2+} because in an acidic solution there is an equilibrium between the conjugate acid and the ion, as shown in the equations:

$$HPO_4^-(aq) + H_2O(l) \rightleftharpoons PO_4^{2-}(aq) + H_3O^+(aq) \qquad K_a = 4.8 \times 10^{-13}$$

The K_a value is very small so in acidic solution there are insufficient PO_4^{2-} to produce a precipitate. Adding an alkali will remove the H_3O^+ ions, causing the equilibrium to shift to the right, increasing the concentration of PO_4^{2-} ions enough to allow precipitation to occur.

Worked example 14.1

1 Volume $AgNO_3$ used = 12.6 mL

Volume of blank = 0.20 mL

Volume to reach end point = 12.6 − 0.20 = 12.4 mL

Calculate moles of Ag^+:

$n = cV$

$n(AgNO_3) = c \times V = 1.60 \times 0.0124 = 0.0198$ mol

$n(Ag^+) = n(AgNO_3) = 0.0198$ mol

Calculate moles of Br^-:

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

$n(Ag^+) = n(Br^-) = 0.0198$ mol

Calculate concentration of Br^-:

$$c = \frac{n}{V} \qquad V = 50 \text{ mL}$$

$$[Br^-] = \frac{0.0198}{0.050} = 0.396 \text{ mol L}^{-1}$$

2 Volume $AgNO_3$ used = 20.6 mL

Volume of blank = 0.50 mL

Volume to reach end point = 20.6 − 0.50 = 20.1 mL

Calculate moles of Ag^+:

$n = cV$

$n(AgNO_3) = c \times V = 0.12 \times 0.0201 = 2.41 \times 10^{-3}$ mol

$n(Ag^+) = n(AgNO_3) = 2.41 \times 10^{-3}$ mol

Calculate moles of Cl^-:

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

$n(Ag^+) = n(Cl^-) = 2.41 \times 10^{-3}$ mol

$n(Cl^-) = n(NaCl) = 2.41 \times 10^{-3}$ mol

$m(NaCl) = 2.41 \times 10^{-3} \times 58.5 = 0.141$ g

$\% \text{ NaCl} = \left(\frac{0.141}{3.06}\right) \times 100 = 4.6\%$

Worked example 14.2

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(aq)$

Calculate the original number of moles of Ag^+ that was added to the sample.

$n_{AgNO_3} = c_{AgNO_3} \times V_{AgNO_3} = 0.12 \times 0.025 = 3.0 \times 10^{-3}$ mol

$n_{AgNO_3} = n_{Ag^+} = 3.0 \times 10^{-3}$ mol

Calculate the number of moles of Ag^+ that reacted with SCN^-. (This is the excess Ag^+ in 25 mL.)

$n_{SCN^-} = C_{SCN^-} \times V_{SCN^-} = 0.11 \times 0.0123 = 1.35 \times 10^{-3}$ mol

$n_{Ag^+} = n_{SCN^-} = 1.35 \times 10^{-3}$ mol

In 50 mL solution:

$n_{Ag^+} = 2 \times 1.35 \times 10^{-3} = 2.7 \times 10^{-3}$ mol

$n(Ag^+ \text{ that reacted with } Cl^-) = 3.0 \times 10^{-3} - 2.7 \times 10^{-3} = 3.0 \times 10^{-4}$ mol, $n_{Ag^+} = n_{Cl^-} = 3 \times 10^{-4}$ mol

$c(Cl^-)$ in 25 mL diluted sample $= \frac{n}{V} = \frac{3 \times 10^{-4}}{0.025} = 0.012 \text{ mol L}^{-1}$

$c(Cl^-)$ in original sample = 0.012 × 10 = 0.12 mol L^{-1}

Worked example 14.3

1 $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

Mass AgCl = 0.437 g

$$\text{Mass } Cl^- = \left(\frac{35.5}{143.4}\right) \times 0.437 = 0.108 \text{ g}$$

$$n(Cl^-) = \frac{0.108}{35.5} = 3.04 \times 10^{-3} \text{ mol} \qquad V = 10.0 \text{ mL} = 0.010 \text{ L}$$

$$c(Cl^-) = \frac{3.04 \times 10^{-3}}{0.010} = 0.0304 \text{ mol L}^{-1}$$

2 $(NH_4)_2C_2O_4(aq) + Ca^{2+}(aq) \rightarrow CaC_2O_4(s) + 2NH_4^+(aq)$

Mass $CaC_2O_4(s)$ = 2.43 g

$$\text{Mass } Ca^{2+} = \left(\frac{40.1}{128.1}\right) \times 2.43 = 0.761 \text{ g}$$

$$\%Ca = \left(\frac{0.761}{2.00}\right) \times 100 = 38.1\%$$

3 $2As^{3+}(aq) + 3S^{2-}(aq) \rightarrow As_2S_3(s)$

Mass $As_2S_3(s)$ = 0.185 g

$$\text{Mass } As^{3+} = \left(\frac{74.9}{246}\right) \times 0.185 = 0.0563 \text{ g}$$

$$\%As = \left(\frac{0.0563}{1.5}\right) \times 100 = 3.75\%$$

Check your understanding 14.5

1 A precipitation titration is a volumetric analysis technique that uses an indicator and the amount/concentration of analyte is determined from the volume and concentration of the titrant. A gravimetric analysis involves adding excess reactant to precipitate the desired ion, which is removed by filtration, dried and weighed. The amount of the species being analysed is calculated using masses.

2

Method	pH	Titration type	Species analysed
Mohr	Needs pH 6–9	Direct titration	Cl^-, Br^-, CN^-
Volhard	Need low pH	Direct titration for Ag^+ Back titration for anions	Cl^-, Br^-, I^-, CN^-, PO_4^{3-}, CrO_7^{2-}, S^{2-}, CO_3^{2-}
Fajan	Needs specific pH for indicator	Direct titration	Cl^-, Br^-, I^-

3 Errors include:

- contamination with other species
- loss of sample due to inefficient filtering, spillage or rinsing of containers
- not all the desired species precipitating out of solution
- water still remaining in the final sample.

4 Volume $AgNO_3$ used = 24.5 mL

Volume of blank = 0.60 mL

Volume to reach end point = 24.5 − 0.60 = 23.9 mL

a $n(AgNO_3) = c \times V = 0.12 \times 0.0239 = 2.87 \times 10^{-3}$ mol

$n(Ag^+) = n(AgNO_3) = 2.87 \times 10^{-3}$ mol

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

$n(Ag^+) = n(Cl^-) = 2.87 \times 10^{-3}$ mol (in 25 mL)

b In 100 mL diluted sample (= number of moles in 20 mL original sample):

$n(Cl^-) = 2.87 \times 10^{-3} \times 4 = 0.0115$ mol

c $m(NaCl) = 0.0115 \times 58.5 = 0.672$ g in 20 mL

$$m(NaCl) = \frac{0.0672}{20} = 0.0336 \text{ g mL}^{-1}$$

5 $Ag^+(aq) + CN^-(aq) \rightarrow AgCN(s)$

$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(aq)$

Calculate the original number of moles of Ag^+ that was added to the sample.

$n_{AgNO_3} = c_{AgNO_3} \times V_{AgNO_3} = 0.12 \times 0.05 = 6.0 \times 10^{-3}$ mol

$n_{\text{AgNO}_3} = n_{Ag^+} = 6.0 \times 10^{-3}$ mol

Calculate the number of moles of Ag^+ that reacted with SCN^- (This is the excess Ag^+)

$n_{\text{SCN}^-} = c_{\text{SCN}^-} \times V_{\text{SCN}^-} = 0.27 \times 0.0144 = 3.89 \times 10^{-3}$ mol

$n_{\text{Ag}^+} = n_{\text{SCN}^-} = 3.89 \times 10^{-3}$ mol

$n\left(\text{Ag}^+ \text{that reacted with CN}^-\right) = 6.0 \times 10^{-3} - 3.89 \times 10^{-3} = 2.11 \times 10^{-3}$ mol

$n_{\text{Ag}^+} = n_{\text{CN}^-} = 2.11 \times 10^{-3}$ mol

$$c(\text{CN}^-) = \frac{n}{V} = \frac{2.11 \times 10^{-3}}{0.025} = 0.0844 \text{ mol L}^{-1}$$

6 **a** $Pb^{2+}(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2H^+(aq)$

Mass $PbSO_4(s)$ = 1.69 g

$$\text{Mass Pb}^{2+} = \left(\frac{207.2}{303.3}\right) \times 1.69 = 1.15 \text{ g}$$

$$\% \text{ Pb} = \left(\frac{1.15}{3.00}\right) \times 100 = 38.3\%$$

b Mass Pb = 1.15 g

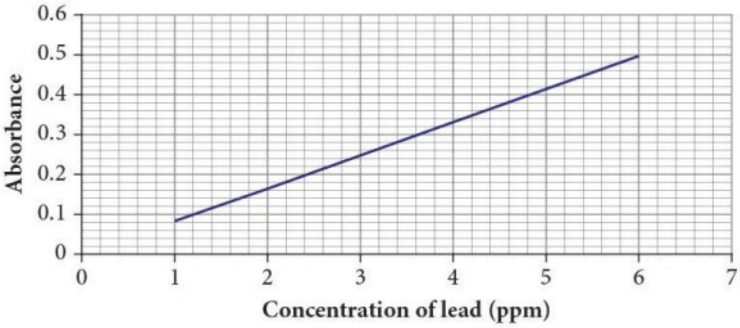
Mass Cu = 3.00 − 1.15 = 1.85 g

Worked example 14.4

1 **a** 3.5 ppm

b 1.5 ppm

2 **a**



b 3.6 ppm

c The sample is 3.6 ppm. As such, it is not under 3.5 ppm and would not be safe.

