Chapter 1 Working scientifically

1.1 Questioning and predicting

1.1 Review

1 An inquiry question ends with a question mark and guides the investigation. A hypothesis is a cause-and-effect statement that can be tested through an investigation. The purpose is a statement outlining the aim of the investigation.

2 A. This is a question and could be used to guide an investigation. Options B, C and D are statements.

3 Qualitative. If you observe that the colour of a precipitate, for example, is ‘white’ or ‘light green’ then this is a descriptive quality, not a numerical value.

4 A. The phosphate concentration of various types of laundry detergent can be measured using gravimetric analysis or UV-visible spectroscopy. Option B does not specify the type of organism that detergent might be toxic to. Option C does not specify what is meant by 'best'. Option D does not specify the type of washing and how dirty it is.

5 A. Temperature and pH of water can be measured. Option B is not specific. Options C and D are not inquiry questions.

6 C. This hypothesis is written as a cause-and-effect statement that could be tested in an investigation.

1.2 Planning investigations

1.2 Review

1 **a** valid
   b reliable
   c accurate.

2 F. Water can be sampled from various possible locations in the field.

3 C and D. Gloves and rubber boots prevent contact with pollutants, and rubber boots also reduce the risk of slipping on wet rocks or soil.

4 B. Repeating an experiment multiple times increases the reliability of an investigation. If the values reported are close to each other, then the values are also precise. Accuracy refers to how close the measured values are to the actual value, and can be increased by reducing systematic errors.

5 **a** pH of water; this is the factor that is being varied
   b mass of mussel; this is the factor that may change when the independent variable changes
   c temperature of water, method of pH measurement, equipment used to measure mass, type of mussel; these are other factors that could affect the mass if they were not kept constant

6
- Weigh approximately 10 g of marble chips into a conical flask. Record the mass to the number of decimal places displayed on the digital balance.
- Add a plug of cotton wool to the mouth of the conical flask.
- Tare the weighing balance to read exactly 0 g when the conical flask, marble chips and cotton wool plug are on the balance.
- Use a measuring cylinder to measure 100 mL of 0.5 mol L^{-1} hydrochloric acid.
- Remove the cotton wool plug.
- Immediately add the hydrochloric acid to the conical flask, add the cotton wool plug, and record the mass shown on the balance.

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1.3 Conducting investigations

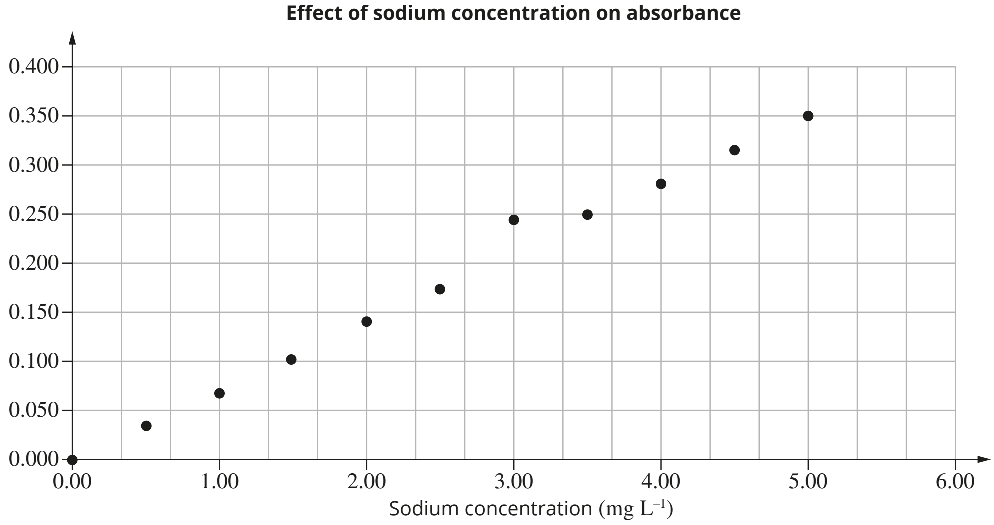
1.3 Review

1. Observations and measurements should be recorded in a logbook, so that you have a permanent record for future reference.
2. **a** systematic error: Because of improper calibration, every recorded mass will be incorrect. Time should be taken to learn how to calibrate all equipment properly before starting an experiment.
   b mistake: The different flasks of hydrochloric acid have not been correctly labelled, or were incorrectly selected. All materials should be labelled clearly and checked before they are used in experiments.
   c random error: This result is an outlier. Repeating an experiment will make outliers obvious.
   d systematic error: Because of poor definitions of the variables, the results will be inconsistent. Variables should be clearly defined before starting an experiment.
3. **a** 17.92, 17.98 and 18.02 mL; these are all within 0.10 mL of each other.
   b $\frac{17.92+17.98+18.02}{3}=17.97\,\text{mL}$
   c random error
4. **a** systematic error: This error will affect all volumes measured out using the pipette.
   b mistake: This was an error made by the student.
   c random error: This was caused by a random fault in the equipment that did not affect other measurements.

1.4 Processing data and information

1.4 Review

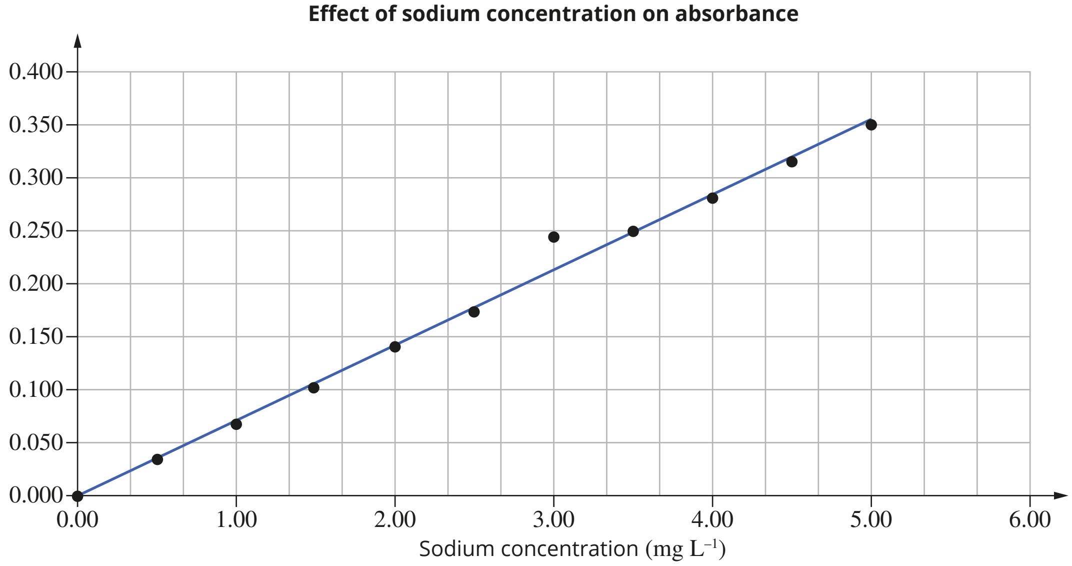
1. **a** $\frac{21+27+19+21+24+26+22}{7}=23$
   b 21: This is the most frequent number in the data set.
   c 22: This is the middle number when the data set it is arranged in numerical order.
2. **a** 4: All the figures in the value are significant.
   b Report the calculation to the least number of significant figures.
   c Report the calculation to the least number of decimal places.
3. **a** *y*-axis
   b *x*-axis
4. The tallest peak occurs at an *m*/*z* value of 31.
5. **a** As the temperature of a solution increases, the solubility of CH_4, O_2 and CO decreases. This is an inverse non-linear relationship. The solubility of He in solution decreases slightly as the temperature increases from 3°C to 35°C, then is relatively constant.
   b In general, the solubility of gases in solution decreases as the temperature of the solution increases.
6. **a**



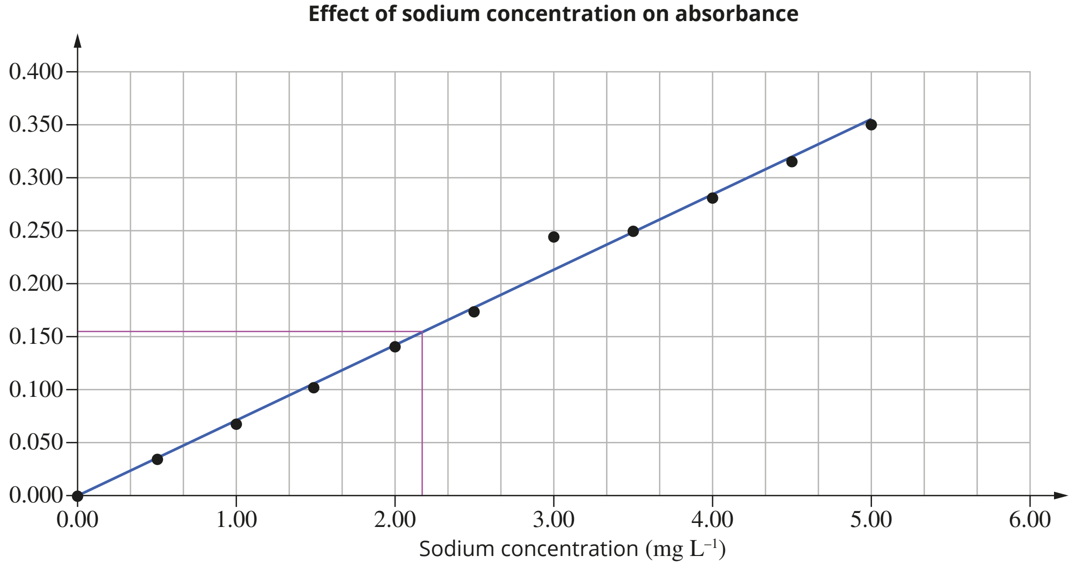
b An outlier is any data point that does not fit an observed pattern or trend. It could alter the gradient of a line of best fit if left in.

c The data point at 3 mg L^{-1} is an outlier.

d


Effect of sodium concentration on absorbance

e


Effect of sodium concentration on absorbance

From the graph, the concentration of sodium in the solution is 2.17 mg L^{-1}.

7 Label the *x*-axis ‘time’ with units, include units (g) on the *y*-axis, have a consistent scale on the *x*-axis, use a scale from 0 to 12 on the *y*-axis, use a scatter plot instead of a bar graph, and include a more descriptive title.

8 **a** The volume is least likely to be accurate because it is difficult to estimate the volume to the nearest 1 mL.

b The measured volume is likely to be more accurate than using a beaker, because a measuring cylinder has a graduated scale that enables the volume to be estimated to the nearest 0.1 mL.

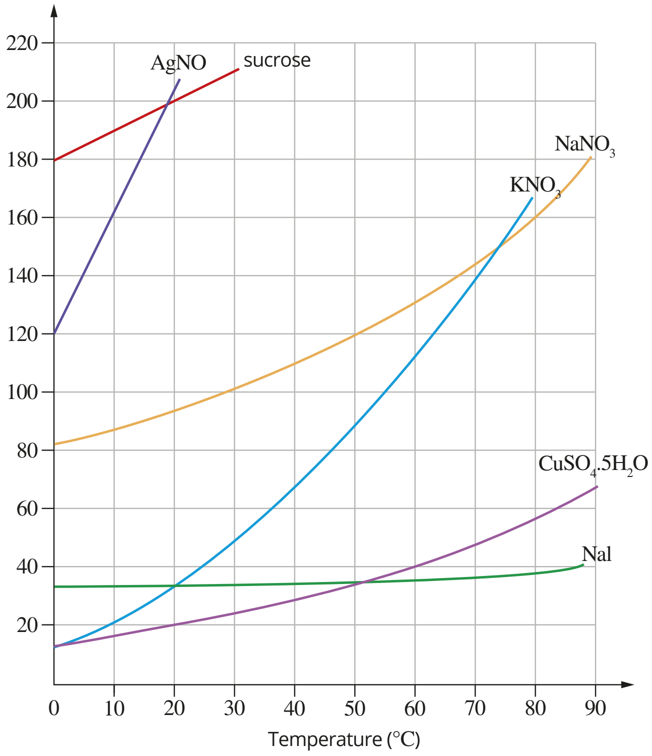
c The volume is likely to be the most accurate, because a burette is calibrated to estimate the volume to 2 decimal places.

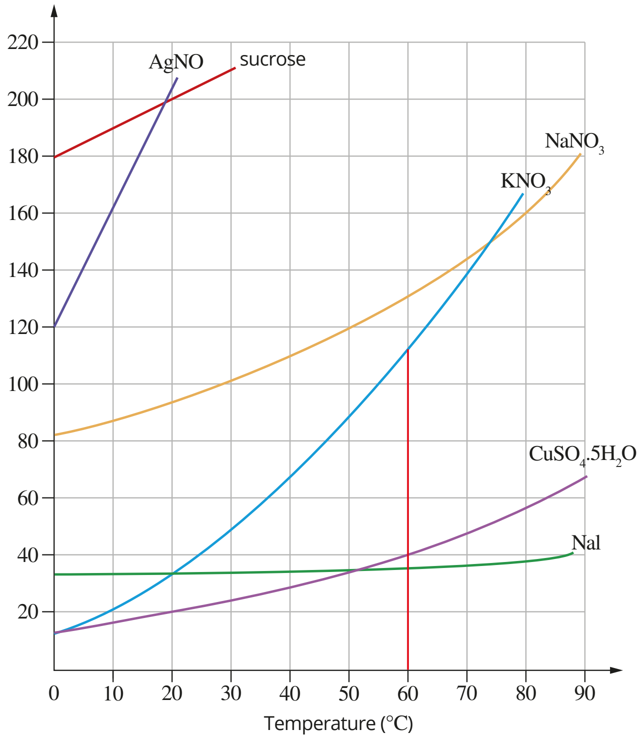
1.5 Analysing data and information

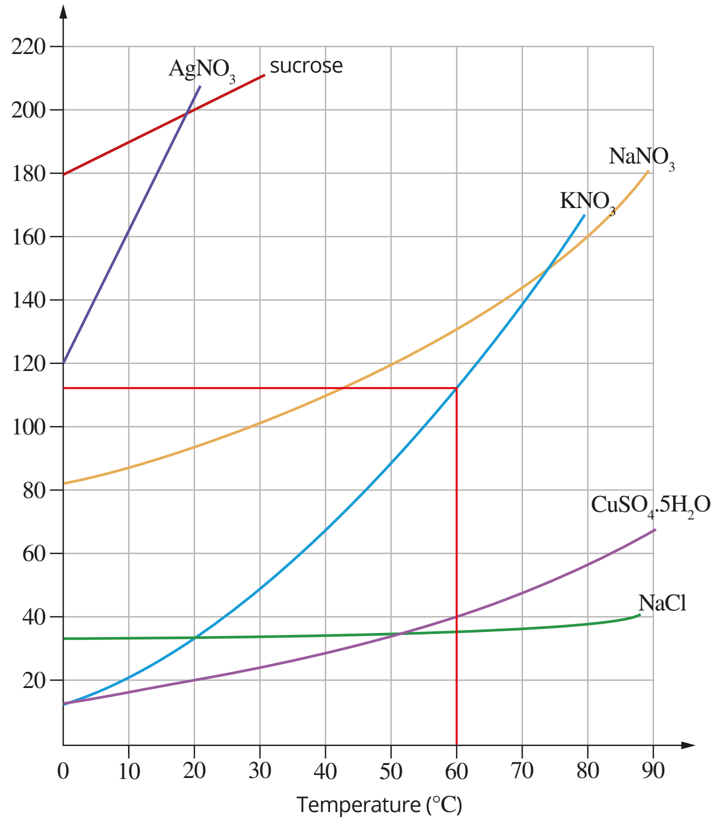
Worked example: Try yourself 1.5.1

READING INFORMATION FROM A GRAPH

Using the graph below, determine the mass of potassium nitrate (KNO_3) that will dissolve in 100 g of water at 60°C.



Thinking	**Working**
The solubility curve represents the maximum mass of solute that will dissolve in 100 g of water at a given temperature. Draw a vertical line from the required temperature on the x-axis to intersect with the solubility curve of the substance.	Draw a vertical line from 60°C on the *x*-axis to intersect with the solubility curve for KNO_3. 

Draw a horizontal line from the intersection point of the solubility curve to the *y*-axis. The point on the *y*-axis represents the mass of dissolved substance per 100 g of water.	
Read the solubility of the substance at the particular temperature from the graph.	The horizontal line intersects the *y*-axis at 112 g. Therefore the maximum mass of KNO_3 that will dissolve in 100 g of water at 60°C is 112 g.

1.5 Review

1 Bar graphs, histograms and pie diagrams are suitable for displaying discrete data, because the data in those graphs do not have to be continuous.