Check your understanding 14.6

1 **a** In AAS, a hollow cathode lamp of the metal being analysed is used. This provides the specific wavelengths of light particular to that element. The sample is vaporised in a flame, which turns the ions back into atoms. The light from the lamp passes through the vaporised sample. The element being investigated will absorb the specific wavelengths of light. A particular chosen wavelength is selected using a monochromator and the intensity of that light is measured by a detector. When the substance is not present, the maximum amount of light will be detected. When the concentration of the substances increases, the element will absorb more of the specific wavelength of light and less of this light will get through.

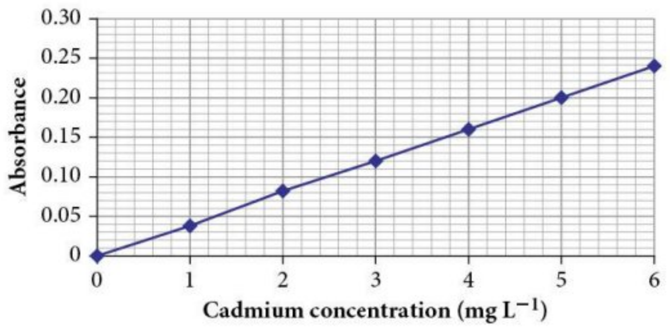
b AAS uses a lamp of the metal being analysed. The sample being tested is vaporised and one wavelength of light is selected. Colourimetry uses a filter of the complimentary colour to that of the solution being analysed. The sample is in solution and the wavelength of a particular colour is used. Both measure the amount of light being absorbed and both require a calibration curve.

2 Standards at about the expected concentration are produced. These are run in the AAS and the absorbance recorded. A calibration curve of the absorbance against concentration is prepared.

3 Each element has specific energy levels for the electrons around the nucleus. Each element requires a specific wavelength of light to provide the energy to excite the electrons to the higher energy levels. The lamp made from the element being tested can be excited and emit the specific wavelength required.

4 A blue filter would not be appropriate since blue is not absorbed by a blue solution. Using a blue filter would cause the solution to look black since blue is the colour that passes through the solution, and is not the absorbed colour. A complimentary coloured filter needs to be used.

5 **a**



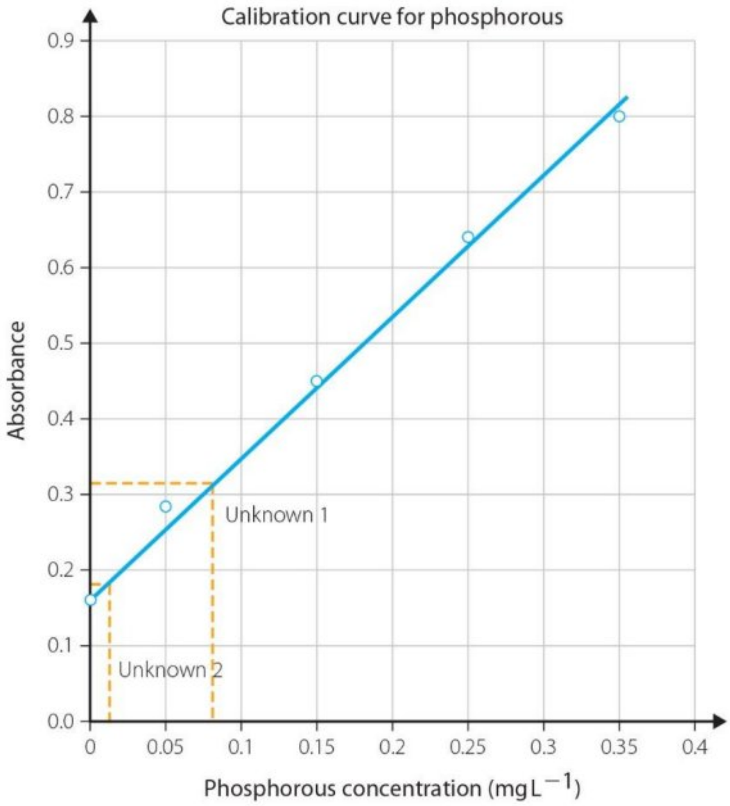
b 2.7 mg L^{-1}

6 **a** 600 ppm

b Dilution factor is 100; original concentration = 600 × 100 = 60 000 ppm

c The original solution had a high concentration, so it would have been quite dark and therefore difficult to measure absorbance. Diluting allows a better measurement between concentrations.

7 **a**



b Unknown site 1 phosphorous concentration = 0.056 mg L^{-1}

Unknown site 2 phosphorous concentration = 0.025 mg L^{-1}

c Site 1 is 56 μg L^{-1}., Site 2 is 25 μg L^{-1}. Both sites are within acceptable levels although site 1 is very close to being at the maximum limit.

d A blue filter is used because it is the complimentary colour for the yellow solution.

Chapter review questions

1 Many of the flame colours are similar, so confirmation tests should be used.

2 Student responses will vary, but answers should consider impact of pollutant on organisms within the environment.

3 **a** $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow 2NaCl(aq) + BaSO_4(s)$

b $3CuSO_4(aq) + 2K_3PO_4(aq) \rightarrow Cu_3(PO_4)_2(s) + 3K_2SO_4(aq)$

c $CaCl_2(aq) + 2NaNO_3(aq) \rightarrow 2NaCl(aq) + Ca(NO_3)_2(aq)$

d $AgNO_3(aq) + NaBr(aq) \rightarrow AgBr(s) + NaNO_3(aq)$

e $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

4 **a** Silver forms precipitates with all three of the solutions, while barium does not form precipitates with Cl^- or OH^-, so the solution must contain silver nitrate.

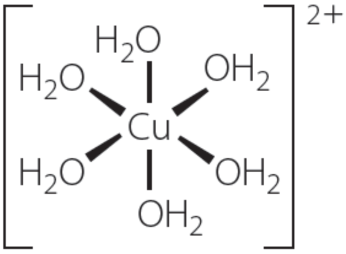
b Both lead and calcium ions form precipitate with SO_4^{2-} ions; however, calcium has a brick- red flame colour, while lead has a light blue-grey flame colour, so the solution must contain calcium chloride.

c Both carbonate and iodide ions form a precipitate with Ag^+; however, a carbonate reacts with acid to produce bubbles of CO_2 gas. Since no bubbles were produced with HNO_3, the solution must contain sodium iodide.

5 The most appropriate tests would be two confirmatory tests. If Fe^{3+} is present, it reacts with SCN^- ion to produce a deep red colour, while Fe^{2+} can be identified because it decolourises an acidified dilute potassium permanganate solution.

6 **a** A complex ion where one or more small molecules or ions are attached to a central cation. This results in a complex that has different properties to the individual species.

For example, hexaaquacopper(II) is a complex copper ion that has six water molecules bonded to it.



b The formula represents that of a complex compound in which an aluminium ion is the central ion with six water molecules attached to it.

c The bond between the metal ion and ligand is a coordinate covalent bond, where both electrons are donated by the ligand to an empty orbital of the metal ion.

d The complex ion is often omitted to simplify the reaction, which shows the combinations of ions responsible for the precipitant. For example, copper forms a precipitate with hydroxide ion and the reaction is usually written simply as:

$Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_2(s)$

However, the product is actually a complex ion:

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^{-}(aq) \rightarrow [Cu(H_2O)_4(OH)_2](s) + 2H_2O(l)$

7 **a** $[CuCl_4]^{2-}$

b The addition of ammonia solution to a copper(II) hydroxide precipitate causes the precipitate to dissolve because the NH_3 replaces the hydroxide ion ligands.

$[Cu(H_2O)_4(OH)_2](s) + 4NH_3(aq) \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) + 2OH^{-}(aq) + 2H_2O(l)$

8

Anion	CO_3^{2-}	Cl^-	PO_4^{3-}	SO_4^{2-}
Reaction with Ag^+	ppt	Ppt – darkens in sunlight	ppt	NP
Reaction with HNO_3	Bubbles	NR	NR	NR

The solution contains the CO_3^{2-} and Cl^- anions.

9 $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(aq)$

Calculate the original number of moles of Ag^+ that was added to the sample.

$$n_{AgNO_3} = c_{AgNO_3} \times V_{AgNO_3} = 2.1 \times 0.0540 = 0.113 \text{ mol}$$

$$n_{AgNO_3} = c_{Ag^+} = 0.113 \text{ mol}$$

Calculate the number of moles of Ag^+ in 20 mL that reacted with SCN^- :

$$n_{SCN^-} = c_{SCN^-} \times V_{SCN^-} = 0.6973 \times 0.0310 = 0.0216 \text{ mol}$$

$$n_{Ag+} = n_{SCN^-} = 0.0216 \text{ mol}$$

$n(Ag^+)$ in 100 mL sample = 0.0216 × 5 = 0.108 mol

$n(Ag^+$ that reacted with $I^-)$ = 0.113 – 0.108 = 5.0×10^{-3} mol

$$n_{Ag^+} = n_{I^-} = 5.0 \times 10^{-3} \text{ mol}$$

$$c(I^-) = \frac{n}{V} = \frac{5.0 \times 10^{-3}}{0.046} = 0.109 \text{ mol L}^{-1}$$

10 **a** $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

b Volume $AgNO_3$ used = 25.0 mL

Volume of blank = 0.20 mL

Volume to reach endpoint = 25.0 − 0.20 = 24.8 mL

$n(AgNO_3) = c \times V = 0.100 \times 0.0138 = 1.38 \times 10^{-3}$ mol

$n(Ag^+) = n(AgNO_3) = 1.38 \times 10^{-3}$ mol

$n(Ag^+) = n(Cl^-) = 1.38 \times 10^{-3}$ mol (in 25 mL)

c $c(Cl^-) = \dfrac{1.38 \times 10^{-3}}{0.025} = 0.0552 \text{ mol L}^{-1}$

d Original sample was diluted by 10 × factor.