2 The reaction rate was constant between time t_0 and t_1. At t_1 there was an instantaneous increase in reaction rate, which gradually reduced until time t_2. The rate of reaction from t_2 onwards was constant, but greater than the reaction rate up until t_1.

3 **a** The solubility curve for potassium nitrate shows that 140 g of solute will dissolve in 100 g of water at 70°C. The mass in 500 g of water is $\frac{140\times500}{100}=700$ g.

b The solubility curve for potassium nitrate shows that 140 g of solute will dissolve in 100 g of water 70°C. The mass in 50 g of water is $\frac{140\times50}{100}=70$ g. The mass required to be added is 70 – 25 = 45 g.

c The solubility curve for potassium nitrate shows that 68 g of solute will dissolve in 100 g of water 40°C. The mass in 50 g of water is $\frac{68\times50}{100}=34$ g. The mass the will remain undissolved is 100 – 34 = 66 g.

4 The features of a credible primary or secondary source are: qualified authors, published in a reputable peer-reviewed journal, method detailed enough that the reader could replicate experiment, valid, reliable, accurate, precise, limitations outlined, assumptions outlined, and includes suggested future improvements or research directions.

1.6 Problem solving

1.6 Review

1 A. In UV–visible spectroscopy a wavelength should be selected where the substance absorbs strongly. The greatest absorbance occurs at 260 nm.

2 The procedure was repeated five times to minimise random errors.

3 Add a precipitating agent to precipitate the sodium ions and then use gravimetric analysis, or use atomic absorption spectroscopy.

4 **a** the equipment set-up, the time required for each step
  b **i** C_2HCl_3
    ii $C_2H_2ClF_3$
    iii $C_2HBrClF_3$

1.7 Communicating

1.7 Review

1 C. Options A, B and D are not in scientific style, because they use subjective language.
2 A, B and C. Option D is written in first-person narrative.
3 **a** 2.35×10^5
  b 6.55×10^{-7}
  c It allows very large and very small numbers to be expressed easily.
4 Stierwalt, S. (2016). Will salt water quench the world's thirst? *Scientific American, 315*(5). https://www.scientificamerican.com/article/will-salt-water-quench-the-world-s-thirst

CHAPTER 1 REVIEW

1 **a** bar graph
  b line graph
  c scatter graph with trend line
  d pie diagram.
2 B. Emotive language is not appropriate for a scientific report. Options A, C and D are written using objective language.
3 C. A periodic table, a scientific article summarised on a science website, a science documentary and this textbook are all examples of secondary sources of information, summarising findings by other researchers. A practical report written by a Year 12 student and an article published in a peer-reviewed scientific journal are examples of primary sources of information.
4 A. A is an example of an in-text citation written in APA style. B gives an in-text citation but in footnote style, not that of APA. C and D contain information that should be listed in the reference list at the end of the communication.
5 A purpose is a statement outlining the purpose of an investigation. A hypothesis is a cause and effect statement that can be tested through an investigation. The variables are the factors that can change in an investigation. The independent variable is the variable changed on purpose by the researcher, the dependent variable is the variable observed or measured in an investigation, controlled variables are all other variables that are maintained in the investigation.
6 **a** dependent variable
  b controlled variables
  c independent variable.
7 The independent variable is the source of water. The dependent variable is lead concentration. The controlled variables are method of lead analysis, sample size, and temperature of sample.
8 **a** The independent variable is the type of organic acid; the dependent variable is the dissociation constant.
  b The independent variable is the type of ionic compound; the dependent variable is the solubility of substance in water at 50°C.
  c The independent variable is the type of alcohol; the dependent variable is the property.
9 **a** corrosive chemical
  b toxic chemical
  c flammable chemical.
10 0.070 50 L; the final 0 is significant and must be retained.
11 **a** The mean is the average of a set of data.
  b The mode is the most frequent value in a set of data.
  c The median is the middle value in a set of data.

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12 $\frac{16.05+15.98+16.80+15.92+16.20+17.01}{6}=16.33$

The range of values is 17.01 – 15.92 = 1.09. Therefore the uncertainty of the average of the values is $16.33 \pm (1.09 \div 2) = 16.33 \pm 0.55$

13 The mean is most affected by an outlier.

14 **a** Answers will vary. Sample answer is: 2 significant figures 0.032, 3 significant figures 0.0302, 4 significant figures 0.030 20, 5 significant figures 0.030 200

b Report the final calculation to the least number of significant figures of the measurement used in the calculation.

c Report the final calculation to the least number of decimal places of the measurement used in the calculation.

15 **a** mistake: This is an error made by the student.

b random error: Random errors result in small differences in measurements either side of the mean.

c systematic error: This error will affect every measurement made with the scale.

16 **a** Accuracy refers to how close a measurement is to the true value. Precision refers to how close measurements are to each other.

b It might be invalid if more than one independent variable was changed at a time, an inappropriate method was used, outliers were included in data analysis, or an insufficient sample size was used.

c There are many possible answers e.g. the experiment was repeated only three times.

17 **a** reliability

b accuracy

c validity

d precision.

18 It gives appropriate credit to others, avoids plagiarism, and enables the reader to obtain further information.

19 **a** Purpose: To investigate the effect of temperature on the pH of water.

b The independent variable would be the water temperature; the dependent variable would be the measured pH; the controlled variables would be the source of water, sample size, method used, and calibration technique.

c pH is numerical so the data collected would be quantitative.

d universal indicator and colour chart: low precision

calibrated pH data-logging equipment: high precision e.g. ±0.1 pH unit

e It should be an indirect linear relationship, because the pH scale is logarithmic.

20 Similarities include credible sources for all sources stated, 2016 year of publication for Stierwelt and Li articles, Stierwelt and Romanok articles use data from the USA, the Elmahdi and BOM articles use Australian information, and all sources related to water quality.

Differences include that the Stierwalt article information has been fully summarised, but the summaries of the other articles are in progress, and the Stiewalt and Li articles have different focuses and therefore different conclusions.

21 Student answers will vary. For example, the student could design a valid experiment, with a control, to test the manufacturer's claim and compare to published findings from a consumer magazine such as Choice.

22 Student answers will vary. The data shows a strong correlation between per capita cheese consumption and the number of people who died from entanglement in bedsheets. To investigate whether the consumption of cheese could have caused death from entanglement in bedsheets, the student would need to propose a hypothesis for the causation and test the hypothesis (assuming ethical approval could be obtained). This could include investigating whether people who died from entanglement in bedsheets had consumed cheese on the night of their death, the type of cheese, allergies towards cheese, the quantity of cheese consumed, etc.

23 Student answers will vary. Possible answers include checking that: the inquiry question, hypothesis and purpose for the investigation are stated clearly; an appropriate risk assessment been undertaken; the variables have been clearly defined; the investigation has used an appropriate methodology to achieve an accurate, precise, reliable and valid answer to an inquiry question or hypothesis; all sources of information not created by the author have been acknowledged using in-text citations and following a consistent referencing style; the strengths and weaknesses of the investigation including limitations and suggested future improvements have been discussed; patterns and trends in data have been identified and discussed; appropriate chemical nomenclature and scientific conventions have been followed; tables and figures included in the communication are clearly labelled, relevant and signposted for the reader; and the writing style is appropriate for the intended audience.

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24 **a** 132 g $NaNO_3$ per 100 g of water.

b 161 g $AgNO_3$ per 100 g of water

c 68 g

d From the graph, 40 g of $CuSO_4.5H_2O$ will dissolve in 100 g of water at 60°C.

$$\frac{x}{40}=\frac{150}{100}$$
$$x=\frac{150}{100}\times 40$$
$$=60\,g$$

e from the graph, 120 g of $NaNO_3$ will dissolve in 100 g of water at 50°C.

$$\frac{x}{120}=\frac{83}{100}$$
$$x=\frac{83}{100}\times 120$$
$$=99.6=100\,g$$

25 The flowchart does not show: the state of each reactant, the reaction conditions and catalysts required for each step, the percentage yield of carbon dioxide in the two pathways, the rate of reaction, or the equilibrium constant for each step.

26 Student answers will vary.

27 Student answers will vary.

28

Measurement	**Value**	**Number of significant figures in measured or calculated value**
mass of crucible and lid (g)	41.893	5
mass of crucible, lid and Mg ribbon (g)	42.633	5
mass of crucible, lid and MgO (g)	43.143	5
mass of Mg (g)	42.633 – 41.893 = 0.740	3
mass of MgO (g)	43.143 – 41.893 = 1.250	4
% Mg in MgO	(0.740 ÷ 1.250) × 100% = 59.2%	3
% O in MgO	100 – 59.2 = 40.8%	3

29 **a** $BaCl_2$

b The mass of $BaSO_4$ precipitate was constant after the addition of 90 mL of 0.100 mol L^{-1} $BaCl_2$. This showed that all of the sulfate ions had precipitated as $BaSO_4$, and the $BaCl_2$ was in excess at the end of the experiment.

c Consider adding smaller volumes of $BaCl_2$, e.g. 15 mL increments. The graph shows that increments of 30 mL volumes of $BaCl_2$ were added in order to precipitate $BaSO_4$. The addition of smaller volumes of $BaCl_2$ would help determine more accurately when the $BaCl_2$ would be in excess. This could be compared to stoichiometric calculations.

Chapter 2 Static and dynamic equilibrium

2.1 Chemical systems

2.1 Review

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

2 Equilibrium occurs when there is a *reversible* reaction in a closed system. *Energy* can be added to the system but *matter* cannot be added or removed. At equilibrium, the *rates* of the forward and reverse reactions are equal. The total mass of reactants and products present in the reaction *remains constant*.

3 **a** closed
  b open
  c closed
  d open.

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

4 130 kJ mol^{-1}

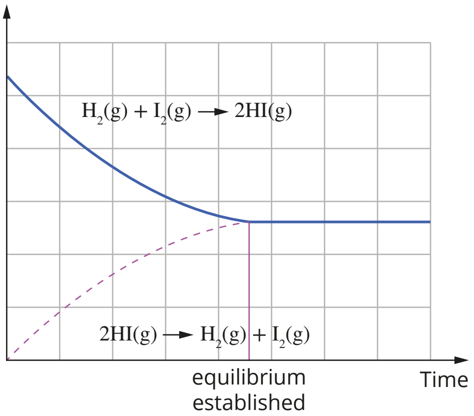
The reverse reaction is exothermic, and the activation energy is the difference between 390 kJ mol^{-1} and 260 kJ mol^{-1}, which is 130 kJ mol^{-1}.

2.2 Dynamic equilibrium

2.2 Review

1 C. A and D are false because the extent of reaction gives no indication of the rate of reaction. Option B is false because the extent of reaction only indicates the relative amounts of reactants and products when equilibrium is achieved. It does not necessarily mean that there are an equal amount of reactants and products when equilibrium is achieved.

2



Only reactants are present initially, and they undergo reaction to form the products. As the concentration of the reactants decreases, the rate of this reaction will decrease. The upper curve therefore shows the rate of the forward reaction.

The lower curve shows the rate of the reverse reaction. As the number of product particles increases, the rate of the reverse reaction increases. When the rates of the forward and reverse reactions become equal, equilibrium is established.

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3 In a *closed* system, as the concentrations of the reactants decreases, the rate of the forward reaction also *decreases*. The collisions between these reactant molecules occur *less* frequently. Once some product starts to form, the *reverse* reaction occurs and the frequency of collisions between product molecules *increases*. At equilibrium, the rates of the forward and backward reactions are *equal* and the concentrations of all species do not change.

4 **a** 0.07 mol L^{-1}

- **b** 0.00 mol L^{-1}
- **c** 0.03 mol L^{-1}
- **d** 0.08 mol L^{-1}
- **e** 0.04 mol
- **f** The horizontal regions of the graph indicate that there is no change in concentration of NO_2 or N_2O_4. This is when the system is at equilibrium and both the forward and reverse reactions are occurring at the same rate.
- **g** 6 s
- **h** As the reaction proceeds, the intensity of the brown colour will increase as the concentration of NO_2 increases until equilibrium is reached. Once equilibrium is reached, the colour of the reaction mixture will remain constant.

5 B. From the equation for photosynthesis, there are 6 molecules of gas on each side of the equation, but there is a decrease in the number of particles in the system. Hence ΔS will be negative. (Another way of looking at this is that the production of a large product molecule from many smaller reactant molecules is creating greater order.)

6 **a** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= 6.01 - (298 \times 0.0220)$ (T is in kelvin and ΔS° is converted to kJ mol^{-1} K^{-1})

$= 6.01 - 6.556$

$= -0.55$ kJ mol^{-1}

b Since ΔG is negative, the melting of ice is spontaneous at 25°C.

(You knew that of course, but it's good to see that thermodynamics can prove it.)

CHAPTER 2 REVIEW

1 A.

2 C. In a saturated solution, an equilibrium exists between a solid and the solute dissolved in solution. No gas is produced in this system, so matter is not being exchanged with the surroundings.

3 D. A reversible process can occur in both open and closed systems. For a process to be reversible, the reactant and product particles must continuously react. However, for equilibrium to be established the process must be reversible and the system must be closed. Both physical and chemical changes can be reversed under appropriate conditions.

4 **a** open, because both energy and matter (carbon dioxide and water vapour) are exchanged with the surroundings

- **b** closed, because only energy is exchanged with the surroundings. While the door is shut, no matter is exchanged.
- **c** open, because both energy and matter is exchanged with the surroundings
- **d** closed, because only energy is exchanged. Temperature changes result in changes in volume, but there is no exchange of matter.

5 **a** False. The stable product, MgO, under normal conditions, cannot be converted back to the reactants, Mg and O_2. The process is therefore irreversible. Furthermore, it is a chemical reaction, not a physical change, because a new compound is formed due to the breaking of reactant bonds and reforming of bonds in the product.

- **b** True. It is a reversible reaction, as shown by the use of the double-headed reaction arrow. Both the forward and reverse reactions can occur.
- **c** True. Energy is released to the surroundings when petrol and oxygen from the air react, indicating that it is an exothermic reaction. Because CO_2 and H_2O are released to the atmosphere, matter is also exchanged with the surroundings. It is irreversible because the products are stable and are not converted back to reactants under normal conditions.
- **d** False. It is an open system and equilibrium cannot be achieved in open systems. However, it is a reversible process because water can evaporate and condense again.

6 **a** Chemical equilibrium is 'dynamic' because both forward and reverse reactions occur at the same rate. An equilibrium develops between water vapour and liquid water when wet clothes are in a sealed bag, with water evaporating as rapidly as water vapour condenses, so the clothes remain wet.

- **b** When the bag is opened, water vapour escapes and the rate of evaporation exceeds the rate of condensation. The system is not in equilibrium and the clothes dry.

7 iii, iv, ii, i.

The forward reaction will occur as the concentrations of CO and Cl_2 decrease, the rate of the production of $COCl_2$ decreases.

As $COCl_2$ is formed, some $COCl_2$ molecules decompose to re-form CO and Cl_2.

When the rates of the forward and reverse reactions become equal, $COCl_2$ is formed at the same rate as it is breaking down.

Equilibrium has been reached and the concentrations of CO, Cl_2 and $COCl_2$ will now remain constant.

8 Equilibrium can occur only in a closed system.

In b, at the molecular level, some of the sugar in the saturated sugar solution will continue to dissolve at the same rate as some is precipitated. This system is at equilibrium.

In f, the dissolved carbon dioxide will be in equilibrium with the gaseous carbon dioxide. This system is at equilibrium.

In all of the other situations, the reverse reaction is not occurring at the same rate as the forward reaction, because the systems are open. These cannot be at equilibrium.

9 Initially, collisions between SO_2 and O_2 reactant molecules occur frequently, with sufficient molecules having the correct energy and orientation to produce product molecules, SO_3. As more product molecules are formed they collide with sufficient energy to decompose to the reactant molecules, SO_2 and O_2. The forward and reverse reactions continue to occur with the rate of the forward reaction decreasing over time and the rate of the reverse reaction increasing over the same time interval. Finally, the rates of both reactions become equal and equilibrium is established.

10 In physics, a static equilibrium occurs when all forces are in balance; there is no overall force and there is no movement. In chemistry, a static equilibrium occurs when the rates of the forward and reverse reactions of a system are equal and almost zero. There is no movement of reactant and product particles in either the forward or reverse direction. For example: graphite $\rightleftharpoons$ diamond

Dynamic equilibrium occurs when the rate of the forward reaction is equal to the rate of the reverse reaction. Although the concentrations of the reactants and products do not change over time, at the atomic level the reactants are continually forming products and the products continually forming reactants. For example: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

11 Combustion reactions are irreversible because the products, CO_2 and H_2O, are stable molecules and do not react to re-form the reactants at normal temperatures. Non-equilibrium systems are irreversible, so combustion may be considered to be a non-equilibrium system.

12 There is a decrease in entropy of the cards (ΔS_{system}) when they are arranged in order. However, the person is using energy to carry out the process, releasing significant amounts of gaseous CO_2 and H_2O and heat to the atmosphere. The entropy of the surroundings ($\Delta S_{surroundings}$) increases significantly as these gases and heat are released. Overall, $\Delta S_{surroundings}$ is greater than ΔS_{system} and the entropy of the universe increases overall, in accord with the second law of thermodynamics.

13 The reaction and entire process of the deployment of air bags is irreversible. This means that this system could be considered to be a non-equilibrium system.

14 $\Delta G° = \Delta H° - T\Delta S°$

$= -2803 - (298 \times 0.212)$ (T is in kelvin and $\Delta S°$ is converted to $kJ\,mol^{-1}\,K^{-1}$)

$= -2803 - 63.18$

$= -2866\,kJ\,mol^{-1}$

Since $\Delta G°$ is negative, this indicates that respiration is spontaneous.

15

	Photosynthesis	**Room**
a	decrease (–)	decrease (–)
b	non-spontaneous (+)	non-spontaneous (+)
c	increases	increases

16 **a** HR_w is red and R_w^- is green.

b $R_w^-(aq) + H^+(aq) \rightarrow HR_w(aq)$

c The formation of R_w^- from HR_w can be described as reversible because once R_w^- is formed by adding a base it can be converted back to HR_w by adding an acidic substance such as vinegar.

(Later in this module you will learn that substances such as red wine pigment form an equilibrium in solution. In this case the equilibrium can be represented as:

$$HR_w(aq) \rightleftharpoons R_w^-(aq) + H^+(aq)$$

If a base is added to red wine, the OH^- reacts with the H^+ and the forward reaction is forced forward, forming the green R_w^- pigment. Adding an acid causes the reverse reaction to occur.)

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Chapter 3 Calculating an equilibrium constant

3.1 The equilibrium law

Worked example: Try yourself 3.1.1

DETERMINING THE EXPRESSION FOR THE EQUILIBRIUM CONSTANT FOR AN EQUILIBRIUM SYSTEM

Write the expression for K_{eq} for the reversible reaction:

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

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

Worked example: Try yourself 3.1.2

DETERMINING THE EXPRESSION FOR THE EQUILIBRIUM CONSTANT FOR A HETEROGENEOUS EQUILIBRIUM SYSTEM

Lead(II) iodide is only slightly soluble in water. The equation for its dissolution can be written as:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

Write the expression for the equilibrium constant K_{eq}.

Thinking	**Working**
Identify the reactants and products. The reactants appear in the denominator of the expression and the products in the numerator. The concentration of a pure solid or a pure liquid is assigned as 1.	PbI_2 is a reactant. It is a pure solid so it will not appear in the equilibrium expression. Pb^{2+} and I^- are products so they appear in the numerator of the expression.
Write the expression for K_{eq}. $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$ Remember that the index of each component concentration is the same as its coefficient in the balanced chemical equation.	$K_{eq} = [Pb^{2+}][I^-]^2$

3.1 Review

1 $Q = \frac{[HCl]^2}{[H_2\ Cl_2]}$

2 The reaction quotient $Q < K_{eq}$. The reaction will shift to the right to establish equilibrium. This causes the concentration of the products to increase.

3 **a** A homogeneous system is a system in which all the species are in the same phase.

b A heterogeneous system is a system in which the species are in different phases.

c $Q = \frac{[\text{products}]^{\text{coefficient}}}{[\text{reactants}]^{\text{coefficient}}}$

Q is equal to K_{eq} at equilibrium.

d The equilibrium constant is the ratio of the equilibrium concentrations of the products divided by the equilibrium concentrations of the reactants raised to the power of their coefficients. It is given the symbol K_{eq} and the value for the equilibrium constant changes with temperature.

4 $K_{eq} = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

Since $Q > K_{eq}$, the concentration of $[Cu(NH_3)_4]^{2+}$ must decrease and the concentration of the reactants must increase in order to reach equilibrium. This will occur if the reaction moves to the left, producing more reactants.

5 **a** $K_{eq} = [NH_3][H_2S]$

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

c $K_{eq} = \frac{1}{[Ag^+]^2[CO_3^{\ 2-}]}$

d $K_{eq} = \frac{[H_2O]^2[C]_2^{\ 2}}{[HCl]^4[O_2]}$

3.2 Working with equilibrium constants

3.2 Review

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

b Since $\frac{[N_2][H_2]^3}{[NH_3]^2} = 100$

$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{1}{100} = 0.01$

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

d Since $\frac{[N_2][H_2]^3}{[NH_3]^2} = 100$

$\frac{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}{[NH_3]} = \sqrt{100} = 10$

e **i** When an equation is reversed, the value of the equilibrium constant is the reciprocal of the original constant.

ii When the coefficients are halved, the new equilibrium constant has a value equal to the square root of the original constant.

2 **a** $K_{eq} = \frac{[HCl]^2[O_2]^{\frac{1}{2}}}{[H_2O\ \ C]_2}$

$= \sqrt{4.0 \times 10^{-4}}$

$= 0.020$

b $K_{eq} = \frac{[H_2O\ \ C]_2}{[HCl]^2[O_2]^{\frac{1}{2}}}$

$= \frac{1}{0.020}$

$= 50$

3 **a** $K_{eq} = 8.35$

b $K_{eq} = 0.767$

c $K_{eq} = 1.30$

d $K_{eq} = 0.346$

4 B. The largest value of K_{eq} indicates that the reaction favours the products.

5 **a** increased

b decreased

c increased

d decreased

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3.3 Calculations involving equilibrium

Worked example: Try yourself 3.3.1

CALCULATING THE EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Calculate the value of the equilibrium constant, K_{eq}, for the reaction at that temperature.

Thinking	Working
Find the molar concentrations for all species at equilibrium. Convert mol to mol L^{-1} using $c = \frac{n}{V}$.	Volume of vessel = 3.00 L $[N_2O_4] = \frac{n(N_2O_4)}{V}$ $= \frac{0.120}{3.00}$ $= 0.0400 \text{ mol L}^{-1}$ $[NO_2] = \frac{n(NO_2)}{V}$ $= \frac{0.500}{3.00}$ $= 0.167 \text{ mol L}^{-1}$
Write the expression for K_{eq}.	$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$
Substitute values into the expression for K_{eq} to determine the value of K_{eq}.	$K_{eq} = \frac{0.167^2}{0.0400}$ $= 0.694$

Worked example: Try yourself 3.3.2

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following reaction, which has an equilibrium constant of 0.72 at 250°C.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

An equilibrium mixture contains 0.040 mol L^{-1} N_2O_4 at 250°C. What is the concentration of NO_2 in this mixture?

Thinking	Working
Write the expression for K_{eq}.	$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$
Substitute the known values into the expression for K_{eq}.	$0.72 = \frac{[NO_2]^2}{0.040}$
Rearrange the expression to make the unknown the subject and calculate the concentration of this species.	$[NO_2] = \sqrt{0.72 \times 0.040}$ $= 0.17 \text{ mol L}^{-1}$

Worked example: Try yourself 3.3.3

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

During one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetroxide (N_2O_4) at 60°C.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

0.350 mol of N_2O_4 was placed in a 2.00 L vessel. When equilibrium was achieved at 60°C, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at this temperature.

Thinking	**Working**
Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled I (initial), C (change) and E (equilibrium):	Initially, there is 0.350 mol of $N_2O(g)$ and 0 mol of the product $NO_2(g)$. Let x mol of N_2O_4 react; $2x$ mol of NO_2 is produced. At equilibrium there is 0.120 mol of $NO_2(g)$.

	Reactants ⇌ Products	
I		
C		
E		

	$N_2O_4(g)$ ⇌	$2NO_2(g)$
I	0.350 mol	0 mol
C	$-x$	$+2x$
E	$0.350 - x$	$2x = 0.120$ mol

Thinking	**Working**
Enter the data provided in the table. When a species is consumed, the change is negative; when a species is produced, the change is positive.	
Using the coefficients from the equation, calculate the moles of all species at equilibrium.	Initially no NO_2 was present, so because 0.120 mol NO_2 has been produced at equilibrium: $2x = 0.120$ mol $x = 0.0600$ mol We can enter these values in the table:

	$N_2O_4(g)$ ⇌	$2NO_2(g)$
I	0.350 mol	0 mol
C	$-x = -0.0600$	$+2x = 0.120$
E	$0.350 - 0.0600 = 0.290$ mol	$2x = 0.120$ mol

Thinking	**Working**
Using the volume of the vessel, calculate the equilibrium concentrations for all species at equilibrium. Use the formula $c = \frac{n}{V}$.	The volume of the vessel is 2.00 L. $[N_2O_4] = \frac{n}{v} = \frac{0.290}{2.00} = 0.145 \text{ mol L}^{-1}$ $[NO_2] = \frac{n}{v} = \frac{0.120}{2.00} = 0.0600 \text{ mol L}^{-1}$
Write the expression for K_{eq} and substitute the equilibrium concentrations. Calculate the equilibrium constant, K_{eq}.	$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.0600^2}{0.145} = 0.0248$

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3.3 Review

1 From the equation, write the expression for the equilibrium constant:

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

Calculate equilibrium concentrations of reactants and products.

$$\begin{aligned}[NO_2] &= \frac{n}{V}\\ &= \frac{0.40}{2.0}\\ &= 0.20\ mol\ L^{-1}\end{aligned}$$

$$\begin{aligned}[N_2O_4] &= \frac{0.80}{2.0}\\ &= 0.40\ mol\ L^{-1}\end{aligned}$$

Substitute equilibrium concentrations into the equilibrium expression and calculate the value of the equilibrium constant.

$$\begin{aligned}K_{eq} &= \frac{[NO_2]^2}{[N_2O_4]}\\ &= \frac{0.20^2}{0.40}\\ &= 0.10\end{aligned}$$

2

$$\begin{aligned}K_{eq} &= \frac{[COCl_2]}{[CO][Cl_2]}\\ &= \frac{0.28}{2.4 \times 10^{-2} \times 0.108}\\ &= 1.1 \times 10^2\end{aligned}$$

3

$$\begin{aligned}K_{eq} &= \frac{[NO_2]^2}{[NO]^2[O_2]}\\ 6.44 \times 10^5 &= \frac{15.5^2}{0.0542^2 \times [O_2]}\\ [O_2] &= \frac{15.5^2}{0.0542^2 \times 6.44 \times 10^5}\\ &= 0.127\ mol\ L^{-1}\end{aligned}$$

4

	$PCl_3(g)$ +	$Cl_2(g)$ ⇌	$PCl_5(g)$
I	4.45 mol	5.50 mol	0 mol
C	$-x = -0.35$	$-x = -0.35$	$+x = 0.35$
E	$4.45 - x$ $= 4.45 - 0.35$ $= 4.10$ mol	$5.50 - x$ $= 5.50 - 0.35$ $= 5.15$ mol	$x = 0.35$ mol

Vessel volume = 2.00 L

$$[PCl_3] = \frac{4.10}{2.00} = 2.05\ mol\ L^{-1}$$

$$[Cl_2] = \frac{5.15}{2.00} = 2.58\ mol\ L^{-1}$$

$$[PCl_5] = \frac{0.35}{2.00} = 0.18\ mol\ L^{-1}$$

$$\begin{aligned}K_{eq} &= \frac{[PCl_5]}{[PCl_3\ Cl_2]}\\ &= \frac{0.18}{2.05 \times 2.58}\\ &= 3.3 \times 10^{-2}\end{aligned}$$

5

	$N_2(g)$ +	$3H_2(g)$ ⇌	$2NH_3(g)$
I	5.89 mol	8.23 mol	0 mol
C	$-x = -0.24$	$-3x = -0.72$	$+2x = 0.48$
E	$5.89 - x$ $= 5.89 - 0.24$ $= 5.65$ mol	$8.23 - 3x$ $= 8.23 - 0.72$ $= 7.51$ mol	$2x = 0.48$ mol

Volume of vessel = 5.00 L

$[N_2] = \frac{5.65}{5.00} = 1.13\ \text{mol L}^{-1}$

$[H_2] = \frac{7.51}{5.00} = 1.50\ \text{mol L}^{-1}$

$[NH_3] = \frac{0.48}{5.00} = 0.0960\ \text{mol L}^{-1}$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
$$= \frac{0.0960^2}{1.13 \times 1.50^3}$$
$$= 2.41 \times 10^{-3}$$

6 **a** From the equation, write the expression for the equilibrium constant.

$$K_{eq} = \frac{[H_2][I_2]}{[HI]^2}$$

Calculate equilibrium concentrations of reactants.

$[H_2] = \frac{0.220}{2.0} = 0.110\ \text{mol L}^{-1}$

$[I_2] = \frac{0.110}{2.0} = 0.055\ \text{mol L}^{-1}$

Substitute equilibrium concentrations into the equilibrium expression and calculate the concentration of HI.

$$48.8 = \frac{0.110 \times 0.055}{[HI]^2}$$
$$[HI]^2 = \frac{0.110 \times 0.055}{48.8}$$
$$[HI] = \sqrt{\frac{0.110 \times 0.055}{48.8}}$$
$$= 0.011\ \text{mol L}^{-1}$$

b

	$2HI(g)$ ⇌	$H_2(g)$ +	$I_2(g)$
I	4.00 mol	0 mol	0 mol
C	$-2x = -0.88$	$+x = 0.44$	$+x = 0.44$
E	$4.00 - 2x$ $= 4.00 - 0.88$ $= 3.12$ mol	$x = 0.44$ mol	$x = 0.44$ mol

Volume of vessel = 2.0 L

$[HI] = \frac{3.12}{2.0} = 1.56\ \text{mol L}^{-1}$

$[H_2] = \frac{0.44}{2.0} = 0.22\ \text{mol L}^{-1}$

$[I_2] = \frac{0.44}{2.0} = 0.22\ \text{mol L}^{-1}$

$$K_{eq} = \frac{[H_2][I_2]}{[HI]^2}$$
$$= \frac{0.22 \times 0.22}{1.56^2}$$
$$= 0.020$$

c The reaction quotient for this reaction is $\frac{[H_2][I_2]}{[HI]^2}$

Calculate concentrations of all substances.

$[H_2] = \frac{0.240}{2.0} = 0.12\,mol\,L^{-1}$

$[I_2] = \frac{0.320}{2.0} = 0.16\,mol\,L^{-1}$

$[HI] = \frac{1.00}{2.0} = 0.50\,mol\,L^{-1}$

The value of the reaction quotient is:

$\frac{0.12 \times 0.16}{0.50^2} = 0.077$

The value of the reaction quotient is greater than the value of the equilibrium constant at the same temperature as calculated in part **b**. Thus the system is not at equilibrium. A net backwards reaction will occur. As the reaction moves towards equilibrium, the concentrations of H_2 and I_2 will decrease and the concentration of HI will increase until the value of the reaction quotient is equal to the equilibrium constant.

CHAPTER 3 REVIEW

1 B. Given the form of the expression for K_{eq}, the concentration of SO_3 must be in the numerator and the concentrations of SO_2 and O_2 in the denominator. Their indices are equal to their coefficients in the equation.

2 $K_{eq} = \frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}]^2[Sn^{2+}]}$

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

4 **a** $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

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

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

5 **a** $K_{eq} = \frac{1}{[Cu^{2+}][CO_3^{2-}]}$

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

c $K_{eq} = \frac{[PCl_5]^4}{[Cl_2]^{10}}$

d $K_{eq} = \frac{[Cl_2]^{20}}{[PCl_5]^8}$

6 The reaction quotient is the ratio of the concentrations of the products to the concentration of the reactants, with the index of each concentration the same as the coefficient of the substance in the reaction equation. The value of the reaction quotient becomes equal to the equilibrium constant at equilibrium.

7 As Q for the reaction is larger than K_{eq}, the reaction must move to decrease Q. This will happen with a decrease in the concentration of the products. There will be a net backwards reaction, decreasing the concentration of ethyl ethanoate as the mixture reaches equilibrium.

8 **a** If $K_{eq} = 0.0001$ for a particular reaction, at equilibrium the concentrations of products will be *less than* the concentrations of reactants.

b For the reaction with the equation $2H_2(g) + 2NO(g) \rightleftharpoons 2H_2O(g) + N_2(g)$ the expression for the equilibrium constant, K_{eq}, is $\frac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$

c When the reaction quotient is smaller than K_{eq}, the reaction *moves to the right* to establish equilibrium.

9 **a** No. K_{eq} is very small.

b 10^{10}

c Yes. K_{eq} is very large (provided the rate is sufficiently fast).