$c(Cl^-) = 0.0552 \times 10 = 0.552 \text{ mol L}^{-1}$

e $c(Cl^-) = c(Na^+) = c(NaCl) = 0.552 \text{ mol L}^{-1}$

$M(NaCl) = 58.5$ g

$c(NaCl) = 0.552 \times 58.5 = 32.3 \text{ g L}^{-1}$

11 **a** $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

Volume $AgNO_3$ used = 19.7 mL

$n(AgNO_3) = c \times V = 0.100 \times 0.0197 = 1.97 \times 10^{-3}$ mol

$n(Ag^+) = n(AgNO_3) = 1.97 \times 10^{-3}$ mol

$n(Ag^+) = n(Cl^-) = 1.97 \times 10^{-3}$ mol

b $n(Cl^-) = n(NaCl) = 1.97 \times 10^{-3}$ mol

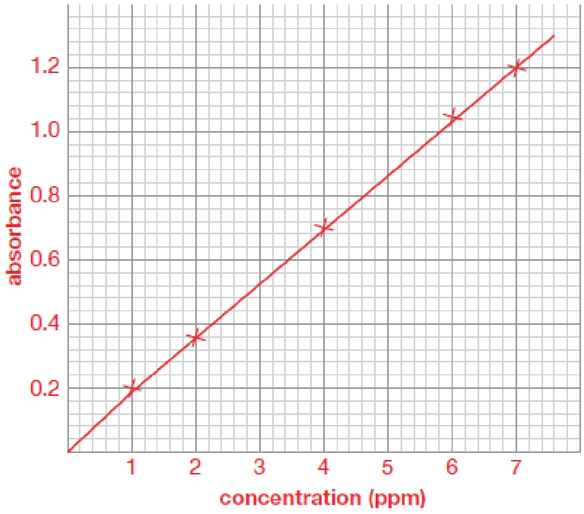
$m(NaCl) = 1.97 \times 10^{-3} \times 58.5 = 0.115$ g

c $\%(NaCl) = (\dfrac{0.115}{0.12}) \times 100 = 95.8\%$

d A blank titration was not conducted, so the volume of Ag^+ would be larger than the actual volume, resulting in a higher number of moles of NaCl and thus a higher % than actual.

12 Student responses will vary. Answers should include a precipitation reaction to identify the presence of lead and a gravimetric analysis to determine the quantity in 100 mL of drink.

13 a



b A = 1.7 ppm; B = 5.1 ppm; C = 7.5 ppm (all ± 0.1)

14

$$\text{absorbance} \propto \frac{1}{c}$$

$\therefore Ac = \text{constant}$

$A_1c_1 = A_2c_2$

For sample A

$0.85 \times 5 = 0.8 \times c$

$$c = \frac{0.85 \times 5}{8} = 5.3\text{ppm}$$

Concentration A = 5.3 ppm = 5.3 mgL^{-1}

V_{sampleA} = 250 mL

$\therefore\ c = 5.3 \times 0.25$

= 5.3 mg in 250 mL

= 5.3 mg Fe in 100 mg tablet

= 5.3 % (w/w)

Sample B

7.08 ppm, 1.8 % (w/w)

Sample C

4.0 ppm, 1.0 % (w/w)

15 **a** **i** $KCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + KNO_3(aq)$

Mass $AgCl(s) = 0.840$ g

$$\text{Mass } Cl^- = \left(\frac{35.5}{143.4}\right) \times 0.840 = 0.208 \text{ g}$$

$$n(Cl^-) = \frac{0.208}{35.5} = 5.86 \times 10^{-3} \text{ mol} = n(KCl)$$

$m(KCl) = 5.86 \times 10^{-3} \times 74.6 = 0.437$ g

ii $$\% \text{ KCl} = \left(\frac{0.437}{0.450}\right) \times 100 = 97.1\%$$

b Test for magnesium or barium – add NaOH solution to a sample. If white precipitate forms, then Mg^{2+} is present. If no precipitate, then Ba^{2+} could be present; check for Ba^{2+} with flame test (pale green flame).

16 **a** **i** $Ca^{2+}(aq) + Na_2SO_4(aq) \rightarrow CaSO_4(s) + 2Na^+(aq)$

Mass $CaSO_4(s) = 666$ mg $= 0.666$ g

$$\text{Mass } Ca^{2+} = \left(\frac{40.1}{136.2}\right) \times 0.666 = 0.196 \text{ g} = 196 \text{ mg}$$

ii $Mg^{2+}(aq) + Na_2CO_3(aq) \rightarrow MgCO_3(s) + 2Na^+(aq)$

Mass $MgCO_3(s) = 149$ mg $= 0.149$ g

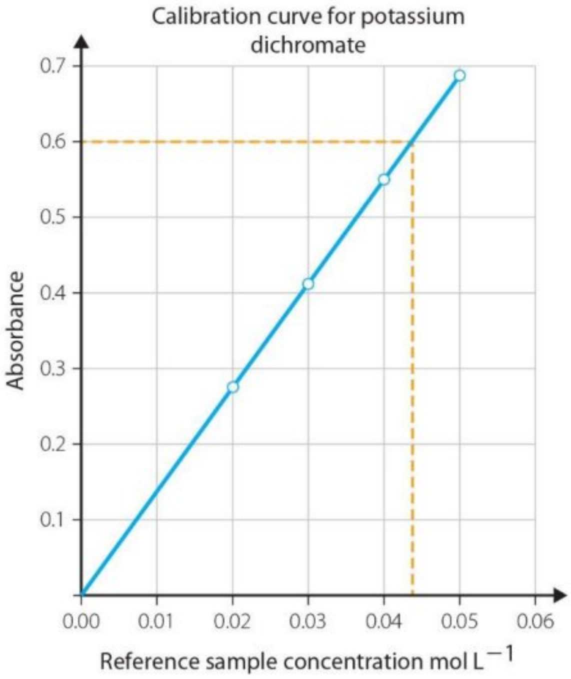
$$\text{Mass } Mg^{2+} = \left(\frac{24.3}{84.3}\right) \times 0.149 = 0.0429 \text{ g} = 42.9 \text{ mg}$$

b For both elements, the test results found less in the tables than given on the label. The results of the test found 198 mg calcium compared to the label value of 229 mg, while the magnesium value of 42.9 mg was quite a lot less than the label value of 115 mg.

c Possible errors could include:

- loss of precipitate through filtering process
- some precipitate left in beaker while transferring to funnel
- loss of precipitate by spilling
- contamination of precipitate by other substances in solution
- loss of precipitate while washing
- incomplete drying improvements.

17 a



b Concentration = 0.044 mol L^{-1}

18 a 0.5 ppm

b Sample had been diluted by a factor of 10 (20 mL to 200 mL).

Concentration of original sample = 5 ppm

c 5 ppm = 5 mgL $^{-1}$, so the level of copper is above drinking water regulations of 1.3 mg L^{-1}

Module 8: Applying chemical ideas

Chapter 15: Analysis of organic substances

Check your understanding 15.1

1 **a** Small alcohols and carboxylic acids are soluble in water, while those with longer hydrocarbon chain are not. Alkenes are not soluble in water.

b Solubility would not be a suitable way to distinguish between alcohols, carboxylic acids and alkenes, because if larger molecules were present, they all would be insoluble.

2 **a** Alkene; *trans*-2-pentene

b Carboxylic acid; propanoic acid

c Alcohol; 2-butanol

d Carboxylate anion; sodium butanoate

3 **a** $Br_2(aq) + CH_2{=}CH{—}CH_3(l) \rightarrow CH_2BrCHBrCH_3(l)$

Products: 1,2-dibromopropane

b $2CH_3CH_2CH_2CH_2OH(l) + 2Na(s) \rightarrow 2CH_3CH_2CH_2CH_2O^-Na^+(aq) + H_2(g)$

Products: Sodium butoxide and hydrogen gas

c $CH_3CH_2OH(aq) + HCOOH(aq) \rightarrow HCOOCH_3CH_2 + H_2O(l)$

Products: ethyl methanoate and water

d $CH_3CH_2CH_2COOH(aq) + Na_2CO_3(aq) \rightarrow 2CH_3CH_2CH_2COONa(aq) + CO_2(g) + H_2O(l)$

Products: sodium butanoate, carbon dioxide gas and water

e $2CH_3OH(l) + 2Na(s) \rightarrow 2CH_3O^-Na^+(aq) + H_2(g)$

Products: Sodium methoxide and hydrogen gas

4 **a** Reactants needed: carboxylic acid, an alcohol, and concentrated sulfuric acid

b While an ester produced should be identifiable by its smell reaction, it would be more accurate and simpler to use sodium carbonate or litmus.

5 The ester methyl methanoate would have the lowest boiling point of 32°C because its intermolecular bonding is not as strong as that in an acid or alcohol.

Ethanoic acid would have the highest boiling point of 118°C because the OH and C=O groups are polar, so carboxylic acids can form strong hydrogen bonds.

1-propanol would have a boiling point of 97°C because the presence of the OH means it can also form hydrogen bonds, so it would have a higher boiling point than the ester but a lower boiling point than the carboxylic acid.

6 **a** A is water because it is soluble in itself, is not flammable, and does not react with bromine.

B is hexene because it is the only one that would decolourise bromine due to the presence of a double bond.

C is pentane because it is insoluble in water and does not decolourise bromine.

D is ethanol because it is soluble in water and flammable.

b Reactions of 1-hexene (B):

$C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

$Br_2(aq) + CH_2{=}CHCH_2CH_2CH_2CH_3(l) \rightarrow CH_2BrCHBr\,CH_2CH_2CH_2CH_3(l)$

Reactions for pentane (C):

$C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$

Reactions for ethanol (D):

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

Check your understanding 15.2

1 Mass spectroscopy has high energy electrons as the energy source, while the other techniques use electromagnetic radiation as the energy source. Mass spectroscopy destroys the original sample, while the other techniques keep the sample intact. The data produced in mass spectroscopy is a mass/charge ratio, while the other techniques shows frequencies of energy absorbance.