10 **a** $K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

b **i** The coefficients of each species has been halved. $K_{eq} = \sqrt{32} = 5.7$

ii The reaction is the reverse of that in part **a**. $K_{eq} = \frac{1}{32} = 0.031$

iii Each of the coefficients has been doubled. $K_{eq} = 32^2 = 1.0 \times 10^3$

iv The reaction is reversed and the coefficients halved. $K_{eq} = \frac{1}{\sqrt{32}} = 0.18$

11 The reaction is not at equilibrium and will shift towards the left to reach equilibrium.

$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.25^2}{1.0 \times 1.0^3} = 0.063$

The reaction quotient is greater than K_{eq} so the reaction will move to decrease Q, so the equilibrium will shift to the left, to produce more reactants.

12 Container is 2.0 L

$[H_2O] = \frac{0.020}{2.0} = 0.010\,mol\,L^{-1}$

$[H_2] = \frac{0.030}{2.0} = 0.015\,mol\,L^{-1}$

$[CO] = \frac{0.040}{2.0} = 0.020\,mol\,L^{-1}$

$[CO_2] = \frac{0.050}{2.0} = 0.025\,mol\,L^{-1}$

$$K_{eq} = \frac{[H_2O][CO]}{[H_2\ \ CO_2]}$$
$$= \frac{0.010 \times 0.020}{0.015 \times 0.025}$$
$$= 0.53$$

13 $K_{eq} = \frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}]^2[Sn^{2+}]}$
$$= \frac{0.40^2 \times 0.20}{0.30^2 \times 0.10}$$
$$= 3.6$$

14 Write the expression for the equilibrium constant.

$$K_{eq} = \frac{[C_3H_6O][H_2]}{[C_3H_8O]}$$

Calculate equilibrium concentrations of reactants and products.

$[C_3H_6O] = \frac{0.082}{20}$

$= 0.0041\,mol\,L^{-1}$

$[H_2] = \frac{0.082}{20}$

$= 0.0041\,mol\,L^{-1}$

$[C_3H_8O] = \frac{0.018}{20}$

$= 0.00090\,mol\,L^{-1}$

Substitute equilibrium concentrations in the equilibrium expression and find the value of the equilibrium constant.

$$K_{eq} = \frac{0.0041 \times 0.0041}{0.00090}$$
$$= 0.019$$

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

b Calculate equilibrium concentrations of reactants and products.

$[PCl_5] = \frac{4.50}{3.00}$

$= 1.50\,mol\,L^{-1}$

$[Cl_2] = \frac{0.900}{3.00}$

$= 0.300\,mol\,L^{-1}$

$[PCl_3] = \frac{6.00}{3.00}$

$= 2.00\,mol\,L^{-1}$

Use the expression for the equilibrium constant from part **a**.

Substitute equilibrium concentrations in the equilibrium expression.

$$K_{eq} = \frac{[PCl_3\ \ Cl_2]}{[PCl_5]}$$
$$= \frac{2.00 \times 0.300}{1.50}$$
$$= 0.400$$

c Rearrange the expression to find $[Cl_2]$.

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

Substitute equilibrium concentrations in the equilibrium constant expression and find the value of $[Cl_2]$.

$$[Cl_2] = 0.400 \times \frac{0.0020}{0.0010}$$

$$= 0.80\ mol\ L^{-1}$$

d Note that the equation is reversed and the temperature is constant. For the reverse reaction the equilibrium constant is the reciprocal of the forward reaction.

$$K_{eq} = \frac{1}{0.400} = 2.50$$

16

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
I	0.540 mol	0 mol
C	$-x = -0.140$	$+2x = 0.280$
E	$0.540 - x$ $= 0.540 - 0.140$ $= 0.400$ mol	$2x = 0.280$ mol

Volume of vessel = 2.0 L

$[N_2O_4] = \frac{0.400}{2.0} = 0.20\ mol\ L^{-1}$

$[NO] = \frac{0.280}{2.0} = 0.14\ mol\ L^{-1}$

Substitute equilibrium concentrations in the equilibrium expression and find the value of the equilibrium constant.

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

$$= \frac{0.14^2}{0.20}$$

$$= 0.098$$

17

	$2NO(g)\ +$	$2H_2(g) \rightleftharpoons$	$N_2(g)\ +$	$2H_2O(g)$
I	0.100 mol	0.051 mol	0 mol	0.100 mol
C	$-x = -(0.100 - 0.062)$ $= -0.038$	$-x = -0.038$	$+\frac{x}{2} = \frac{+0.038}{2}$ $= +0.019$	$+x = +0.038$
E	0.062 mol	$0.051 - x$ $= 0.051 - 0.038$ $= 0.013$ mol	$0 + \frac{x}{2}$ $= 0 + 0.019$ $= 0.019$ mol	$0.100 + x$ $= 0.100 + 0.038$ $= 0.138$ mol

Volume of vessel = 1.0 L so amount in moles = molar concentration

$$K_{eq} = \frac{[H_2O]^2[N_2]}{[H_2]^2[NO\ ^2}$$

$$= \frac{0.138^2 \times 0.019}{0.013^2 \times 0.062^2}$$

$$= 557$$

18 **a** Write the expression for the equilibrium constant.

$$K_{eq} = \frac{[C]^2[D]}{[A][B]^3}$$

Calculate equilibrium concentrations of reactants and products.

$$[A] = \frac{2.0}{2.0}$$

$$= 1.0\ mol\ L^{-1}$$

$$[B] = \frac{0.50}{2.0}$$

$$= 0.25\ mol\ L^{-1}$$

$$[D] = \frac{3.0}{2.0}$$

$$= 1.5\ mol\ L^{-1}$$

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b Substitute equilibrium concentrations into the equilibrium expression and calculate the equilibrium concentration of C.

$$K_{eq} = 0.024 = \frac{[C]^2 \times 1.5}{1.0 \times 0.25^3}$$

$$[C]^2 = \frac{0.024 \times 1.0 \times 0.25^3}{1.5}$$

$$[C] = \sqrt{\frac{0.024 \times 1.0 \times 0.25^3}{1.5}}$$

$$= 0.016\,\text{mol}\,\text{L}^{-1}$$

c Convert the equilibrium concentration of C into a mole value.

$[C] = 0.016\,\text{mol}\,\text{L}^{-1}$

$n(C) = c \times V$

$= 0.016 \times 2.0$

$= 0.032\,\text{mol}$

19 **a** Write the expression for the equilibrium constant.

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

$$= 0.052$$

Because a 1 L vessel is used, the molar concentrations are the same as the amount in moles. Substitute the concentration values into the reaction quotient.

$$Q = \frac{0.20^2}{0.20 \times 0.20^3}$$

$$= 25$$

$Q > K_{eq}$; therefore the system is not at equilibrium. The system will shift in the direction that makes $Q = K_{eq}$.

Since $Q > K_{eq}$, the reaction must shift to the left, resulting in a net reverse reaction.

b Because a 1 L vessel is used, the molar concentrations are the same as the amount in moles. Substitute the given concentration values into reaction quotient.

$$Q = \frac{0.0^2}{0.050 \times 0.050^3}$$

$$= 0.0$$

$Q < K_{eq}$, so, the system is not at equilibrium. The system will shift in the direction that makes $Q = K_{eq}$.

Because $Q < K_{eq}$, the reaction must shift to right, resulting in a net forward reaction.

20 **a** For the initial mixture:

$$Q = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

$$= \frac{0.300 \times 0.400}{0.100 \times 0.200^3}$$

$$= 150$$

$Q > K_{eq,}$ so a net reverse reaction will occur to make this ratio equal to K_{eq}.

i increase

ii increase

iii decrease

iv decrease

b The enthalpy change was endothermic.

21 A closed system, because the bottle cap is tightly closed and therefore matter cannot be exchanged with the surroundings. This is a dynamic equilibrium system.

Chapter 4 Factors that affect equilibrium

4.1 Le Châtelier's principle

Worked example: Try yourself 4.1.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT ON EQUILIBRIUM OF ADDING A REACTANT OR PRODUCT

Consider the following equilibrium system:

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

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

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

4.1 Review

1 In each case the system will react by decreasing the concentration of hydrogen gas.

- **a** net forward reaction
- **b** net reverse reaction
- **c** net forward reaction

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

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

3 **a** There will be a net reverse reaction, so the position of equilibrium will shift to the left.

b There will be a net forward reaction, so the position of equilibrium will shift to the right.

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

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4.2 Further applications of Le Châtelier's principle

Worked example: Try yourself 4.2.1

USING LE LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A CHANGE IN VOLUME

Consider the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Predict the shift in equilibrium position and the effect on the amount of Cl_2 when the volume is doubled at a constant temperature.

Thinking	Working
Determine the immediate effect of the change of volume on the pressure.	Doubling the volume will halve the pressure of all species at equilibrium.
The system will try to partially oppose the change in pressure by reducing or increasing the pressure in the system. (For a volume decrease, the system will shift in the direction of the fewest particles, and vice versa for a volume increase.) Decide how the equilibrium will respond.	There are 2 molecules of gas on the reactant side and 1 molecule of gas on the product side, so the system will shift to the left. This increases the amount of the reactants, including Cl_2. Note that the PCl_3 and Cl_2 concentrations will still be lower than they were at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.

Worked example: Try yourself 4.2.2

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

Consider the following reaction:

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

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

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

4.2 Review

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

2 **a** net forward reaction

b no effect

c net forward reaction

3 **a** Doubling the pressure causes increased frequency of collisions and an increased rate of both the forward and reverse reactions. Since there are more particles on the left side there will be more successful collisions in the forward direction, so a net forward reaction results.

b Increasing the pressure causes an increased frequency of collisions and an increased rate of both the forward and reverse reactions. Because there is an equal chance of reactant molecules colliding and forming a product, or product molecules colliding and forming the reactants (2 mol of reactants and 2 mol of products), there is no overall net reaction.

c A temperature increase means all reactant and product molecules have more energy and move faster. There will be more frequent collisions and more molecules will have the necessary energy to overcome the activation energy barrier. An increased temperature favours an endothermic reaction because a greater proportion of molecules at the higher temperature will have the necessary energy to overcome the activation energy barrier than for the exothermic reaction. Hence there will be a net reaction in the direction of the endothermic reaction, i.e. a net forward reaction.

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

a As the volume increases, the concentration of NO_2 will decrease, although the reaction will favour the formation of NO_2 according to Le Châtelier's principle. The adjustment can only partially oppose the change, so the corresponding increase in concentration will not reach the initial NO_2 concentration.

b The mass of NO_2 will be higher. By favouring the forward reaction, the shift in equilibrium will result in a higher yield of NO_2.

CHAPTER 4 **REVIEW**

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

b $A + B \rightleftharpoons C + D$

When the products C and D are removed, a net forward reaction occurs. Applying Le Châtelier's principle, the system can be regarded as partially opposing the change and trying to restore equilibrium.

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

a SO_2 is a reactant. Adding a reactant causes a net forward reaction.

b O_2 is a reactant. Removing a reactant causes a net reverse reaction.

c SO_3 is a product. Removing a product causes a net forward reaction.

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

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

4 If Ca^{2+} ions were inefficiently absorbed from food, decreased concentrations of these ions could occur in body fluids. As a consequence, a net forward reaction would occur, resulting in decreased amounts of calcium phosphate in bones.

5 **a** Increase. Heating favours the endothermic reaction, which is the reverse reaction, increasing H_2 concentration.

b Increase. Heating favours the endothermic reaction, which is the forward reaction, increasing H_2 concentration.

6 B and D. The Ag^+ ions react with SCN^- ions to form a white-coloured precipitate of AgSCN. The concentration of SCN^- ions in the solution is reduced, causing the equilibrium to shift to the left, reducing the concentration of red-coloured $FeSCN^{2+}$ ions.

Adding a small volume of water dilutes the mixture, so the concentration of all species is decreased. The position of equilibrium shifts to the side with more particles, so shifts to the left, further reducing the concentration of red-coloured $FeSCN^{2+}$ ions.

7 C. The amount of $COCl_2$ will increase because, with an increased pressure, the system will move to decrease the pressure by moving in the direction of the fewest particles. Hence a net forward reaction occurs.

8 **a** Curve A represents NO_2.
Curve B represents N_2O_4.
The graph shows that when the concentration of B decreases from 0.10 to 0.05 $mol\,L^{-1}$, the concentration of A rises from 0 to 0.10 $mol\,L^{-1}$. B must be N_2O_4 and A must be NO_2, because the ratio of N_2O_4 to NO_2 in the equation is 1:2.

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

9 D. Only a change in temperature changes K_{eq} of a reaction.

10 **a** **i** increase temperature
ii increase temperature
iii decrease temperature
b **i** cannot cause forward reaction
ii increase volume
iii cannot cause forward reaction

11 **a** net reverse reaction
b net forward reaction
c no effect

12 C. A catalyst changes the activation energies of the forward and reverse reactions. It does not change K_{eq} or the ΔH of the reaction.

13 **a** **i** net forward reaction
ii no change
iii net forward reaction
b **i** increase
ii no change
iii no change
c likely to be large, since the reaction will be almost complete

14

	Colour change	**Explanation using Le Châtelier's principle and collision theory**
a The temperature is increased to 450°C at constant volume.	lighter	Le Châtelier's principle: Increasing the temperature of the system increases the energy of the substances in the mixture. The reaction opposes an increase in energy by absorbing energy. Because the reverse reaction is endothermic, this favours a net reverse reaction (K_{eq} will decrease). Collision theory: A higher temperature causes all molecules to have more energy and there are more frequent collisions. The temperature increase affects the rate of the endothermic reaction more than the exothermic reaction because a higher proportion of molecules have the necessary energy to overcome the activation energy barrier. So, the net reaction will be the reverse, endothermic reaction, producing more colourless NO and O_2.
b The volume of the container is increased at constant temperature.	lighter	Le Châtelier's principle: An increase in volume causes a decrease in pressure. The system will oppose the change by increasing the pressure, so the equilibrium position moves in the direction of the most particles, producing more NO and O_2. Collision theory: Decreased pressure means there will be less frequent collisions. The rate of the reaction involving the smaller number particle (the reverse reaction) will decrease the least. Therefore the equilibrium shifts to the left.
c A catalyst is added at constant volume and temperature.	no change	Le Châtelier's principle: The system cannot adjust to oppose the addition of a catalyst. There is therefore no net reaction. Collision theory: Adding a catalyst increases the rates of the forward and back reactions equally. There is no net reaction because the change in the frequency of collisions is equal in both directions.
d More oxygen is added at constant volume and temperature.	darker	Le Châtelier's principle: The reaction opposes the change by consuming the added O_2 and shifts toward the right to produce more brown NO_2. Collision theory: Adding O_2 increases its concentration and causes the rate of the forward reaction to increase. As O_2 is consumed the rate of the forward reaction decreases and the rate of the reverse reaction increases until a new equilibrium is established. Overall, there is a net forward reaction.

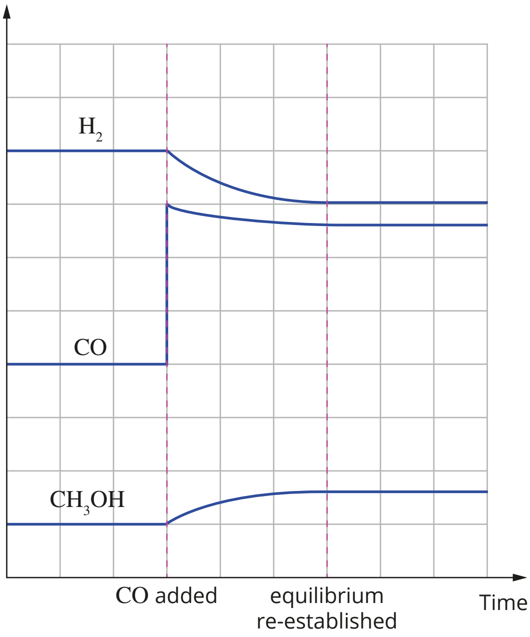
15 **a** Decreasing the temperature would favour the forward exothermic process, resulting in a net forward reaction.

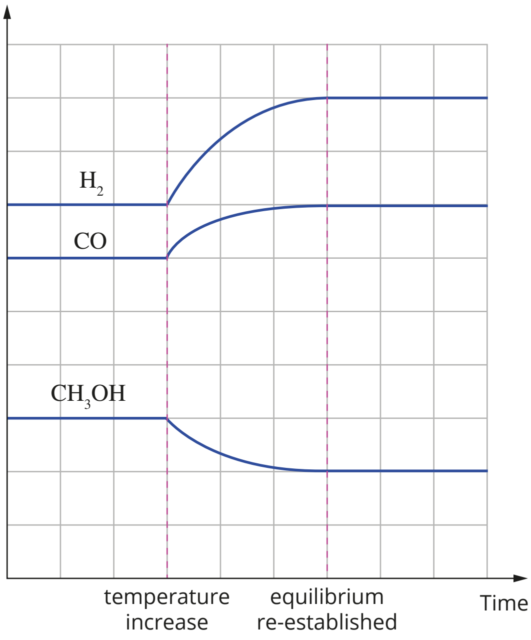
b There are five particles on the reactant side and three particles on the product side. A decrease in volume would increase the pressure of the system. This would cause the system to favour the forward reaction in order to reduce the overall number of particles.

16 **a** **i** decrease
ii decrease
iii increase
iv no change
v no change

b **i** increase
ii increase
iii increase
iv increase
v no change

17





18 **a** Between t_0 and t_1: The rates of the forward and reverse reactions are equal and the rate of production of ammonia is constant. The system is at equilibrium. The frequency of effective collisions between N_2 and H_2 molecules is constant.

b At t_1: When the volume is decreased, the concentrations of all species will increase. The system will adjust to reduce the concentrations overall and will favour the forward reaction. According to collision theory, an increase in concentration causes the frequency of all collisions in both directions to increase. An increase in the rate of production of ammonia is favoured.

c Between t_1 and t_2: The reactant molecules collide and produce ammonia. As the concentrations of these reactant molecules decrease, the rate of production of ammonia decreases. As more ammonia is formed, the reverse reaction increases. After t_2 equilibrium is re-established.

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

b $K_{eq} = \frac{[CS_2]\,O_2]^4}{[SO_3]^2[CO_2]}$

c **i** $n(O_2) = 4 \times n(CS_2) = 4 \times 0.028 = 0.11\ \text{mol}$

ii $[CS_2] = \frac{0.028}{20} = 0.0014 = 1.4 \times 10^{-3}\ \text{mol L}^{-1}$

$[O_2] = \frac{0.11}{20} = 0.0056 = 5.6 \times 10^{-3}\ \text{mol L}^{-1}$

$[SO_3] = \frac{0.022}{20} = 0.0011 = 1.1 \times 10^{-3}\ \text{mol L}^{-1}$

$[CO_2] = \frac{0.014}{20} = 0.00070 = 7.0 \times 10^{-4}\ \text{mol L}^{-1}$

$$K_{eq} = \frac{[CS_2]\,O_2]^4}{[SO_3]^2[CO_2]}$$

$$= \frac{0.0014 \times 0.0056^4}{0.0011^2 \times 0.00070}$$

$$= 1.6 \times 10^{-3}$$

d **i** increase

ii increase

iii no effect

iv decrease

v no effect

20 **a** $K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

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

c 1.56

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

e 3.50

f The volume was decreased, which resulted in an increased pressure. Because the value of K_{eq} at 25–30 minutes is larger than at 15–20 minutes and this is an exothermic reaction, a decrease in temperature must also have occurred.

21 When the rates at which water is transferred between the containers becomes equal, a dynamic equilibrium is established and no further change in water levels occurs.

In part B of the activity, when more water is added to one container, a new equilibrium is formed but the relative amounts of water in the containers is different to that of the first equilibrium. This is an illustration of Le Châtelier’s principle.

Chapter 5 Solubility and equilibria

5.1 Process of dissolution of ionic compounds

Worked example: Try yourself 5.1.1

DETERMINING WHETHER A PRECIPITATE WILL FORM FROM TWO IONIC SOLUTIONS

Determine whether a precipitate will be formed when a solution of sodium hydroxide and a solution of barium acetate are mixed. If so, identify the precipitate.

Thinking	**Working**
Identify the ions that are present in each ionic solution.	Sodium (Na^+), hydroxide (OH^-), barium (Ba^{2+}) and acetate (CH_3COO^-)
Identify any spectator ions.	Sodium (Na^+) and acetate (CH_3COO^-) never form precipitates.
Identify the remaining ions.	Hydroxide (OH^-) and barium (Ba^{2+})
Use the solubility tables to determine if this combination of ions is insoluble.	Hydroxide (OH^-) and barium (Ba^{2+}) form a soluble compound, therefore no precipitate will form.

5.1 Review

1 $NaNO_3(s) \xrightarrow{H_2O\ l} Na^+(aq) + NO_3^-(aq)$
$Ca(OH)_2(s) \xrightarrow{H_2O\ l} Ca^{2+}(aq) + 2OH^-(aq)$

2 When an ionic compound is added to water, the positive ion attracts the partial negative charges on the oxygen atoms in water molecules and the negative ion attracts the partial positive charges on the hydrogen atoms in water molecules. When potassium bromide is added to water, the attraction of the ions to the water molecules is enough to overcome the attraction between the ions in the lattice, and the ions enter solution, where they are hydrated (surrounded by water molecules).

3 **a** Na^+/CO_3^{2-}
b Ca^{2+}/NO_3^-
c K^+/Br^-
d Fe^{3+}/SO_4^{2-}
e Cu^{2+}/Cl^-

4 A, D, E, G, H, J

5 **a** Yes, silver chloride will precipitate.
b Yes, aluminium hydroxide will precipitate.
c Yes, copper(II) phosphate will precipitate.
d No precipitate will form.
e Yes, lead(II) iodide will precipitate.
f No precipitate will form.

5.2 Solubility of ionic compounds and equilibrium

Worked example: Try yourself 5.2.1

WRITING EQUILIBRIUM EXPRESSIONS IN TERMS OF K_{sp}

Write the equilibrium expression for a saturated solution of silver carbonate.

Thinking	**Working**
Check the solubility tables to determine if this combination of ions is insoluble.	Silver (Ag^+) and carbonate (CO_3^{2-}) are insoluble.
Write a balanced ionic equation.	$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$
Write the expression for K_{sp}.	$K_{sp} = [Ag^+]^2[CO_3^{2-}]$

Worked example: Try yourself 5.2.2

CALCULATING K_{sp} FROM SOLUBILITY DATA

Magnesium hydroxide is a white solid that is commonly used in antacids. At 25°C, 1 L of water can dissolve 1.12×10^{-4} mol of $Mg(OH)_2$. Calculate K_{sp} for magnesium hydroxide at this temperature.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr>
<td>Construct an ICE table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled I (initial), C (change) and E (equilibrium):
<table>
<tr><td></td><td colspan="2">Reactants ⇌ Products</td></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
</td>
<td>Initially, there is no Mg^{2+} or OH^- present, so the initial amounts of both are zero.
When the maximum amount of magnesium hydroxide that can dissolve in 1 L of water (1.12×10^{-4} mol) is added, 1.12×10^{-4} mol of Mg^{2+} ions and $2 \times 1.12 \times 10^{-4}$ mol of OH^- ions enter the solution.
Therefore, the amount of Mg^{2+} and OH^- ions at equilibrium is 1.12×10^4 mol and 2.24×10^4 mol respectively.
<table>
<tr><td></td><td>$MgOH(s) \rightleftharpoons$</td><td>$Mg^{2+}(aq)$ +</td><td>$2OH^-(aq)$</td></tr>
<tr><td>I</td><td></td><td>0</td><td>0</td></tr>
<tr><td>C</td><td></td><td>$+1.12 \times 10^{-4}$ mol</td><td>$+2 \times (1.12 \times 10^{-4})$
$= +2.24 \times 10^{-4}$ mol</td></tr>
<tr><td>E</td><td></td><td>1.12×10^{-4} mol</td><td>2.24×10^{-4} mol</td></tr>
</table>
</td>
</tr>
<tr>
<td>Write the expression for K_{sp} and substitute the equilibrium concentrations.
Calculate the equilibrium constant, K_{sp}.</td>
<td>Since there is 1 L of solution:
$[Mg^{2+}] = 1.12 \times 10^{-4}$ mol L^{-1}
$[OH^-] = 2.24 \times 10^{-4}$ mol L^{-1}
$K_{sp} = [Mg^{2+}][OH^-]^2$
$= (1.12 \times 10^{-4})(2.24 \times 10^{-4})^2$
$= 5.62 \times 10^{-12}$</td>
</tr>
</table>

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Worked example: Try yourself 5.2.3

CALCULATING MOLAR SOLUBILITY FROM K_{sp}

Zinc hydroxide has a K_{sp} value of 3.8×10^{-17} at 25°C. Calculate the molar solubility of zinc hydroxide at this temperature.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr>
<td>Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled I (initial), C (change) and E (equilibrium):
<table>
<tr><th></th><th colspan="2">Reactants $\rightleftharpoons$ Products</th></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
</td>
<td>Initially there is no Zn^{2+} or OH^- present. When the zinc hydroxide is added to water, zinc ions and hydroxide ions enter the water in a 1:2 ratio. This can be represented by <i>s</i>.
<table>
<tr><th></th><th>$Zn(OH)_2(s) \rightleftharpoons$</th><th>$Zn^{2+}(aq)$ +</th><th>$2OH^-(aq)$</th></tr>
<tr><td>I</td><td></td><td>0</td><td>0</td></tr>
<tr><td>C</td><td></td><td>$+s$</td><td>$+2s$</td></tr>
<tr><td>E</td><td></td><td>s</td><td>$2s$</td></tr>
</table>
</td>
</tr>
<tr>
<td>Write the expression for K_{sp} and substitute <i>s</i> for the equilibrium concentrations.
Calculate the molar solubility, including the correct units.</td>
<td>$K_{sp} = [Zn^{2+}][OH^-]^2$
$3.8 \times 10^{-17} = (s)(2s)^2$
$3.8 \times 10^{-17} = 4s^3$
$9.5 \times 10^{-18} = s^3$
Take the cube root of both sides:
$s = 2.1 \times 10^{-6}$
The molar solubility of zinc hydroxide is 2.1×10^{-6} mol L^{-1}</td>
</tr>
</table>

Worked example: Try yourself 5.2.4

PREDICTING THE FORMATION OF A PRECIPITATE GIVEN K_{sp}

Calcium fluoride has a K_{sp} value of 3.2×10^{-11} at 25°C. If 1.0×10^{-3} g of calcium fluoride is added to 1 L of water at 25°C, predict whether a precipitate will form.

Thinking	**Working**
Calculate the concentrations for the ions at equilibrium. Use the formulae: $n = \frac{m}{M}$ and $c = \frac{n}{V}$	There is 1.0×10^{-3} g of calcium fluoride. $n(CaF_2) = \frac{m}{M}$ $= \frac{1.0 \times 10^{-3}}{78.08}$ $= 1.3 \times 10^{-5}$ mol $c = \frac{n}{V}$ $= \frac{1.3 \times 10^{-5}}{1}$ $= 1.3 \times 10^{-5}$ mol L^{-1}
Calculate the ionic product.	Assume that each mole of calcium fluoride (CaF_2) dissociates to form 1 mol of calcium ions and 2 mol of fluoride ions. Therefore, when 1.3×10^{-5} mol of calcium fluoride is added to 1 L of water, 1.3×10^{-5} mol of barium ions and 2.6×10^{-5} mol of fluoride ions are formed ionic product $= [Ca^{2+}][F^-]^2$ $= (1.3 \times 10^{-5})(2.6 \times 10^{-5})^2$ $= 8.4 \times 10^{-15}$
Compare the ionic product to the value of K_{sp}.	The ionic product is 8.4×10^{-15}. This value is smaller than the K_{sp} value of 3.2×10^{-11} at 25°C. No precipitate will form.

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Worked example: Try yourself 5.2.5

PREDICTING THE FORMATION OF A PRECIPITATE WHEN SOLUTIONS ARE MIXED

5.0 mL of 0.010 mol L^{-1} barium chloride and 20 mL of 0.010 mol L^{-1} sodium sulfate are mixed together. Predict whether a precipitate will form and, if so, identify the precipitate.

Thinking	**Working**
Identify the ions that are present in each solution, and determine whether any combination of these ions is insoluble.	Barium (Ba^{2+}), chloride (Cl^-), sodium (Na^+) and sulfate (SO_4^{2-}) ions are present. Barium and sulfate ions combine to form an insoluble compound, so they could form a precipitate.
Identify the value of K_{sp} for the compound that could form a precipitate.	The value of K_{sp} for barium sulfate is 1.08×10^{-10}
Calculate the concentration of the ions that would form the precipitate. The concentrations of the solutions and the final volume of the mixture determine the concentration of these ions. Use the formula: $c_1V_1 = c_2V_2$	$[Ba^{2+}]_{mixture} = \frac{c_1V_1}{V_2}$ $= \frac{0.010 \times 0.0050}{0.025}$ $= 2.0 \times 10^{-3}$ mol L^{-1} $[SO_4^{2-}]_{mixture} = \frac{c_1V_1}{V_2}$ $= \frac{0.010 \times 0.020}{0.025}$ $= 8.0 \times 10^{-3}$ mol L^{-1}
Calculate the ionic product for this salt.	ionic product $= [Ba^{2+}][SO_4^{2-}]$ $= (2.0 \times 10^{-3})(8.0 \times 10^{-3})$ $= 1.6 \times 10^{-5}$
Compare this to the value of K_{sp} for the salt.	This is greater than the value of K_{sp} for barium sulfate. A precipitate will form.

Worked example: Try yourself 5.2.6

CALCULATING THE EFFECT OF A COMMON ION ON THE MOLAR SOLUBILITY OF AN IONIC COMPOUND

Silver bromide has a K_{sp} value of 5.35×10^{-13} at 25°C. Calculate its molar solubility in a 0.50 mol L^{-1} solution of NaBr.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled I (initial), C (change) and E (equilibrium):
<table>
<tr><td></td><td colspan="2">Reactants ⇌ Products</td></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
</td><td>Initially, there is no Ag^+ present and 0.50 mol L^{-1} of Br^-. When the silver bromide is added to water, silver ions and bromide ions enter the water in a 1:1 ratio. This can be represented by <i>s</i>. For 1 L of solution:
<table>
<tr><td></td><td colspan="3">$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$</td></tr>
<tr><td>I</td><td></td><td>0</td><td>0.50</td></tr>
<tr><td>C</td><td></td><td>$+s$</td><td>$+s$</td></tr>
<tr><td>E</td><td></td><td>s</td><td>$0.50 + s$</td></tr>
</table>
</td></tr>
<tr><td>Assume that the solute that is being added makes a negligible contribution of the common ion in the solution. Assume that all of the common ion comes from the solute already in solution.</td><td>Since the amount of bromide ions contributed from dissolving silver bromide is so small, it can be assumed that all of the bromide ions come from the NaBr solution, hence this value is used for the equilibrium concentration of Br^-.
<table>
<tr><td></td><td colspan="3">$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$</td></tr>
<tr><td>I</td><td></td><td>0</td><td>0.50</td></tr>
<tr><td>C</td><td></td><td>$+s$</td><td>0</td></tr>
<tr><td>E</td><td></td><td>s</td><td>0.50</td></tr>
</table>
</td></tr>
</table>

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Write the expression for K_{sp} and substitute *s* for the equilibrium concentrations. Calculate the molar solubility, including the correct units.	$K_{sp} = [Ag^+][Br^-]$ $5.35 \times 10^{-13} = s \times 0.50$ $s = \frac{5.35 \times 10^{-13}}{0.50}$ $= 1.1 \times 10^{-12}\ mol\ L^{-1}$ The solubility of silver bromide in 0.50 mol L^{-1} NaBr is $1.1 \times 10^{-12}\ mol\ L^{-1}$.

5.2 Review

1 **a** $K_{sp} = [Ca^{2+}][SO_4{}^{2-}]$

b $K_{sp} = [Zn^{2+}][CO_3{}^{2-}]$

c $K_{sp} = [Pb^{2+}][I^-]^2$

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

2

	$Cu(OH)_2(s) \rightleftharpoons$	$Cu^{2+}(aq)$ +	$2OH^-(aq)$
I		0	0
C		$+3.8 \times 10^{-7}$	$+2 \times (3.8 \times 10^{-7})$ $= +7.6 \times 10^{-7}$
E		1.3×10^{-5}	7.6×10^{-7}

$$K_{sp} = [Cu^{2+}][OH^-]^2$$
$$= (3.8 \times 10^{-7})(7\ 6 \times 10^{-7})^2$$
$$= 2.2 \times 10^{-19}$$

3

	$SrSO_4(s) \rightleftharpoons$	$Sr^{2+}(aq)$ +	$SO_4^{2-}(aq)$
I		0	0
C		$+s$	$+s$
E		s	s

$$K_{sp} = [Sr^{2+}][SO_4^{2-}]$$
$$3.2 \times 10^{-7} = s \times s$$
$$s = \sqrt{3.2 \times 10^{-7}}$$
$$= 5.6 \times 10^{-4}\ mol\ L^{-1}$$

4 $n(PbBr_2) = \frac{m}{M} = \frac{4.5}{367.0} = 0.012\ mol$

$c = \frac{n}{V} = \frac{0.012}{1} = 0.012\ mol\ L^{-1}$

	$PbBr_2(s) \rightleftharpoons$	$Pb^{2+}(aq)$ +	$2Br^-(aq)$
I		0	0
C		+0.012	$+2 \times 0.012$ $= +0.024$
E		0.012	0.024

$$K_{sp} = [Pb^{2+}][Br^-]^2$$
$$= 0.012 \times (0.024)^2$$
$$= 6.9 \times 10^{-6}$$

This value is greater than the K_{sp} for $PbBr_2$ at 25°C, so a precipitate will form.