2 Advantages include keeping the original sample intact (except mass spectroscopy), while chemical techniques change the original sample, very small sizes can be used, more detail about the molecular structure is gained, and a much greater range of sample types can be identified.

3 The statement is correct because UV–vis spectroscopy uses wavelengths of electromagnetic radiation in both the UV and visible ranges of the spectrum, while colourimetry uses only wavelengths in the visible spectrum.

Worked example 15.1

1 Hexane – $CH_3CH_2CH_2CH_2CH_2CH_3$, mass = 86

Check Table 15.4 to identify possible common fragments.

$15 = CH_3^+$

$29 = CH_2CH_3^+$

Check masses of fragments ± H

$41 = CH_2CHCH_2^+$ (loss of 2 × H from 43)

$43 = CH_3CH_2CH_2^+$

$57 = CH_3CH_2CH_2CH_2^+$

2 **a** 3-pentanol – $CH_3CH_2CHOHCH_2CH_3$, mass = 88

59 is the base peak

$59 = CHOHCH_2CH_3^+$

Produced by a split next to the COH group giving CH_3CH_2 and $CHOHCH_2CH_3^+$ fragments

$31 = CH_2OH^+$

$41 = (59 - 18)$

Loss of water = $CHCHCH_3^+$

b The fragment at 31 would possibly be CH_2OH^+.

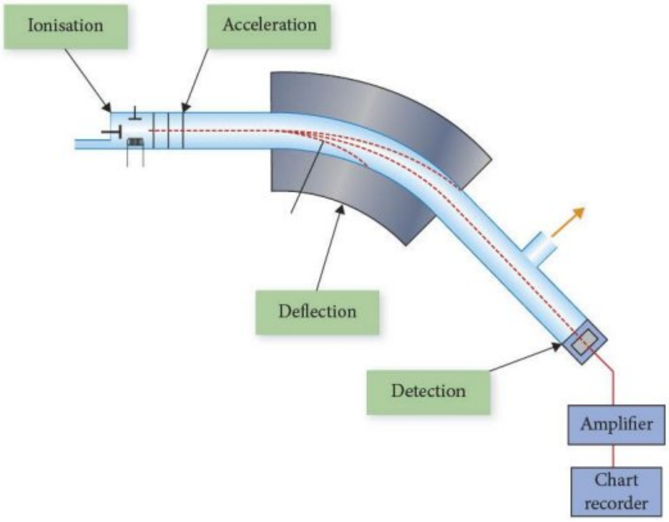
If the primary alcohol produced a fragment by splitting next to the C containing the alcohol (similar to above), the fragments would be CH_2OH ($m = 31$) and $CH_3CH_2CH_2CH_2$ ($m = 57$). It is expected that fragmentation is different because the functional group is at different points in the chain.

Check your understanding 15.3

1 **a** Mass/charge ratio is the mass of an ion relative to the charge of the ion; this determines the deflection in the mass spectrometer.

b Base peak is the most common peak in the mass spectrum, which is assigned a value of 100%.

2



3 The parent peak, the heaviest one based upon the most common elements in the compound.

4 When there may be isotopes of the elements present; for example, in CH_3Cl, the parent peak would be at 50 due to $CH_3{}^{35}Cl$, but there would be a smaller peak (about 25% of the height) at 52 m/z due to ^{37}Cl ion present.

5 The cations are repelled by the ion repeller, accelerated through the magnetic field and attracted to the negative plates at the detector. Radicals do not get accelerated or attracted to the detector.

6 The mass spectrum can show the molar mass (parent ion), isotopes can be detected and the fragmentation pattern can indicate the way the molecules are arranged; for example, the presence of a peak at 29 m/z could indicate a $CH_3CH_2{}^+$ fragment.

7 **a** The peak at 15 could be due a $CH_3{}^+$, the peak at 29 could be due to $CH_3CH_2{}^+$, the peak at 46 is the parent ion, and the peak at 45 would be due to the loss of ^1H.

b The peak at 31 is the most stable fragment since it is the most abundant. It would be a CH_2OH^+ ion.

8 Main peaks

m/z value at 100 parent peak: $C_7H_{16}{}^+$

m/z value at 71: loss of a $CH_3CH_2{}^*$ (i.e. a $C_5H_{11}{}^+$ cation)

m/z value at 57: $CH_3CH_2CH_2CH_2{}^+$

m/z value at 43: $CH_3CH_2CH_2{}^+$ fragment

Peak at the m/z value of 43 is the base peak with three carbons and at m/z value 57 has 4 carbons and the peak at a m/z value of 71 has five carbons. These indicate that it likely to be a straight chain isomer.

9 **a** The mass spectrum of the contaminated sample shows a peak at 32, which is not present in the spectrum of pure ethanol, and the peak at 29 is larger in the contaminated sample than in the pure sample.

b A peak at 32 could be the parent peak for methanol (CH_3OH^+), while the increase at 29 could be due to the fragment CHO^+ fragment. Based on this it is highly likely that the contaminant is methanol.

10 **a** Parent ion indicates molar mass, so the mass/charge ratio is expected to be 86

b Structure A mass/charge ratio of 43 indicates a CH_3CO^+ fragment.

Structure B mass/charge ratio of 57 indicates a $CH_3CH_2CO^+$ fragment.

c A peak at 29 would indicate a $CH_3CH_2{}^+$ fragment, which is unlikely to occur in a mass spectrum of structure A but is very likely in structure B.

Worked example 15.2

1 1-butanol $CH_3—CH_2—CH_2—CH_2—OH$

There are four hydrogen environments. The proton on the $—CH_2OH$ would have a shift around 3.3–4.5. The proton in the CH_3 group would have a shift around 0.9. The protons in the CH_2 groups would have shifts around 1.3. The protons on the oxygen in the OH group would have a shift between 1–6

2 There are two hydrogen environments: the first near 0.9 for the methyl hydrogens and the second CH=CH around 4.6–6.

Worked example 15.3

1 1-butanol $CH_3—CH_2—CH_2—CH_2—OH$

There are four carbon environments. The carbon in the $CH_2—OH$ group would have a shift between 50–90 ppm, the carbon in the CH_3 group would have a shift between 8–25, the carbons in the CH_2 groups would have two different shifts both between 20–45, one for the CH_2 between the CH_3 and CH_2 and the other for the CH_2 between the CH_2 and CH_2OH

2 The molecule is symmetrical, so there are two carbon environments. The carbon in the CH_3 group would have a shift between 8–25, the carbons in the C=C would have a shift between 110–150.

Check your understanding 15.4

1 ^1H and ^{13}C. These two isotopes have an uneven number of nucleons.

2 Radio waves

3 The number of different environments for the hydrogens, the number of hydrogens in each environment, the type of proton and, if it is high resolution, the number of hydrogens on the adjacent carbon atoms

4 The number of different carbon environments in the molecule and the type of carbon present

5 **a** ^1H NMR: 1 ^{13}C NMR: 1

b ^1H NMR: 1 ^{13}C NMR: 1

c ^1H NMR: 3 ^{13}C NMR: 2

d ^1H NMR: 4 ^{13}C NMR: 4

e ^1H NMR: 1 ^{13}C NMR: 1

f ^1H NMR: 4 ^{13}C NMR: 4

g ^1H NMR: 2 ^{13}C NMR: 2

h ^1H NMR: 5 ^{13}C NMR: 5

i ^1H NMR: 3 ^{13}C NMR: 3

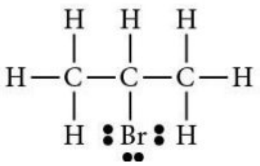
6 **a** The amount of shielding a nuclei will experience will depend upon the chemical environment. Oxygen is highly electronegative and would attract the electrons towards it, thereby exposing or de-shielding the nuclei. If the nuclei are de-shielded, less energy is needed to flip. If the nuclei are more shielded, then more energy is needed to flip the nuclei.

b The splitting pattern of a doublet corresponds to a single H present on the adjacent carbon. A triplet is caused by two H atoms attached to the adjacent carbon atom. The formula used is $(n + 1)$ = pattern. The pattern is the result of the adjacent nuclei either lining up with the field and shielding the nuclei more or against the field (de-shielding the nuclei). The pattern follows Pascal's triangle since it represents the possible combinations.

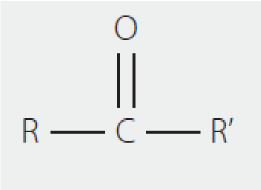
c There are no ^{1}H nuclei present that would interfere with the spectrum.

7 At a shift near 2 ppm there is a doublet – which indicates a single proton in an adjacent carbon. The single proton caused this splitting pattern. The multiplet at just over a 4 ppm shift indicates multiple protons on the adjacent carbons. The other protons caused this splitting pattern.

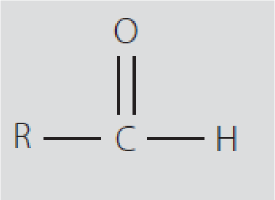
Two environments as indicated by the two peaks, one very strong peak with approximately six times. This indicates six protons in the one environment, which are split into a doublet by one proton; this suggests symmetry. The height of the peak just over 4 ppm with a relative height of 1 suggests one proton that is split into a multiplet by the six protons on adjacent carbons. The structure is:



8 Propanone has the structure:

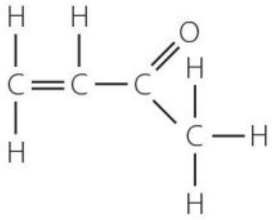


and propanal has the structure:



Propanone is symmetrical and has two different carbon environments so would have two peaks, while propanal has three different carbon environments so would have three peaks.