5

	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$		
I		0	0.15
C		$+s$	0
E		s	0.15

$$K_{sp} = [Ag^+][Cl^-]$$
$$1.77 \times 10^{-10} = s \times 0.15$$
$$s = \frac{1.77 \times 10^{-10}}{0.15}$$
$$s = 1.2 \times 10^{-9}\ \text{mol L}^{-1}$$

6 The toxin is cycasin. The seeds are either roasted briefly and then leached in water for a short time, or only leached but for a longer time.

CHAPTER 5 REVIEW

1 **a** dissociation
  b **i** $Cu^{2+}(aq)$, $NO_3^-(aq)$
    ii $Zn^{2+}(aq)$, $SO_4^{2-}(aq)$
    iii $NH_4^+(aq)$, $PO_4^{3-}(aq)$

2 **a** K^+/CO_3^{2-}
  b Pb^{2+}/NO_3^-
  c Na^+/OH^-
  d Na^+/SO_4^{2-}
  e Mg^{2+}/Cl^-
  f Zn^{2+}/NO_3^-
  g K^+/S^{2-}
  h Fe^{3+}/NO_3^-

3 **a** $Mg(CH_3COO)_2(s) \xrightarrow{H_2O\ l} Mg^{2+}(aq) + 2CH_3COO^-(aq)$
  b $AgNO_3(s) \xrightarrow{H_2O\ l} Ag^+(aq) + NO_3^-(aq)$
  c $KBr(s) \xrightarrow{H_2O\ l} K^+(aq) + Br^-(aq)$
  d $Ba(OH)_2(s) \xrightarrow{H_2O\ l} Ba^{2+}(aq) + 2OH^-(aq)$
  e $Na_3PO_4(s) \xrightarrow{H_2O\ l} 3Na^+(aq) + PO_4^{3-}(aq)$

4 B. The ionic compound dissociates into positive and negative ions, and water molecules are dipolar. The interaction of the ions with the water is therefore an ion–dipole attraction.

5 Magnesium ions have a positive charge. This means the partially negatively charged oxygen atoms in the water molecules are attracted to them. The water molecules are arranged around the magnesium ion with their oxygen atoms pointed towards the magnesium ion.

Chloride ions have a negative charge. This means the hydrogen atoms in the water molecules, which have a partial positive charge, are attracted to them. The water molecules are arranged around the chloride ion with their hydrogen atoms pointed towards the chloride ion.

6 There are numerous possible answers to this question. Use the information in Tables 5.1.2 and 5.1.3.
  a Examples: Na_2CO_3, $(NH_4)_2CO_3$ and K_2CO_3
  b Examples: $CaCO_3$, $MgCO_3$ and Ag_2CO_3

7 There are numerous possible answers to this question. Use the information in Tables 5.1.2 and 5.1.3.
  a Examples: Na_2SO_4, K_2SO_4 and $(NH_4)_2SO_4$
  b Examples: $CaSO_4$, $BaSO_4$ and $PbSO_4$

8 According to Table 5.1.1, the solubility of sodium chloride is 6.3 mol L^{-1}. Therefore, the solubility of sodium chloride in 150 mL of water is:

$$n = c \times V$$
$$= 6.3 \times 0.150$$
$$= 0.95\ \text{mol}$$

$m = n \times M$

$= 0.95 \times 58.44$

$= 55\,\text{g}$

This is the mass of sodium chloride that will dissolve in 150 mL of water. Any amount greater than this will not dissolve.

9 **a** silver chloride
b iron(II) hydroxide
c lead(II) iodide
d none

10 **a** **i** magnesium sulfide
ii barium sulfate
iii iron(III) hydroxide
iv silver chloride

b **i** $Na_2S(aq) + MgI_2(aq) \rightarrow 2NaI(aq) + MgS(s)$
ii $K_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + BaSO_4(s)$
iii $FeCl_3(aq) + 3NaOH(aq) \rightarrow 3NaCl(aq) + Fe(OH)_3(s)$
iv $NH_4Cl(aq) + AgCH_3COO(aq) \rightarrow NH_4CH_3COO(aq) + AgCl(s)$

c **i** $Mg^{2+}(aq) + S^{2-}(aq) \rightarrow MgS(s)$
ii $Ba^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow BaSO_4(s)$
iii $Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$
iv $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

11 Reaction i: sodium and iodide
Reaction ii: potassium and nitrate
Reaction iii: sodium and chloride
Reaction iv: ammonium and acetate

12

	$MgSO_4$	**KCl**	**NaOH**	**$AgNO_3$**	**$FeBr_2$**
$Pb(CH_3COO)_2$	$PbSO_4$	$PbCl_2$ (slightly soluble)	$Pb(OH)_2$	–	$PbBr_2$ (slightly soluble)
K_2CO_3	$MgCO_3$	–	–	Ag_2CO_3	$FeCO_3$
BaI_2	$BaSO_4$	–	–	AgI	–
Na_3PO_4	$Mg_3(PO_4)_2$	–	–	$Ag_3(PO_4)_2$	$Fe_3(PO_4)_2$
NH_4S	MgS	–	–	Ag_2S	FeS

13 D. Pure solids and liquids are not included in equilibrium expressions so A, B and C are incorrect.

14 **a** $FeCl_2(s) \rightleftharpoons Fe^{2+}(aq) + 2Cl^-(aq)$
b $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$
c $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4{}^{2-}(aq)$
d $Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq)$

15 **a** $K_{sp} = [Pb^{2+}][C]^{-\ 2}$
b $K_{sp} = [Zn^{2+}][OH^-]^2$
c $K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$
d $K_{sp} = [Ba^{2+}][SO_4{}^{2-}]$

16 **a** $BaCO_3$ has a greater value of K_{sp}, so it is more soluble than $BaSO_4$.
b $Fe(OH)_2$ has a greater value of K_{sp}, so it is more soluble than $Zn(OH)_2$.
c $PbCl_2$ has a greater value of K_{sp}, so it is more soluble than PbI_2.

17 Molar solubility is the number of moles of a solute that will dissolve per litre of water to form a saturated solution.

18 Sodium chloride is very soluble in water, so it can be considered to dissociate completely. Because only the forward reaction occurs, no equilibrium arrow is used.

Silver chloride is only sparingly soluble in water. When silver chloride is added to water, very little solid dissolves, and ions dissociate into solution at the same rate that others return to the ionic lattice. This is an equilibrium system, so the equation has an equilibrium arrow.

19 There are no ions present in pure water before the addition of the sparingly soluble salt. Therefore, the initial concentration of ions is zero. When the salt is added, ions enter the solution. Therefore, the change in concentration is always positive.

20 a

	$PbBr_2(s) \rightleftharpoons$	$Pb^{2+}(aq)$ +	$2Br^-(aq)$
I		0	0
C		$+1.18 \times 10^{-2}$	$+2 \times (1.18 \times 10^{-2})$ $= +2.36 \times 10^{-2}$
E		1.18×10^{-2}	$= 2.36 \times 10^{-2}$

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

$= (1.18 \times 10^{-2})(2.36 \times 10^{-2})^2$

$s = 6.57 \times 10^{-6}$

b

	$BaSO_4(s) \rightleftharpoons$	$Ba^{2+}(aq)$ +	$SO_4^{\ 2-}(aq)$
I		0	0
C		$+1.04 \times 10^{-5}$	$+1.04 \times 10^{-5}$
E		1.04×10^{-5}	1.04×10^{-5}

$K_{sp} = [Ba^{2+}][SO_4^{\ 2-}]$

$= (1.04 \times 10^{-5}) \times (1.04 \times 10^{-5})$

$s = 1.08 \times 10^{-10}$

c

	$Ag_2CrO_4(s) \rightleftharpoons$	$2Ag^{2+}(aq)$ +	$CrO_4^{\ 2-}(aq)$
I		0	0
C		$+2 \times (8.7 \times 10^{-5})$ $= +1.74 \times 10^{-4}$	$+8.7 \times 10^{-5}$
E		1.74×10^{-4}	8.7×10^{-5}

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

$= (1.74 \times 10^{-4})^2(8.7 \times 10^{-5})$

$= 2.6 \times 10^{-12}$

21 a

	$ZnS\ (s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$		
I		0	0
C		$+s$	$+s$
E		s	s

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

$2.0 \times 10^{-25} = s \times s$

$s = \sqrt{2.0 \times 10^{-25}}$

$= 4.5 \times 10^{-13}\ mol\ L^{-1}$

b

	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$		
I		0	0
C		$+s$	$+s$
E		s	s

$$\begin{aligned} K_{sp} &= [Ag^+][Br^-] \\ 5.35 \times 10^{-13} &= s \times s \\ s &= \sqrt{5.35 \times 10^{-13}} \\ &= 7.31 \times 10^{-7}\ \text{mol L}^{-1} \end{aligned}$$

c

	$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{\ 2-}(aq)$		
I		0	0
C		$+2s$	$+s$
E		$2s$	s

$$\begin{aligned} K_{sp} &= [Ag^+]^2[SO_4^{\ 2-}] \\ 1.20 \times 10^{-5} &= (2s)^2 \times s \\ &= 4s^3 \\ s^3 &= \frac{1.20 \times 10^{-5}}{4} \\ &= 3.00 \times 10^{-6} \\ s &= \sqrt[3]{3.00 \times 10^{-6}} \\ &= 1\ 44 \times 10^{-2}\ \text{mol L}^{-1} \end{aligned}$$

22 Ionic compounds that dissociate to produce different numbers of ions have different relationships to K_{sp}. Because silver cyanide dissociates to form two ions, Ag^+ and CN^-, it has a different relationship to K_{sp} than alumiunium hydroxide, which produces four ions in solution.

23 a

	$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{\ 2-}(aq)$		
I		0	0
C		$+s$	$+s$
E		s	s

$$\begin{aligned} K_{sp} &= [Pb^{2+}][SO_4^{\ 2-}] \\ 2.53 \times 10^{-8} &= s \times s \\ s &= \sqrt{2.53 \times 10^{-8}} \\ &= 1.59 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned}$$

$$\begin{aligned} n &= c \times V \\ &= 1.59 \times 10^{-4} \times 1 \\ &= 1.59 \times 10^{-4}\ \text{mol} \\ m &= n \times M \\ &= 1.59 \times 10^{-4} \times 303.3 \\ &= 4.82 \times 10^{-2}\ \text{g} \end{aligned}$$

b

	$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$		
I		0	0
C		$+2s$	$+s$
E		$2s$	s

$$K_{sp} = [Ag^+]^2[S^{2-}]$$

$$8.0\times10^{-51} = (2s)^2 \times s = 4s^3$$

$$s^3 = \frac{8.0\times10^{-51}}{4}$$

$$= 2.0\times10^{-51}$$

$$s = \sqrt[3]{2.0\times10^{-51}}$$

$$= 1.3\times10^{-17}\text{ mol L}^{-1}$$

$$n = c \times V$$

$$= 1.3 \times 10^{-17} \times 1$$

$$= 1.3 \times 10^{-17}\text{ mol}$$

$$m = n \times M$$

$$= 1.3 \times 10^{-17} \times 247.9$$

$$= 3.1 \times 10^{-15}\text{ g}$$

24 **a** **i** $n(Ag_2CO_3)_3 = \frac{m}{M} = \frac{0.0010}{275.8}$

$$= 3.6 \times 10^{-6}\text{ mol}$$

$$c = \frac{n}{V} = \frac{3.6 \times 10^{-6}}{0.100}$$

$$= 3.6 \times 10^{-5}\text{ mol L}^{-1}$$

	$Ag_2CO_3(s) \rightleftharpoons$	$2Ag^+(aq)$ +	$CO_3^{2-}(aq)$
I		0	0
C		$+2 \times (3.6 \times 10^{-5})$	$+3.6 \times 10^{-5}$
E		7.25×10^{-5}	3.6×10^{-5}

$$\text{ionic product} = [Ag^+]^2[CO_3^{2-}]$$

$$= (7.25 \times 10^{-5})^2(3.6 \times 10^{-5})$$

$$= 1.9 \times 10^{-13}$$

The ionic product is smaller than the value of K_{sp} for Ag_2CO_3 so no precipitate will form.

ii $n(CuCl) = \frac{m}{M} = \frac{0.20}{99.00}$

$$= 2.02 \times 10^{-3}\text{ mol}$$

$$c = \frac{n}{V} = \frac{2.02 \times 10^{-3}}{1.0}$$

$$= 2.02 \times 10^{-3}\text{ mol L}^{-1}$$

	$CuCl(s) \rightleftharpoons$	$Cu^+(aq)$ +	$Cl^-(aq)$
I		0	0
C		$+2.02 \times 10^{-3}$	$+2.02 \times 10^{-3}$
E		2.02×10^{-3}	2.02×10^{-3}

$$\text{ionic product} = [Cu^+][Cl^-]$$

$$= (2.02 \times 10^{-3})(2.02 \times 10^{-3})$$

$$= 4.1 \times 10^{-6}$$

The ionic product is greater than the value of K_{sp} for CuCl at 25°C so a precipitate will form.

iii $n(SrCrO_4) = \frac{m}{M} = \frac{3.0 \times 10^{-5}}{203.61}$

$$= 1.47 \times 10^{-7}\text{ mol}$$

$$c = \frac{n}{V} = \frac{1.47 \times 10^{-7}}{1.0} = 1.47 \times 10^{-7}\text{ mol L}^{-1}$$

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	$SrCrO_4(s) \rightleftharpoons$	$Sr^{2+}(aq)$ +	$CrO_4^{2-}(aq)$
I		0	0
C		$+1.47 \times 10^{-7}$	1.47×10^{-7}
E		1.47×10^{-7}	1.47×10^{-7}

$$\begin{aligned}\text{ionic product} &= [Sr^{2+}][CrO_4^{2-}]\\ &= (1.47 \times 10^{-7})(1.47 \times 10^{-7})\\ &= 2.2 \times 10^{-14}\end{aligned}$$

The ionic product is smaller than the value of K_{sp} for $SrCrO_4$ so no precipitate will form.

b i

	$Ag_2CO_3\ (s) \rightleftharpoons$	$2Ag^+(aq) +$	$CO_3^{2-}(aq)$
I		0	0
C		$+2s$	$+s$
E		$2s$	s

$$\begin{aligned}K_{sp} &= [Ag^+]^2[CO_3^{2-}]\\ 8.46 \times 10^{-12} &= (2s)^2(s)\\ &= 4s^3\\ s^3 &= \frac{8.46 \times 10^{-12}}{4}\\ &= 2.115 \times 10^{-12}\\ s &= \sqrt[3]{2.115 \times 10^{-12}}\\ &= 1.28 \times 10^{-4}\ \text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}n &= c \times V\\ &= 1.28 \times 10^{-4} \times 0.100\\ &= 1.28 \times 10^{-5}\ \text{mol}\\ m &= n \times M\\ &= 1.28 \times 10^{-5} \times 275.8\\ &= 3.53 \times 10^{-3}\ \text{g}\end{aligned}$$

iii

	$SrCrO_4(s) \rightleftharpoons$	$Sr^{2+}(aq) +$	$CrO_4^{2-}(aq)$
I		0	0
C		$+s$	$+s$
E		s	s

$$\begin{aligned}K_{sp} &= [Sr^{2+}][CrO_4^{2-}]\\ 2.0 \times 10^{-5} &= s \times s\\ s &= \sqrt{2.0 \times 10^{-5}}\\ &= 4.5 \times 10^{-3}\ \text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}n &= c \times V\\ &= 4.5 \times 10^{-3} \times 1.0\\ &= 4.5 \times 10^{-3}\ \text{mol}\\ m &= n \times M\\ &= 4.5 \times 10^{-3} \times 203.61\\ &= 0.91\ \text{g}\end{aligned}$$

25 **a** Lead(II) iodide is insoluble, and could precipitate. The value of K_{sp} for lead(II) iodide is 9.8×10^{-9}.

$$\begin{aligned}\text{ionic product} &= [Pb^{2+}][I^-]^2\\ &= 0.020 \times (0.0030)^2\\ &= 1.8 \times 10^{-7}\end{aligned}$$

This value is greater than the value of K_{sp} for lead(II) iodide. A precipitate will form.

b Magnesium carbonate is insoluble, and could precipitate. The value of K_{sp} for magnesium carbonate is 6.82×10^{-6}

$$\begin{aligned}\text{ionic product} &= [Mg^{2+}][CO_3{}^{2-}]\\ &= (3.0 \times 10^{-5})(0.0040)\\ &= 1.2 \times 10^{-7}\end{aligned}$$

This value is smaller than the value of K_{sp} for magnesium carbonate. No precipitate will form.

c Silver chloride is insoluble, and could precipitate. The value of K_{sp} for silver chloride is 1.77×10^{-10}.

$$\begin{aligned}\text{ionic product} &= [Ag^+][Cl^-]\\ &= (5.0 \times 10^{-6})(2.0 \times 10^{-4})\\ &= 1.0 \times 10^{-9}\end{aligned}$$

This value is greater than the value of K_{sp} for silver chloride. A precipitate will form.

26 **a** Silver bromide is insoluble, and could precipitate. The value of K_{sp} for silver bromide is 5.35×10^{-13}.

$$\begin{aligned}[Ag^+]_{\text{mixture}} &= \frac{c_1V_1}{V_2}\\ &= \frac{0.0010 \times 0.010}{0.020}\\ &= 5.0 \times 10^{-4}\,\text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}[Br^-]_{\text{mixture}} &= \frac{c_1V_1}{V_2}\\ &= \frac{0.0050 \times 0.010}{0.020}\\ &= 2.5 \times 10^{-3}\,\text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}\text{ionic product} &= [Ag^+][Br^-]\\ &= (5.0 \times 10^{-4})(2.5 \times 10^{-3})\\ &= 1.3 \times 10^{-6}\end{aligned}$$

This value is greater than the value of K_{sp} for silver bromide. A precipitate will form.

b Magnesium hydroxide is insoluble, and could precipitate. The value of K_{sp} for magnesium hydroxide is 5.61×10^{-12}.

$$\begin{aligned}[Mg^{2+}]_{\text{mixture}} &= \frac{c_1V_1}{V_2}\\ &= \frac{6.0 \times 10^{-7} \times 0.0050}{0.0100}\\ &= 3.0 \times 10^{-7}\,\text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}[OH^-]_{\text{mixture}} &= \frac{c_1V_1}{V_2}\\ &= \frac{4.0 \times 10^{-5} \times 0.0050}{0.0100}\\ &= 2.0 \times 10^{-5}\,\text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}\text{ionic product} &= [Mg^{2+}][OH^-]^2\\ &= (3.0 \times 10^{-7})(2.0 \times 10^{-5})^2\\ &= 1.2 \times 10^{-16}\end{aligned}$$

This value is smaller than the value of K_{sp} for magnesium hydroxide. No precipitate will form.

c Lead(II) sulfate is insoluble, and could precipitate. The value of K_{sp} for lead(II) sulfate is 2.53×10^{-8}.

$$\begin{aligned}[Pb^{2+}]_{\text{mixture}} &= \frac{c_1V_1}{V_2}\\ &= \frac{1.0 \times 10^{-4} \times 0.020}{0.025}\\ &= 8.0 \times 10^{-5}\,\text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}[SO_4{}^{2-}]_{\text{mixture}} &= \frac{c_1V_1}{V_2}\\ &= \frac{0.020 \times 0.0050}{0.025}\\ &= 4.0 \times 10^{-3}\,\text{mol L}^{-1}\end{aligned}$$

$$\begin{aligned}\text{ionic product} &= [\mathrm{Pb^{2+}}][\mathrm{SO_4^{2-}}]\\ &= (8.0\times10^{-5})(4.0\times10^{-3})\\ &= 3.2\times10^{-7}\end{aligned}$$

This value is greater than the value of K_{sp} for lead(II) sulfate. A precipitate will form.

27 a

	$\mathrm{PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)}$		
I		0	0.050
C		$+s$	0
E		s	0.050

$$\begin{aligned}K_{sp} &= [\mathrm{Pb^{2+}}][\mathrm{I^-}]^2\\ 9.8\times10^{-9} &= (s)(0.050)^2\\ s &= \frac{9.8\times10^{-9}}{(0.050)^2}\\ &= 3.9\times10^{-9}\ \mathrm{mol\ L^{-1}}\end{aligned}$$

b

	$\mathrm{Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)}$		
I		0	0.020
C		$+s$	0
E		s	0.020

$$\begin{aligned}K_{sp} &= [\mathrm{Fe^{3+}}][\mathrm{OH^-}]^3\\ 2.79\times10^{-39} &= (s)(0.020)^3\\ s &= \frac{2.79\times10^{-39}}{(0.020)^3}\\ &= 3.5\times10^{-34}\ \mathrm{mol\ L^{-1}}\end{aligned}$$

c

	$\mathrm{ZnCO_3(s) \rightleftharpoons Zn^{3+}(aq) + CO_3^{2-}(aq)}$		
I		0	0.20
C		$+s$	0
E		s	0.20

$$\begin{aligned}K_{sp} &= [\mathrm{Zn^{2+}}][\mathrm{CO_3^{2-}}]\\ 1.4\times10^{-11} &= s\times0.20\\ s &= \frac{1.4\times10^{-11}}{0.20}\\ &= 7.0\times10^{-11}\ \mathrm{mol\ L^{-1}}\end{aligned}$$

28 a i

	$\mathrm{AgI(s) \rightleftharpoons Ag^{+}(aq) + I^-(aq)}$		
I		0	0
C		$+s$	$+s$
E		s	s

$$\begin{aligned}K_{sp} &= [\mathrm{Ag^{+}}][\mathrm{I^-}]\\ 8.52\times10^{-17} &= s\times s\\ s &= \sqrt{8.52\times10^{-17}}\\ &= 9.23\times10^{-9}\ \mathrm{mol\ L^{-1}}\end{aligned}$$

ii

	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$		
I		0	1.5
C		$+s$	0
E		s	1.5

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

$$8.52 \times 10^{-17} = s \times 1.5$$

$$s = \frac{8.52 \times 10^{-17}}{1.5}$$

$$= 5.68 \times 10^{-17}\ mol\ L^{-1}$$

b The calculated molar solubility for silver iodide in a 1.5 mol L^{-1} solution of potassium iodide is 5.68×10^{-17} mol L^{-1}, which is much lower that the value in pure water of 9.23×10^{-9} mol L^{-1}. This is because of the presence of a common ion, I^-. Le Châtelier's principle states that a system at equilibrium will shift its position so as to partially oppose the change. Here, the equilibrium position will shift to the left, because of the presence of iodide ions from the potassium iodide. Therefore, the molar solubility of silver iodide is much less in potassium iodide solution than in pure water.

29 One example is the bitter yam. It was picked carefully to avoid damaging the roots, then leached in running water to remove the toxins. Finally, it was roasted before being eaten. Another example is cycad seeds. They are either roasted briefly before leaching in water, or leached for a longer time without roasting.

30 By cutting up the cycad seed, the surface area is increased. This means that more of the seed is exposed to the water, which facilitates the removal of the toxin.

31 The Epsom salts ($MgSO_4$) dissociated in water, yielding Mg^{2+} ions. These ions attach to the polar 'head' group of fatty acid molecules found in soaps and detergents and prevent them from lathering via the precipitation of insoluble soap 'scum'.

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Chapter 6 Properties of acids and bases

6.1 Introducing acids and bases

6.1 Review

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

2 H_2SO_4/HSO_4^- and $H_2NO_3^+/HNO_3$ (one proton difference in each pair)

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

4 The conjugate acids will differ by one proton.
  a NH_4^+
  b CH_3COOH
  c $H_2PO_4^-$
  d HCO_3^-
  e OH^-

5 Brønsted–Lowry acid–base reactions are those involving the exchange of a proton (H^+ ion).

The acid donates the proton to the base. In the reaction below, the HCl loses a proton to the base.

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

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

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

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

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

6.2 Reactions of acids and bases

Worked example: Try yourself 6.2.1

CALCULATING THE AMOUNT OF BASE NEEDED TO NEUTRALISE AN ACID

What volume of a 0.100 mol L^{-1} solution of barium hydroxide ($Ba(OH)_2$) would be required to neutralise 75.0 mL of a 0.0500 mol L^{-1} solution of sulfuric acid (H_2SO_4)?

Thinking	**Working**
Write the general reaction and identify the products.	acid + metal hydroxide → salt + water Products of this reaction are barium sulfate in solution and water.
Write a balanced chemical equation.	$H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow BaSO_4(aq) + 2H_2O(l)$
Calculate the amount, in mol, of known substance using the following relationship: $n = c \times V$	$n(H_2SO_4) = c \times V$ $= 0.0500 \times 0.0750$ $= 3.75 \times 10^{-3}$ mol

Calculate the amount of substance, in mol, of the unknown chemical species using the mole ratio between known and unknown chemical species: $\text{mole ratio} = \frac{\text{coefficient of unknown chemical}}{\text{coefficient of known chemical}}$	$\frac{n(Ba(OH)_2)}{n(H_2SO_4)} = \frac{1}{1}$ $n(Ba(OH)_2) = n(H_2SO_4)$ $= 3.75 \times 10^{-3}$ mol
Knowing the concentration, calculate the required volume for neutralisation using the following relationship: $V = \frac{n}{c}$	$V(Ba(OH)_2) = \frac{n}{c}$ $= \frac{3.75 \times 10^{-3}}{0.100}$ $= 0.0375$ L $= 37.5$ mL

Worked example: Try yourself 6.2.2

DETERMINING THE ENTHALPY OF NEUTRALISATION

25.0 mL of a diluted standard barium hydroxide solution ($Ba(OH)_2$) was added to neutralise 50.0 mL of a 1.5 mol L^{-1} solution of ethanoic acid (CH_3COOH). The temperature of the mixture rose from 21.3°C to a maximum temperature of 34.0°C. Determine the enthalpy of neutralisation.

Thinking	**Working**
Write a balanced chemical equation for the reaction.	$Ba(OH)_2(aq) + 2CH_3COOH(aq) \rightarrow Ca(CH_3COO)_2(aq) + 2H_2O(l)$
Determine the amount, in mol, of acid using the expression: $n = c \times V$	$n(CH_3COOH) = c \times V$ $= 1.5 \times 0.0500$ $= 0.075$ mol
Determine the temperature change, ΔT.	$\Delta T = 34.0 - 21.3$ $= 12.7$°C
Determine the amount of energy released by reaction using the formula: $q = m \times c \times \Delta T$ Assume the density of the mixture is 1 g mL^{-1}. Therefore the mass of the mixture is equivalent to the volume of the mixture.	$q = m \times c \times \Delta T$ $= 75.0 \times 4.18 \times 12.7$ $= 3.98 \times 10^3$ J
Convert energy to kJ.	$\frac{3.98 \times 10^3}{1000} = 3.98$ kJ
Determine the amount of water, in mol, produced in the reaction, using the mole ratio with the limiting reactant.	$\frac{n(H_2O)}{n(CH_3COOH)} = \frac{2}{2}$ $n(H_2O) = n(CH_3COOH)$ $= 0.075$ mol
Determine ΔH_{neut} using: $\Delta H_{neut} = \frac{q}{n(H_2O)}$ Because the temperature increased, the reaction was exothermic and hence ΔH_{neut} is negative.	$\Delta H_{neut} = \frac{q}{n(H_2O)}$ $= \frac{-3.98}{0.075}$ $= -53$ kJ mol^{-1}

Worked example: Try yourself 6.2.3

WRITING IONIC EQUATIONS FOR REACTIONS BETWEEN ACIDS AND METAL CARBONATES

What products are formed when a solution of sulfuric acid is added to a solution of calcium hydrogen carbonate? Write an ionic equation for this reaction.

Thinking	**Working**
Write the general reaction and identify the products.	acid + metal carbonate → salt + water + carbon dioxide Products of this reaction are calcium sulfate in solution, water and carbon dioxide gas.
Identify the reactants and products. Indicate the state of each.	Reactants: sulfuric acid as a diprotic acid is dissociated in solution, forming $H^+(aq)$ and $SO_4^{2-}(aq)$ ions Calcium hydrogen carbonate is an ionic solid, $Ca(HCO_3)_2$. Products: calcium sulfate is dissociated into $Ca^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions. Water has the formula $H_2O(l)$. Carbon dioxide has the formula $CO_2(g)$.
Write the equation showing all reactants and products. (There is no need to balance the equation yet.)	$H^+(aq) + SO_4^{2-}(aq) + Ca(HCO_3)_2(s) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) + H_2O(l) + CO_2(g)$
Identify the spectator ions.	$SO_4^{2-}(aq)$
Rewrite the equation without the spectator ions.	$H^+(aq) + Ca(HCO_3)_2(s) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$
Balance the equation with respect to number of atoms of each element and charge.	$2H^+(aq) + Ca(HCO_3)_2(s) \rightarrow Ca^{2+}(aq) + 2H_2O(l) + 2CO_2(g)$ Note that if hydronium ions are represented as $H_3O^+(aq)$, rather than as $H^+(aq)$, this reaction would be written as: $2H_3O^+(aq) + Ca(HCO_3)_2(s) \rightarrow Ca^{2+}(aq) + 4H_2O(l) + 2CO_2(g)$

Worked example: Try yourself 6.2.4

WRITING IONIC EQUATIONS FOR REACTIONS BETWEEN ACIDS AND REACTIVE METALS

Write an ionic equation for the reaction that occurs when aluminium is added to a solution of nitric acid.

Thinking	**Working**
Write the general reaction and identify the products formed.	Acid + reactive metal → salt + hydrogen Hydrogen gas and aluminium nitrate solution are produced.
Identify the reactants and products. Indicate the state of each.	Reactants: aluminium is a solid, Al(s). Nitric acid is dissociated, forming $H^+(aq)$ and $NO_3^-(aq)$ ions. Products: hydrogen gas, H_2. Aluminium nitrate is dissociated into $Al^{3+}(aq)$ and $NO_3^-(aq)$ ions.
Write the equation showing all reactants and products. (There is no need to balance the equation yet.)	$H^+(aq) + NO_3^-(aq) + Al(s) \rightarrow Al^{3+}(aq) + NO_3^-(aq) + H_2(g)$
Identify the spectator ions.	$NO_3^-(aq)$
Rewrite the equation without the spectator ions. Balance the equation with respect to number of atoms of each element and charge.	$6H^+(aq) + 2Al(s) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

6.2 Review

1 **a** **i** $Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$
ii $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
b **i** $Ca(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2(g)$
ii $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
c **i** $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
ii $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
d **i** $2Al(s) + 6CH_3COOH(aq) \rightarrow 2Al(CH_3COO)_3(aq) + 3H_2(g)$
ii $2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

2 **a** magnesium nitrate
b calcium sulfate
c zinc chloride
d aluminium ethanoate

3 **a** **i** $Al(OH)_3(s) + 3HF(aq) \rightarrow AlF_3(aq) + 3H_2O(l)$
ii $Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$
b **i** $Fe(OH)_2(s) + 2HNO_3(aq) \rightarrow Fe(NO_3)_2(aq) + 2H_2O(l)$
ii $Fe(OH)_2(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + 2H_2O(l)$
c **i** $ZnCO_3(s) + 2CH_3COOH(aq) \rightarrow Zn(CH_3COO)_2(aq) + CO_2(g) + H_2O(l)$
ii $ZnCO_3(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + CO_2(g) + H_2O(l)$
d **i** $Sn(HCO_3)_2(s) + 2HCl(aq) \rightarrow SnCl_2(aq) + 2CO_2(g) + 2H_2O(l)$
ii $Sn(HCO_3)_2(s) + 2H^+(aq) \rightarrow Sn^{2+}(aq) + 2CO_2(g) + 2H_2O(l)$

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

b $n(NaOH) = c \times V$
$= 1.00 \times 25.0 \times 10^{-3}$
$= 0.0250\,\text{mol}$

c $q = m \times c \times \Delta T$
$= (12.5 + 25.0) \times 4.18 \times (28.3 - 19.5)$
$= 1.4 \times 10^3\,\text{J}$
$= 1.4\,\text{kJ}$

d $\frac{n(H_2O)}{n(NaOH)} = \frac{2}{2}$
$n(H_2O) = n(NaOH)$
$= 0.0250\,\text{mol}$

e $\Delta H_{neut} = \frac{q}{n(H_2O)}$
$= \frac{-1.4}{0.0250}$
$= -55\,\text{kJ}\,\text{mol}^{-1}$

5 A. The complete neutralisation of potassium hydroxide and nitric acid produces a salt (potassium nitrate) and water.

CHAPTER 6 REVIEW

1 **a** NH_4^+
b HCl
c HCO_3^-
d H_3O^+
e CH_3COOH

2 Remember that if a substance acts as a base, it will accept a proton. In this question, the proton comes from a water molecule. If a substance acts as an acid, it must be able to donate one or more protons.

a $PO_4^{3-}(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + OH^-(aq)$

b The $H_2PO_4^-$ accepts a proton from water, and acts as a base:

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

The $H_2PO_4^-$ donates a proton to the water, and acts as an acid:

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

c $H_2S(aq) + H_2O(l) \rightarrow HS^-(aq) + H_3O^+(aq)$

3 **a** Cl^-

b H_2O

c OH^-

d SO_4^{2-}

4 **a** Sulfuric acid (H_2SO_4) is a diprotic acid because each molecule can donate two protons to a base:

i.e. $H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$

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

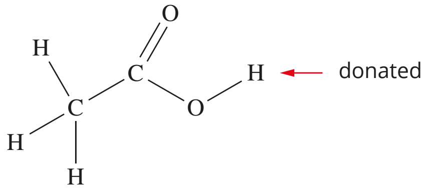
The HSO_4^- ion, however, is amphiprotic because it can act as either an acid or a base, depending on the environment. In water it will undergo both acid and base reactions:

As an acid: $HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$

As a base: $HSO_4^-(aq) + H_2O(l) \rightarrow OH^-(aq) + H_2SO_4(aq)$

b A strong acid is one that dissociates completely in solution (e.g. HCl). A weak acid is one that partially dissociates in solution (e.g. CH_3COOH).