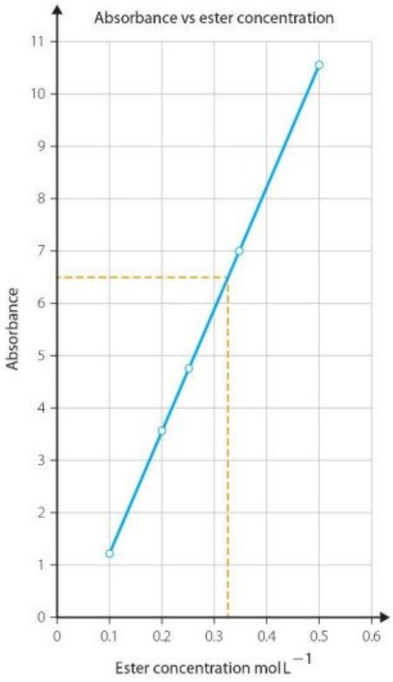
9 The structure of 3-buten-2-one is:



There are four carbon environments. The peak at around 200 must be due to a carbon–oxygen double bond of the ketone group. The two peaks at between 120–140 are due to the carbons at either end of the carbon–carbon double bond. The one closer to the C=O would be more de-shielded due to the electronegative oxygen, so would have the larger value of the two. The peak at 26 is the methyl group, which is joined to the rest of the molecule by a carbon–carbon single bond and slightly de-shielded by its proximity to C=O.

Worked example 15.4

a From the calibration graph, the concentration of ester is 0.325 mol L^{-1} (value will vary depending on line of best fit).



b Ratio ester : drug is 10:3

$$\text{Concentration of drug} = \frac{(0.325 \times 3)}{10} = 0.0975 \text{ mol L}^{-1}$$

Check your understanding 15.5/15.6/15.7

1 IR

2 More information is available to work out the structures. For example, IR determines the functional groups present, while NMR will determine the C—H structure.

3 Diatomic molecules like O_2 or N_2

4 a UV–vis uses the UV and visible part of the spectrum; it relies on the electrons in the molecule being excited to a higher energy state. The amount of light absorbed is recorded. The *x* axis has a uniform scale and shows the wavelength.

The IR uses the IR part of the spectrum. It relies on the energy increasing the vibrations of the molecules. It detects functional groups present and can confirm when they are not present. The amount of light transmitted is recorded. The graph has troughs coming down from the top and the scale changes across the *x* axis, which shows the wavenumber.

Both are non-destructive techniques in which the light is shown on the samples. The identity of substances can be determined by comparing the spectra of a pure sample to the compound. Both are relatively cheap and easy techniques.

b UV–vis would be best for analysing a coloured compound since it will give concentration when using a calibration curve.

5 3300 cm^{-1} is characteristic of the O—H group in alcohols. Broad peak: 1 propanol, 2 propanol, ethanol.

Acids produce a broad beak for the O—H group between 2500–3100 cm^{-1}, so a broad peak close to this region would indicate ethanoic acid, formic acid and butanoic acid.

No broad peak: ethane, ethyl ethanoate, 1-chloroethane and 1-methylamine.

6 a The product is most likely an ester, so X and Y would be an alcohol and a carboxylic acid. The IR spectra of the carboxylic acid would show a broad O—H and a C=O band. The alcohol group would show a broad O—H band and no C=O band.

b An ester has the functional group of RCOOR'. It does not have a O—H functional group. The broad band at approximately 3300 cm^{-1} would be absent. (If the reactants were still present, there may be a band due to the alcohol or carboxylic acid OH group – but this would be diminished.)

c If the student ran a pure standard of methyl ethanoate and the fingerprint region was identical then they would be able to say that the sample is pure.

7 a Ethene would have a band between 1620–1680 cm^{-1} due to the presence of the double bond. This band would be absent for ethane.

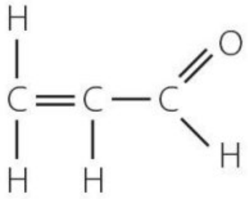
b Differences in the fingerprint regions

c The presence of a C—I band at 500 cm^{-1} compared to C—Cl band at 600–800 cm^{-1} ; differences in the fingerprint regions

d Propanoic acid would have a C=O band at around 1700 cm^{-1}; there would be differences in the fingerprint regions. There would be a difference in the band position for the OH group, with the —OH alcohol in the range of 3230–3550 $cm^{-1}$and the carboxylic acid—OH band would be 2500–3100 cm^{-1}.

8 **a** The value at 162 nm indicates the presence of a double bond C=C, while the band at 270 nm indicates C=O

b Possible structure is:



9 Structure **a** is 1-hexene; there is a trough near 1700 cm^{-1} that indicates a C=C vibration and the sample is more complex.

Structure **b** does not have an absorption band near 1700 cm^{-1}, which indicates no C=C stretch present.

Both have bands less than 1400 cm^{-1} fingerprint region various stretches and bending. There is a band due to the C—H stretch at 3000 cm^{-1}.

Chapter review questions

1 **a** Add drops of sodium carbonate solution to the sample; if bubbles of colourless gas form (CO_2), the compound is butanoic acid.

b Add an oxidising agent such as permanganate. If a reaction occurs, the compound is 2-propanol, which would be oxidised to 2-propanone, while propane will not react.

c Add drops of bromine in an organic solvent; if the solution loses colour, then the compound is 2-pentene.

2 **a** $2CH_3CH_2CH_2CH_2CH_2OHCH_3(l) + 2Na(s) \rightarrow 2CH_3CH_2CH_2CH_2CH_2OCH_3^{-}Na^{+}(aq) + H_2(g)$

Products: Sodium hexoxide and hydrogen gas

b $CH_3CH_2CH_2CH_2COOH(aq) + Na_2CO_3(aq) \rightarrow 2CH_3CH_2CH_2CH_2COONa(aq) + CO_2(g) + H_2O(l)$

Products: sodium pentanoate, carbon dioxide gas and water

c $Br_2(aq) + CH_2{=}CH_2(l) \rightarrow CH_2BrCH_2Br\ (l)$

Products: 1,2-dibromoethane

3 Chemical testing is relatively quick and easy; little sample preparation is required; it does not require expensive equipment; and simple testing can be done in the field. It needs a larger sample; only identifies the presence of functional groups; provides no information on molecular structure; and changes the original sample. It can be inclusive if a number of functional groups that give similar results are present.

Instrumental techniques require expensive equipment and are usually done in a laboratory. They require only a small amount of sample and most techniques are non-destructive. Careful sample preparation is required. Results are accurate and prove details that can be used to determine molecular structure.

4 IR, since the functional groups are different in each class of compounds

5 For ^1H – the number of different environments for the hydrogens, the number of hydrogens in each environment, the type of protons present and if it is high resolution NMR the number of hydrogens on the adjacent atoms

For ^{13}C – the number of different environments for the carbons

NMR provides information about the structure of proteins and biomolecules in solution, which is where they are active.

6 Mass spectroscopy

7 The molar mass uses the RAM for the element. The RAM for each element is determined by a weighted average for each of the isotopes (the RIM) present for that element.

8 Since the compound contains chlorine, it would be expected to have two peaks at 35:37 in the approximate ratio of 3:1 due to the chlorine isotopes that would be present as well as a corresponding set at peaks that correlate to the molar mass of the chloroalkane.

If chloroalkane was a dichloro, then a set of three peaks would be expected, which would correlate to the presence of two ^{35}Cl – a molecule with one ^{35}Cl and one ^{37}Cl and a peak corresponding to two ^{37}Cl isotopes present on the molecule. For dichloromethane, the peaks would be at 84, 86 and 88. The 84 peak would be more abundant because the ^{35}Cl is more abundant than the ^{37}Cl.

9 P decolourised bromine, reacted with sodium metal but not sodium carbonate, so it must be ethanol.

$CH_3CH_2OH(l) + Br_2(soln) + H_2O(l) \rightarrow CH_3COOH(l) + 2Br^-(soln) + 2H^+(aq)$

$2CH_3CH_2OH(l) + 2Na(s) \rightarrow 2CH_3CH_2ONa(soln) + H_2(g)$

Q decolourised bromine but no other reaction, so it must be 3-heptyne.

$CH_3CH_2C{\equiv}CCH_2CH_2CH_3(l) + Br_2(soln) \rightarrow CH_3CH_2CBr_2CHBr_2CH_2CH_2CH_3(l)$

R reacts with sodium carbonate and sodium producing a gas in both instances, so it must be butanoic acid.

$2CH_3CH_2CH_2COOH(aq) + Na_2CO_3(aq) \rightarrow 2Na^+(aq) + 2CH_3CH_2CH_2COO^-(aq) + CO_2(g) + H_2O(l)$

$2Na(s) + 2CH_3CH_2CH_2COOH(aq) \rightarrow 2Na^+(aq) + 2CH_3CH_2CH_2COO^-(aq) + H_2(g)$

10 **a**

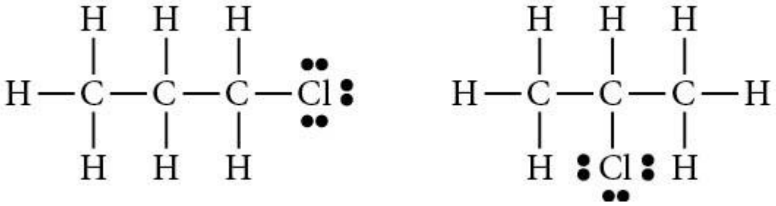
C	H	Cl
46	9	45
46/12	9/1	45/35.5
3.839	9	1.27
3.02	7.09	1

Empirical formula: C_3H_7Cl

b Parent peak is 78 (which is the molecular mass)

c Chlorine has two isotopes: a ^{35}Cl and a ^{37}Cl. The ^{35}Cl is the most abundant isotope and is the one used to determine the parent peak. The ^{37}Cl isotope would have a higher m/z value.

d



e The peak at 43 would be the peak due to the loss of the chlorine; a $CH_3CH_2CH_2^+$.

The peak at 63 would be the parent peak loss of a methyl group.

The peak at 65 would be the parent peak with the ^{37}Cl ion loss of a methyl group.

f The most likely isomer is the second one.

Mass spectra have a base peak at 43, which would be a $CH_3CH_2CH_2^+$. This could be either isomer.

The peak at 63 due to the loss of a methyl group is most likely from the second isomer since there are two methyl groups to be lost.

If it was the first isomer, then a peak due to CH_2Cl^+ at a m/z value of 49 would be expected to be seen. A peak at a m/z value of 29 due to $CH_3CH_2^+$ could be seen. These are not present.

11 IR analysis detects the functional groups present. Drug X would be expected to have a different structure to a perfume and so would have different functional groups. The reaction pathway indicates the many steps involved. Knowing what was being made along the way will indicate that the aim was to produce the drug rather than a perfume, which would have a different pathway.

12 Mass spectra will usually provide the molar mass of a molecule and the fragmentation patterns of molecules can also provide clues to the structure.

NMR gives more information about the structure such as the number of protons of each type. It can provide information about the order in the molecule.

When the molecule is relatively simple (such as ethanol), either technique can be used. When the molecules are more complex, combining techniques is beneficial.

13 1, due to symmetry

14 **a** In 1-nitropropane, there would be three C environments, so three peaks.

In 2-nitropropane, there would be two C environments due to symmetry, so two peaks.

b Yes, the ^1H would also provide the ratio of H on the different carbon atoms.

In 1-nitropropane, there would be three H environments in a ratio of 3:2:2

In 2-nitropropane, there would be two H environments in a ratio of 6:1

15 Alcohols will usually fragment at the C—COH bond.

1-propanol would be expected to produce a peak at 29 m/z due to $CH_3CH_2^+$ and a peak at 21m/z due to CH_2OH^+.

2-propanol would be expected to produce a peak at 15 m/z due to CH_3^+ and a peak at 45 m/z due to CH_3CHOH^+.

16 **a**

C	H	O
48.63	8.18	43.19
48.63/12	8.18/1	43.19/16
4.05	8.18	2.7
1.5	3.03	1
3	6	2

Empirical formula: $C_3H_6O_2$

b **i** The parent peak is 74 so the molar mass is 74. The molecular formula is $C_3H_6O_2$.

ii The peak with a m/z value of 45 could be due to $COOH^+$.

The peak with a m/z value of 29 could be due to $CH_3CH_2^+$ or CHO^+.

c **i** Carboxylic acids have an OH group. The OH stretch is a broad trough at around 2500–3100 cm^{-1} that is not present.

ii C—H band at 3000 cm^{-1}

C—C band at 1100 cm^{-1}

C=O band at about 1700 cm^{-1}

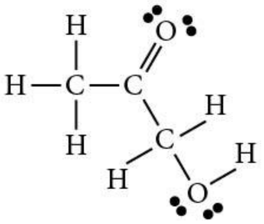
d $CHOOCH_2CH_3$ ethyl methanoate; flavourings: esters

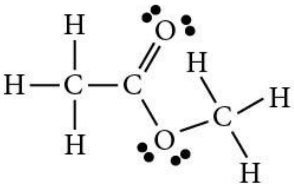
e There are three H environments. One peak with a relative intensity of 3 due to CH_3 probably around 1 ppm, one peak relative intensity of 2 due to the O—CH_2 , and one peak with a relative intensity of 1 due to H—COO.

f Ethanol and methanoic acid; esterification or condensation

$$HCOOH + CH_3CH_2OH \rightarrow HCOOCH_2CH_3$$

g

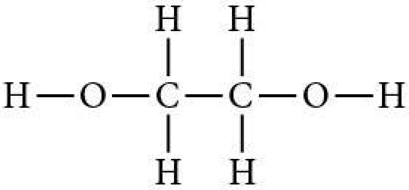




17 1,2-ethanediol; molar mass 62: consistent as peak at m/z of 62.

Symmetrical molecule: CH_2OH^+ fragment peak at m/z 31 consistent.

Other peaks could be due to further fragmentations.



In a low resolution ^1H NMR, two peaks would be expected for the two different proton environments.

In ^{13}C NMR, one peak would be expected as the molecule is symmetrical with both C in the same environment.

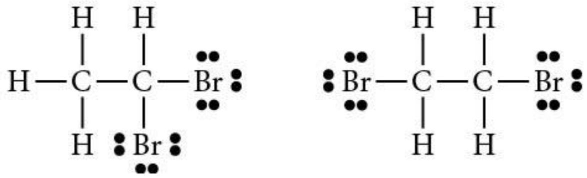
18 Run the sample of salicylic acid in an IR spectrometer. Compare the fingerprint region with a pure sample. If the sample of aspirin was pure, then the fingerprint region would only show the same bands.

If salicylic acid was present in the aspirin, then the broad OH trough would still be present in the IR spectrum of the sample.

UV–vis would be able to determine the purity of the sample. A set of standards could be run with a predetermined amount of salicylic acid and a calibration curve could be developed.

19 The shifts are small, so this is a ^1H NMR spectra. The molecule has two Br – which may account for the shifts being higher than in Table 15.6. There are two environments , one at a shift near 6 ppm with a relative intensity of 1. This is a quartet that indicates three protons in the neighbouring carbon. The peak at 2.5 is a doublet with a relative intensity of 3. This indicates a singlet proton in the neighbouring carbons.

The two possible isomers for $C_2H_4Br_2$ are:



The first structure has two environments, which would have a relative intensity of 3:1. The three protons would be split into a doublet by the single proton that itself would be split into a quartet. This is the structure.

The second structure has only one environment and would not have a splitting pattern and only one peak.

20 ^{13}C NMR:

Ethanol: CH_3CH_2OH, has two peaks, CH_3 with a shift 8–25 ppm, CH_2 with a shift 50–90 Spectra **a**

Ethanoic acid: CH_3COOH, two peaks, CH_3 with a shift 8–25 ppm, COOH with a shift 165–185, Spectra **b**

Ethyl ethanoate: $CH_3COOCH_2CH_3$, four peaks, with the two CH_3 peaks close together, Spectra **c**

IR:

Ethanol: CH_3CH_2OH, broad OH band 3300 cm^{-1} no C=O band, Spectra **d**

Ethanoic acid CH_3COOH, broad OH band at 3300 cm^{-1} C=O band 1700 cm^{-1}, Spectra **f**

Ethyl ethanoate: $CH_3COOCH_2CH_3$, NO OH band, C=O and C—O bands, Spectra **e**

Mass spectra:

Ethanol: CH_3CH_2OH, molar mass 46, Spectra **h**

Ethanoic acid: CH_3COOH, molar mass 60, Spectra **i**

Ethyl ethanoate: $CH_3COOCH_2CH_3$, molar mass 88, Spectra **g**

21 a

C	H	N	O
54.55	9.9	10.7	24.85
4.54	9.9	0.76	1.55
5.97	13	1	2.0

Empirical formula = $C_6H_{13}NO_2$

b With both N and O: amino acids

c The IR spectra show different bands or troughs that indicate they are not the same sample – the fingerprint regions are very different.

Module 8: Applying chemical ideas

Chapter 16: Chemical synthesis and design

Check your understanding 16.1

1 **a** Synthesis, with respect to chemistry, is the process of producing a specific product.

b A reaction pathway is the sequence of chemical reactions for an overall chemical change.

c An intermediate is a product of one reaction that is used as a reactant in the next reaction of a reaction pathway.

2 Students responses will vary. The answer may be specific substances, such as plastic bottles, aspirin, dish washing detergent, or a general group, such as. plastics, pharmaceuticals, soaps and detergents.

3 **a** $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

b This an example of a simple synthesis reaction in which two reactants combine to form a single product. When producing a product such as aspirin, there are many steps in the process and the reactants do not immediately give the desired product.

4 **a** Identify the reactants and determine the reaction pathways to follow.

b In order to produce a particular product, the correct reactants must be used and the way and conditions in which they will react to give this product must be identified.

5 **a** Ethylethanoate is an ester produced from a reaction between ethanol and ethanoic acid. A method such as that used in Investigation 12.1, p.347 would be appropriate.

b Bioethanol is produced by fermentation of carbohydrates such as those found in grain and fruits. For example, sorghum and yeast would be two possible reactants. A method such that used in Investigation 11.3, steps 1–5, p.331 would be appropriate.

c Soap is produced by the hydrolysis of fats. Suitable reactants would be vegetable oil and sodium hydroxide. A method such as that used in Investigation 12.3, p.355 would be appropriate.

Check your understanding 16.2

1 Factors that must be considered when choosing the steps in a reaction pathway are:

- the reactants – safety, cost, availability
- the products – safety, yield, atom economy
- the activation energy – this will affect the rate of the reaction
- any side reactions – this will affect the purity of the product and the amount of waste
- the cost and safety involved with the required conditions.

2 Retrosynthetic analysis involves considering the desired product and then working backwards to determine the steps and the reactants needed. For each step (working backwards), a simple precursor is identified. This process is continued until simple, available reactants are identified

3 In the contact process, the product of one reaction becomes the reactant for the next reaction. This continues until the desired product is achieved. This is a linear sequence.

4 a Ethanol may need to be produced. This could be done using an addition reaction between ethene and water.

Ethanoic acid may also need to be produced and this could be done by oxidising ethanol.

Therefore, production of an ester would be a convergent process.

b Grain and fruit is readily available as a reactant as is yeast so neither of these would need to be produced first.

This is a linear sequence.

c Fats and oils may need to be extracted from nuts or seeds.

Sodium hydroxide would need to be produced and this can be done electrolysis of a concentrated sodium chloride solution.

This would be a convergent process.

5 A synthesis reaction pathway should be designed so the desired product can be produced cheaply, safely and efficiently. This is maximised by having a high yield and purity of the product. This allows the maximum profit to be made. Ideally, the process would also consider reducing the amount of waste produced and the environmental safety of the reactants, products and process.

Worked example 16.1

1 $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

$$n = \frac{V}{22.71} \qquad n(H_2) = \frac{5}{22.71} = 0.220\ \text{mol}$$

$$n(N_2) = \frac{3}{22.71} = 0.132\ \text{mol}$$

$$\text{SR} = \frac{3}{1} = 3$$

$$\text{AR} = \frac{0.220}{0.132} = 1.67$$

SR > AR, therefore hydrogen gas is limiting

$$\therefore n(NH_3) = \frac{n[H_2]\times 2}{3} = \frac{0.220\times 2}{3} = 0.147\ \text{mol}$$

$$m = nM$$

$$\therefore m(NH_3) = 0.147 \times 17.034 = 2.50\ \text{g}$$

2 $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$$n = \frac{m}{M} \qquad n(SO_2) = \frac{1000}{64.07} = 15.61\ \text{mol}$$

$$n(O_2) = \frac{1000}{32} = 31.25\ \text{mol}$$

$$\text{SR} = \frac{2}{1} = 2$$

$$\text{AR} = \frac{15.61}{31.25} = 0.5$$

SR > AR, therefore sulfur dioxide is limiting

$$\therefore n(SO_3) = n(SO_2) = 15.61\ \text{mol}$$

$$m = nM$$

$$\therefore m(SO_3) = 15.61 \times 80.07 = 1249.9\ \text{g} = 1.25\ \text{kg}$$

Worked example 16.2

1 $C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$

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

$$\therefore n(C_7H_6O_3) = \frac{30.0}{138.118} = 0.2172 \text{ mol}$$

$$\therefore n(C_9H_8O_4) = n(C_7H_6O_3) = 0.2172 \text{ mol}$$

$$m = nM$$

$$\therefore m(C_9H_8O_4) = 0.2172 \times 180.154 = 39.1 \text{ g}$$

$$\therefore \%\text{ yield} = \frac{25.0}{39.1} \times 100 = 63.9\%$$

2 $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

200 atm = 200 × 101.3 = 20 260 kPa

400°C = 400 + 273.15 = 673.15 K

$$PV = nRT$$

$$\therefore n(N_2) = \frac{PV}{RT} = \frac{20260 \times 35}{8.314 \times 673.15} = 126.70 \text{ mol}$$

$$n(NH_3) = n(N_2) \times 2 = 253.4 \text{ mol}$$

$$m = nM$$

$$\therefore m(NH_3) = 253.4 \times 17.034 = 4316.4$$

$$\therefore \%\text{ yield} = \frac{1500}{4316.4} \times 100 = 34.8\%$$

Worked example 16.3

1 $$\text{Percent purity} = \frac{\text{mass of useful product}}{\text{total mass of sample}} \times 100\%$$

$$\%\text{ purity} = \left(\frac{5.63}{6.00}\right) \times 100 = 93.8\%$$

2 $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$

$n(HCl) = cV = 1.3 \times 0.0453 = 0.05889$ mol

Use the stoichiometric ratio to calculate the moles of aspirin.

Ratio =2:1

$n(Mg(OH)_2) = ½\, n(HCl) = ½ \times 0.05889 = 0.0294$ mol

$m = nM = 0.0294 \times 58.3 = 1.71$ g

$$\% \text{ purity} = \left(\frac{mass\ product}{mass\ sample}\right) \times 100 = \left(\frac{1.71}{1.75}\right) \times 100 = 97.7\%$$

Check your understanding 16.3

1 The rate of the reaction is how quickly the products are produced. The yield of the reaction is the amount of products that can be produced from the reactants.

2 To maximise the yield of a reaction, the equilibrium should lie to the right.

3 The maximum yield for a reaction is 100%. This would mean that all the reactants have formed products.

4 By removing the product, its concentration is decreased. This will favour the forward reaction, forming more products. This means that more of the reactants will form products and so the yield is increased.

5 a Higher temperatures favour the reverse reaction and would lead to a decrease in yield, so lower temperatures are used, while higher pressure would favour the forward direction, leading to both increased yield and rate. They are not used due to safety risks and cost.

b Temperature: 400–450°C

A compromise is made between the rate of the reaction and the yield. A higher temperature would increase the rate of the reaction. However, since the forward reaction is exothermic, a higher temperature would favour the reverse reaction, decreasing the yield of ammonia.

Pressure: approximately 200 atm.

A high pressure leads to both an increased rate and yield. A high pressure increases the concentration of the reactants and therefore the rate of the reaction. A high pressure will also increase the yield since it will favour the forward reaction that uses four molecules for every two molecules it produces.

Even higher pressures are not used due to the safety risks and cost associated with extreme pressures.

Catalyst: a catalyst is used to increase the rate of the reaction. Catalysts assist in overcoming the effect of the relatively moderate temperature. In the Haber process, an iron/iron oxide catalyst is used.

6 **a** Purity is used to determine the quality of a product. The required level of purity of a product is related to the use of the product. If the product is to be used for human consumption, then a much higher degree of purity is necessary than if it was to be used as a fuel or in a fertiliser.

b Instrumental methods such as mass spectrometry, NMR spectroscopy and IR spectroscopy are used to monitor a product for the presence of impurities.

c Techniques used to determine the quantity of useful product in a sample include volumetric and gravimetric analysis and colourimetric techniques.

7 $Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$

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

$$\therefore n(Al(OH)_3) = \frac{25.0}{78.004} = 0.3205 \text{ mol}$$

$$\therefore n(AlCl_3) = n(Al(OH)_3) = 0.3205 \text{ mol}$$

$$m = nM$$

$$\therefore m(AlCl_3) = 0.3205 \times 133.33 = 42.7 \text{ g}$$

$$\therefore \% \text{ yield} = \frac{20.0}{42.7} \times 100 = 46.8\%$$

8 $C_6H_6(l) + Cl_2(g) \rightarrow C_6H_5Cl(s) + HCl(g)$

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

$$\therefore n(C_6H_6) = \frac{90.0}{78.108} = 1.152 \text{ mol}$$

$$\therefore n(C_6H_5Cl) = n(C_6H_6) = 1.152 \text{ mol}$$

$$m = nM$$

$$\therefore m(C_6H_5Cl) = 1.152 \times 112.55 = 129.7$$

$$\therefore \% \text{ yield} = \frac{125.0}{129.7} \times 100 = 96.4\%$$

9 **a** $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

b A high rate of reaction would be favoured by a high temperature, increased concentrations of H_2 or Cl_2, a high pressure/low volume or the addition of a catalyst.

c A high yield would be favoured by the addition of H_2 or Cl_2, the removal of HCl, and a low temperature.

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

$\therefore n(Cl_2) = \frac{3000}{70.9} = 42.31 \text{ mol}$

$\therefore n(H_2) = \frac{150}{2.016} = 74.4 \text{ mol}$

$SR = \frac{1}{1} = 1$

$AR = \frac{42.31}{74.4} = 0.569$

SR > AR, therefore chlorine is limiting

e Theoretical yield would occur when all the limiting reagent was converted to product.

$n(Cl_2) = 42.31 \text{ mol}$

$n(HCl) = 2 \times n(Cl_2) = 84.62 \text{ mol}$

$m(HCl) = 84.62 \times 36.46 = 3085 \text{ g} = 3.085 \text{ kg}$

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

$n(NaOH) = 0.500 \times 0.02050 = 0.01025 \text{ mol}$

$n(NaOH) = n(HCl) = 0.01025$ mol in 25 mL sample

In 200 mL $n(HCl) = 0.01025 \times 8 = 0.082$ mol

Number of moles HCl in original sample n(HCl) = 0.500 × 0.200 = 0.100 mol

Number of moles HCl reacted with sodium carbonate = 0.100 − 0.082 = 0.018 mol

$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

$n(Na_2CO_3) = ½\ n(HCl) = ½ \times 0.019 = 0.009 \text{ mol}$

$m(Na_2CO_3) = 0.009 \times 109 = 0.95 \text{ g}$

b $m(HCl)$ in sample = 0.082 × 36.5 = 2.99 g

$\% \text{ purity} = (\frac{2.99}{200}) \times 100 = 1.5\%$

Check your understanding 16.4

1 The chemical industry is important because it contributes significantly to Australia's economy, provides a large number of jobs and produces household and industrial chemicals for use in Australia and for export.

2 Student responses will vary but should mention environmental problems.

3 Increasing regulation, better treatment and disposal of wastes, new, cleaner processes being developed

4 The area of chemistry that aims to reduce the impact of chemistry on the environment

5 Student responses will vary, but should mention the need to improve chemical use, reduce waste and find more environmentally friendly production processes.

For example: green chemistry is vitally important to ensure that chemical synthesis is minimising (and hopefully stopping) the negative impacts on the environment. By reducing energy use, less greenhouse gases are emitted. By using renewable resources, we are not depleting sources of non-renewable resources. By reducing waste, we don't have to develop additional steps, using more chemicals, to eliminate the waste. By using and producing less hazardous chemicals, there are fewer risks associated with the synthesis.

Companies that do not implement green chemistry will have a negative impact on the environment. This may lead to future extinction of species, go against the efforts to reduce greenhouse gases or lead to accidents that directly impact on the environment as well as humans.

Chapter review questions

1 The aim of synthesis reactions is to produce a specific product.

2 The reaction mechanism is the sequence of steps for the overall synthesis process.

3 A catalyst will allow the reaction to proceed at a faster rate. This may mean that the process can be carried out at lower temperatures or pressures and reduce the energy consumption. Catalysts are also not consumed in the reaction, meaning that only small quantities are needed, so therefore less chemicals are needed.

4 The position of equilibrium determines the yield of a reaction. During a synthesis reaction, the aim is to produce as much product from the reactants as possible. This means that it is desirable to have equilibrium lie as far to the right as possible.

5 If the efficiencies of the individual steps are similar, a convergent sequence will have an overall higher yield that is preferable.

6 Examples could be the contact process or Haber process.

7 a Yield is the amount or percentage of the possible product that is actually produced, while purity is the degree or percentage to which a mixture contains only the desired synthesised compound or element.

b These are both important in a synthesis reaction because the desired outcome is to produce a high yield (a large amount of product) with few impurities.

8 In the reactions given the ozone (O_3) is the reactant, the oxygen atom (O) is the intermediate and the oxygen molecule (O_2) is the product.

9 When the temperature is decreased, the exothermic reaction will be favoured. Since the exothermic reaction is the forward one in this reaction, a decrease in temperature would increase the yield.

10 **a** **i** Increasing the pressure would drive the reaction to the left, reducing yield.

ii Increasing temperature would drive the reaction to the right, increasing yield.

b Low pressure and increased temperature

c $2CH_4(g) + O_2(g) \rightleftharpoons 2CO(g) + 4H_2(g)$

i Ratio is 2:1, so oxygen would be in excess.

ii Assuming 100 ml methane reacts, 100 mL carbon monoxide would be produced (2:2 ratio).

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

$$n(\mathrm{HCl}) = \frac{1.0}{36.5} = 0.0274 \text{ mol}$$

$$n(\mathrm{CaCO_3}) = \frac{2.5}{100.1} = 0.0250 \text{ mol}$$

Ratio is 2:1 so amount of $CaCO_3$ needed is ½ n(HCl) = 0.0137 mol.

More $CaCO_3$ has been added than needed.

b If the same relative amount of $CaCO_3$ was used on a much larger scale, almost twice as much would have been used than was needed, resulting in an unnecessary cost.

12 For water, 1 mL weighs 1 g. Therefore, 100 mL weighs 100 g.

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

$$\therefore n(\mathrm{H_2O}) = \frac{100}{18.016} = 5.551 \text{ mol}$$

$$\therefore n(\mathrm{O_2}) = \frac{n(H_2O)}{2} = 2.775 \text{ mol}$$

$$m = nM$$

$$\therefore m(\mathrm{O_2}) = 2.775 \times 32 = 88.8$$

$$\therefore \%\text{ yield} = \frac{65.0}{88.8} \times 100 = 73.2\%$$

13 **a** $Ag^+(aq) + NaCl(aq) \rightarrow AgCl(aq) + Na^+(aq)$

$n(NaCl) = 1.00 \times 0.01045 = 0.01045$ mol

$n(NaCl) = n(Ag^+) = 0.01045$ mol (in 25 mL)

In 100 mL:

$n(Ag^+) = 0.01045 \times 4 = 0.0418$ mol

$m(Ag) = 0.0418 \times 107.9 = 4.51$ g

$$\% \text{ Ag} = \left(\frac{4.51}{10}\right) \times 100 = 45.1\%$$

b The coin being analysed is a forgery since it only has 45.1% silver, while the genuine coin is 90% silver.

14 Many answers could be considered, including:

- use of fungi to make penicillin
- increased cost of penicillin
- more deaths due to bacterial infections
- lower populations due to increased deaths
- greater research into alternative treatments.

15 Responses should consider the benefits of the development of a new substance.

16 Responses should present an issue and discuss how the issue could be addressed.

End-of-module 8 review

1 B

2 A

3 D

4 C

5 C

6 B

7 C

8 A

9 B

10 C

11 **a** Student responses may vary, but explanation should mention a specific example and give consequences to environment if monitoring did not occur.

b i

C	H	Br
17.84%	2.97%	79.19%
1.487	2.97	0.9911
1.500	3.00	1

Empirical formula: $C_3H_6Br_2$

Parent peak = 200, which is consistent with the empirical formula so the molecular formula is $C_3H_6Br_2$

ii Bromine has two isotopes one with an amu of 79 and one with an amu of 81, which are in approximately the same proportion. Therefore, a peak due to two 81 Br atoms would occur at 204 m/z.

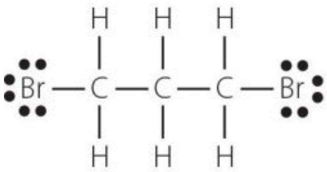
There would also be a peak at 202 due to one 79Br and one 81Br both being present.

iii Two environments, suggesting symmetry for a C3H6Br2.

A muliplet at a shift just over 2 with a relative intensity of 1 indicates more than three protons on the neighbouring carbons.

A triplet with a relative intensity of 2 at around 3.5 ppm this indicates two protons on the neighbouring carbons.

Relative intensity 1:2 with 6 hydrogens present suggests 2 hydrogens in first environment and 4 in the second environment. The structure is:



12 Since the sample contains three ions, each of the ions needs to be identified and removed from the sample separately. Only the carbonate ion will react with HNO_3. The reaction will produce carbon dioxide gas and water, removing the carbonate ion from the sample. This must be done first, otherwise the carbonate ion would precipitate with both Ba^{2+} and Ag^+ . Sulfate ions precipitate with both Ba^{2+} and Ag^+, while chloride ions only precipitate with Ag^+. Therefore, addition of Ba^{2+} will produce a precipitate of $BaSO_4$ that can be removed by filtration leaving only the Cl^- ions. Addition of Ag^+ will produce a precipitate of AgCl that can then be removed.

13 a A = Ca^{2+}, B = Fe^{3+}, C = Ag^+, D = Mg^{2+}, E = Pb^{2+}

b Mg^{2+}, Ag^+

c 1: Add SO_4^{2-} to precipitate Ba^{2+} and filter to obtain $BaSO_4$ precipitate.

2: Add OH^- to filtrate to precipitate both remaining ions then add NH_3 to dissolve Cu^{2+} precipitate. Filter to obtain $Mg(OH)_2$ precipitate. Cu^{2+} ions remain in solution.

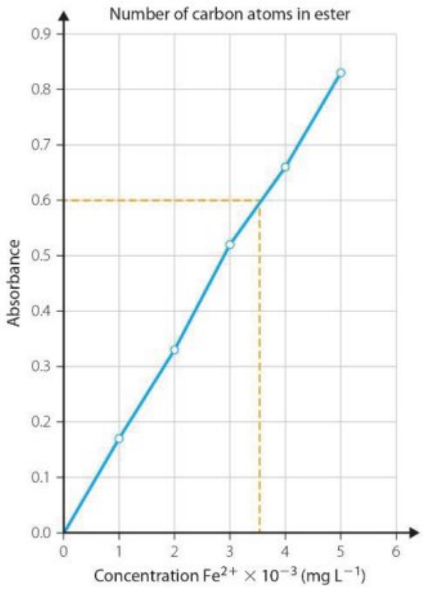
14 **a** 9.308%

b $ZnNH_3PO_4$ has a molar mass of 177.4 g, while ZnP_2O_7 has a molar mass of 239 g. If not all the $ZnNH_3PO_4$ was converted to ZnP_2O_7, the final mass would be less than if all had been converted so the % calculated would be less than actual.

15 **a** $[Cl^-] = 4.5 \times 10^{-3}$ mol L^{-1}

b $[Cl^-] = 160$ mg L^{-1} so sample is within guidelines value.

16 **a**



b $[Fe^{2+}] = 3.5 \times 10^{-3}$ mg L^{-1}

17 **a** 445 millimicrons

b Alizarin is an acid–base indicator so there is a changes colour in the visible region of the spectrum. Therefore, the concentration of each form of the indicator can be determined using wavelengths in the visible region of the spectrum. Colourimetry could also have been used.

18 **a** $58 = [CH_3CH_2CH_2CH_3]^+$. This is the parent peak and it give the relative molecular mass of the compound.

b $15 = [CH_3]^+$

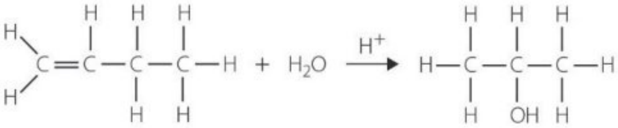
$28 = [CH_3CH]^+$

$43= [CH_3CH_2CH_2]^+$

c The peak at 43 shows the fragment left after a methyl group has split. It is useful in identifying that the butane molecule is a straight chain since an isomer would produce a different fragment pattern.

19 A = 1-butene

The hydration of 1-butene to 2-butanol:



B = 2-butanol

The oxidation of 2-butanol to butanone using permanganate is:

$5CH_3CHOHCH_2CH_3(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3COCH_2CH_3(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

C = butanone

IR spectrum of A shows peak at 3000 cm^{-1}, which is indicative of C—H bond, and peak around 1600–1700 cm^{-1}, which is indicative of double bond.

NMR spectrum of A shows four peaks, which means there are four different carbon environments. The two peaks between 110–140 ppm would be the carbons attached to the double bond, while the other two peaks are C—C bonds. If the compound was 2-butene, there would only be two peaks so the compound must be 1-butene.

IR spectrum of B shows characteristic broad band for alcohols at around 3200–3400 cm^{-1}, no broad band around 2500–3000 cm^{-1}, so it cannot be an acid.

NMR spectrum of B shows four peaks which means four different carbon environments. Peak at 70 ppm shows C—O shift for alcohol. Peaks from 10–40 ppm would be shifts for the three different C—H environments. Spectra could be for 1-butanol or 2-butanol.

IR spectrum for C shows strong band at 1700 cm^{-1}, which is characteristic of C=O cm^{-1}. Absence of broad peak at 2500–3300 cm^{-1} for acid O—H means compound could be an aldehyde or ketone.

20 Percentage yield = 92.5%