5



6 A and D. The first step, as in the development of any equation, is to write the correct chemical formulae for each of the chemicals involved.

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

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

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

B $2HNO_3(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$

This is an acid reacting with a metal, not a Bronsted–Lowry acid–base reaction.

C $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

This a precipitation reaction.

D $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

$CuO(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O(l)$

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

7 **a** A diprotic acid can donate two protons.

b A diprotic acid dissociates in two stages.

Step 1: $H_2CrO_4(aq) + H_2O(l) \rightarrow HCrO_4^-(aq) + H_3O^+(aq)$

Step 2: $HCrO_4^-(aq) + H_2O(l) \rightarrow CrO_4^{2-}(aq) + H_3O^+(aq)$

8 The extent of the dissociation decreases progressively from each subsequent stage. This is because it is harder to remove a proton from a negatively charged species (HA^-) than from a neutral species (H_2A).

9 D. Owing to the negative charge, $H_2PO_4^-$ is able to accept a positively charged proton and it is also able to donate two protons, so it is both diprotic and amphiprotic. Although H_2SO_3 is diprotic, it is not able to accept a proton, so it is diprotic but not amphiprotic. HSO_4^- is amphiprotic, but not diprotic. HCl is neither amphiprotic nor diprotic (it is a monoprotic acid).

10 **a** $Fe(s) + 2HF(aq) \rightarrow FeF_2(aq) + H_2(g)$

b $HClO_4(aq) + LiOH(aq) \rightarrow LiClO_4(aq) + H_2O(l)$

c $HNO_3(aq) + KHCO_3(aq) \rightarrow KNO_3(aq) + CO_2(g) + H_2O(l)$

d $Li_2CO_3(aq) + 2CH_3COOH(aq) \rightarrow 2LiCH_3COO(aq) + CO_2(g) + H_2O(l)$

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11 **a** $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$

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

c $H^+(aq) + HCO_3^-(aq) \rightarrow CO_2(g) + H_2O(l)$

d $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$

12 $n(HF) = c \times V$

$= 0.0500 \times 0.0300$

$= 1.50 \times 10^{-3}\,mol$

$KOH(aq) + HF(aq) \rightarrow KF(aq) + H_2O(l)$

$\frac{n(KOH)}{n(HF)} = \frac{1}{1}$

$n(KOH) = n(HF) = 1.50 \times 10^{-3}\,mol$

$V(KOH) = \frac{n}{c}$

$= \frac{1.50 \times 10^{-3}}{0.0010}$

$= 1.5\,L$

13 **a** $HClO_4(aq) + NaOH(aq) \rightarrow NaClO_4(aq) + H_2O(l)$

b $n(NaOH) = c \times V$

$= 2.00 \times 0.0400$

$= 0.0800\,mol$

$\Delta T = 35.2 - 22.3$

$= 12.9°C$

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

$= 80.0 \times 4.18 \times 12.9$

$= 4.31 \times 10^3\,J = 4.31\,kJ$

$\frac{n(H_2O)}{n(NaOH)} = \frac{1}{1}$

$n(H_2O) = n(NaOH)$

$= 0.0800\,mol$

$\Delta H_{neut} = \frac{q}{n} = \frac{-4.31}{0.0800} = -53.9\,kJ\,mol^{-1}$

c The reaction may not have been carried out under standard conditions; ΔT of the solution is lower than expected due to poor insulation of the calorimeter.

14 **a** $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

b $n(HCl) = c \times V$

$= 12 \times 2.00$

$= 24\,mol$

$\frac{n(NaCO_3)}{n(HCl)} = \frac{1}{1}$

$n(NaHCO_3) = n(HCl) = 24\,mol$

$m(NaHCO_3) = n \times M = 24 \times 84.01 = 2016\,g$. A minimum of 2.0 kg of sodium hydrogen carbonate would be required.

15 Spectator ions are ions which do not participate in a chemical reaction but are still present within the reaction mixture (i.e. ions which do not change from the reactant to the product side in a chemical equation). Because they do not participate, they are not included in ionic equations.

16 **a** **i** A Brønsted–Lowry acid is a proton donor.

ii A strong base is a substance that dissociates completely in water.

iii Molarity is a measure of concentration of a solution expressed in $mol\,L^{-1}$.

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

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

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

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

17 **a** HCl/Cl^- and H_2O/OH^-

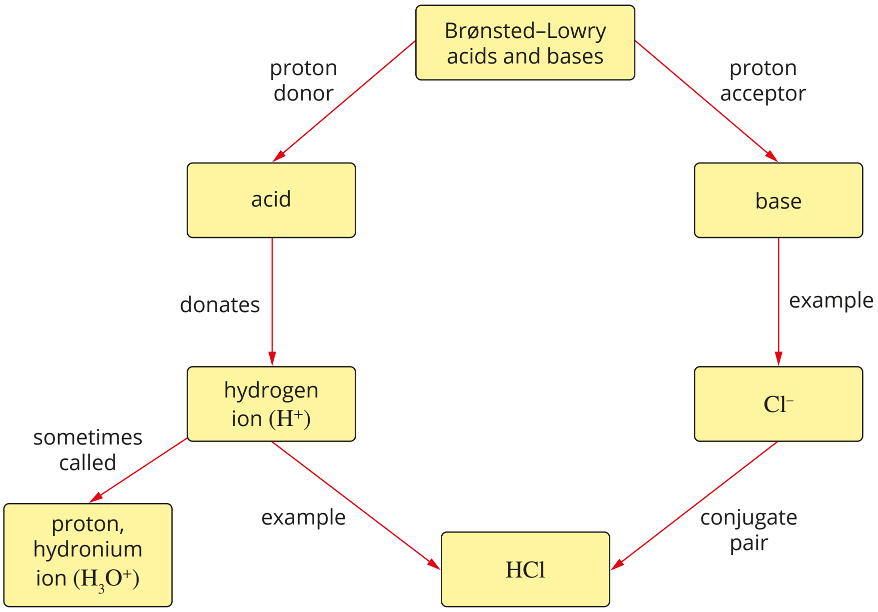
b HNO_3/NO_3^- and NH_4^+/NH_3

c HCO_3^-/CO_3^{2-} and H_3O^+/H_2O

(In **a** Na^+ is a spectator ion, so it is not considered a part of the conjugate acid–base pairs.)

18 As water acts as an amphiprotic substance, it can accept protons. The hydrogen ion in solution readily reacts with water to form the hydronium ion. Writing the hydronium ion in an equation makes it easier to see that a proton transfer has occurred.

19



20 Acid and metal carbonate reaction; vinegar is an acid (ethanoic acid) and bicarbonate of soda is a carbonate.

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Chapter 7 Using the Brønsted–Lowry theory

7.1 Strength of acids and bases

7.1 Review

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

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

3 A. A strong acid readily donates a proton to a water molecule to form the hydronium ion. The complete dissociation of the acid molecule is indicated by the use of a single arrow (→).

4 Stronger acids more readily dissociate, forming ions in solution. Because perchloric acid is stronger, more hydronium ions (and conjugate base ions) would be present in solution than in a solution of ethanoic acid, making it a better conductor of electricity.

7.2 Acidity and basicity of solutions

Worked example: Try yourself 7.2.1

CALCULATING THE CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 5.6×10^{-6} mol L^{-1} HNO_3 solution at 25°C, calculate the concentration of H_3O^+ and OH^- ions.

Thinking	**Working**
Find the concentration of the hydronium (H_3O^+) ions.	HNO_3 is a strong acid, so it will dissociate completely in solution. Each molecule of HNO_3 donates one proton to water to form one H_3O^+ ion: $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$ Because HNO_3 is completely dissociated in water, 5.6×10^{-6} mol L^{-1} HNO_3 will produce a solution with a concentration of H_3O^+ ions of 5.6×10^{-6} mol L^{-1}: $[H_3O^+] = 5.6 \times 10^{-6}$ mol L^{-1}
Use the expression for the ionisation constant of water to calculate the concentration of OH^- ions.	$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ $[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$ $= \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-6}}$ $= 1.8 \times 10^{-9}$ mol L^{-1}

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Worked example: Try yourself 7.2.2

CALCULATING THE pH AND pOH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

Calculate the pH and pOH of a solution in which the concentration of $[H_3O^+]$ is $6 \times 10^{-9}\,mol\,L^{-1}$. Give your answer correct to 2 significant figures.

Thinking	**Working**
Write down the concentration of $[H_3O^+]$ ions in the solution.	$[H_3O^+] = 6 \times 10^{-9}\,mol\,L^{-1}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer (ensure to use log to the base 10 and not the natural logarithm, which may appear as *ln*).	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(6 \times 10^{-9})$ $= 8.2$
Calculate pOH from the relationship: $pOH = 14 - pH$	$pOH = 14 - pH$ $= 14 - 8.2$ $= 5.8$

Worked example: Try yourself 7.2.3

CALCULATING THE pH AND pOH IN A SOLUTION OF A BASE

What is the pH and pOH of a $0.01\,mol\,L^{-1}$ solution of $Ba(OH)_2$ at 25°C?

Thinking	**Working**
Write down the equation for the dissociation of $Ba(OH)_2$ in water.	In water, 1 mol of $Ba(OH)_2$ completely dissociates to release 2 mol of OH^- ions. $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$
Determine the concentration of $[OH^-]$ ions.	$[OH^-] = 2 \times [Ba(OH)_2]$ $= 2 \times 0.01\,mol\,L^{-1}$ $= 0.02\,mol\,L^{-1}$
To calculate the pH, determine the $[H_3O^+]$ in the solution by substituting the $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.0 \times 10^{-14}}{0.02}$ $= 5 \times 10^{-13}\,mol\,L^{-1}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(5 \times 10^{-13})$ $= 12.3$
Determine the pOH by using the pOH formula: $pOH = -\log_{10}[OH^-]$	$pOH = -\log_{10}[OH^-]$ $= -\log_{10}(0.02)$ $= 1.7$
Alternatively, calculate pH from the relationship: $pH = 14 - pOH$	$pH = 14 - pOH$ $= 14 - 1.7$ $= 12.3$

Worked example: Try yourself 7.2.4

CALCULATING pH AND pOH IN A SOLUTION WHERE THE SOLUTE MOLAR CONCENTRATION IS NOT GIVEN

Calculate the pH and pOH of a solution at 25°C that contains 0.50 g KOH in 500 mL of solution.

Thinking	**Working**
Determine the number of moles of KOH.	$n(\text{KOH}) = \frac{m}{M}$ $= \frac{0.50}{56.12}$ $= 8.9 \times 10^{-3}$ mol
Write the equation for dissociation of KOH.	$\text{KOH(aq)} \rightarrow \text{K}^+\text{(aq)} + \text{OH}^-\text{(aq)}$ KOH is completely dissociated in water.
Determine the number of moles of OH^- based on the dissociation equation.	$n(\text{OH}^-) = n(\text{KOH})$ $= 8.9 \times 10^{-3}$ mol
Use the formula for determining concentration given number of moles and volume: $c = \frac{n}{V}$	$n = 8.9 \times 10^{-3}$ mol $V = 0.500$ L $c = \frac{n}{V}$ $= \frac{8.9 \times 10^{-3}}{0.500}$ $= 0.018$ mol L^{-1}
Determine the pOH by using the pOH formula: $\text{pOH} = -\log_{10}[\text{OH}^-]$	$\text{pOH} = -\log_{10}(0.018)$ $= 1.75$
Calculate pH from the relationship: pH = 14 – pOH	pH = 14 – pOH = 14 – 1.75 = 12.25

Worked example: Try yourself 7.2.5

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

Calculate the $[H_3O^+]$ and $[OH^-]$ in a solution of pH 10.4 at 25°C.

Thinking	**Working**
Decide which form of the relationship between pH and $[H_3O^+]$ should be used: $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ or $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$	As you have the pH and are calculating $[H_3O^+]$, use: $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
Substitute the value of pH into the relationship expression and use a calculator to determine the answer.	$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$ $= 10^{-10.4}$ $= 4 \times 10^{-11}$ mol L^{-1}
Determine the $[OH^-]$ in the solution by substituting the $[H_3O^+]$ into the ionic product of water: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ $[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$ $= \frac{1.0 \times 10^{-14}}{4 \times 10^{-11}}$ $= 3 \times 10^{-4}$ mol L^{-1}

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7.2 Review

1 $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$

$= \frac{1.0 \times 10^{-14}}{0.001}$

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

2 $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$

$= \frac{1.0 \times 10^{-14}}{5.70 \times 10^{-9}}$

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

3 $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$

$= \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}}$

$= 1.0 \times 10^{-9}\ mol\ L^{-1}$

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

$= -\log_{10}(0.01)$

$= 2.0$

$pOH = 14 - pH$

$= 14 - 2.0$

$= 12.0$

5 Nitric acid is a strong monoprotic acid and therefore dissociates completely, so $[H_3O^+] = 0.001\ mol\ L^{-1}$.

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

$= -\log_{10}(0.001)$

$= 3.0$

$pOH = 14 - pH$

$= 14 - 3.0$

$= 11.0$

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

$= 10^{-6.0}$

$= 1 \times 10^{-6}\ mol\ L^{-1}$

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

$= \frac{1.0 \times 10^{-14}}{1 \times 10^{-6}}$

$= 1 \times 10^{-8}\ mol\ L^{-1}$

7 $n(HCl) = \frac{m}{M} = \frac{0.365}{36.46} = 0.0100\ mol$

$[HCl] = \frac{n}{V} = \frac{0.0100}{0.200} = 0.0500\ mol\ L^{-1}$

As HCl completely dissociates to H_3O^+ and Cl^-, $[HCl] = [H_3O^+]$, therefore $[H_3O^+] = 0.0500\ mol\ L^{-1}$.

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

$= -\log_{10}(0.0500)$

$= 1.301$

$pOH = 14 - pH$

$= 14 - 1.301$

$= 12.699$

7.3 Dilution of acids and bases

Worked example: Try yourself 7.3.1

CALCULATING MOLAR CONCENTRATION AFTER DILUTION

Calculate the molar concentration of nitric acid when 80.0 mL of water is added to 20.0 mL of 5.00 mol L^{-1} HNO_3.

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

Worked example: Try yourself 7.3.2

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 15.0 mL of 10.0 mol L^{-1} NaOH to dilute the solution to 2.00 mol L^{-1}?

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

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Worked example: Try yourself 7.3.3

CALCULATING THE pH OF A DILUTED ACID

10.0 mL of 0.1 mol L^{-1} HCl is diluted to 30.0 mL. Calculate the pH of the diluted solution.

Thinking	**Working**
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.10\ \text{mol L}^{-1}$ $V_1 = 10.0\ \text{mL}$ $V_2 = 30.0\ \text{mL}$ $c_2 = ?$
Calculate c_2, which is the concentration of H_3O^+ after dilution, by transposing the formula: $c_1V_1 = c_2V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.10 \times 10.0}{30.0}$ $= 0.033\ \text{mol L}^{-1}$
Calculate the pH using: $\text{pH} = -\log_{10}[H_3O^+]$	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.033)$ $= 1.48$

Worked example: Try yourself 7.3.4

CALCULATING THE pH AND pOH OF A DILUTED BASE

15.0 mL of 0.02 mol L^{-1} KOH is diluted to 60.0 mL. Calculate the pH and pOH of the diluted solution.

Thinking	**Working**
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.02\ \text{mol L}^{-1}$ $V_1 = 15.0\ \text{mL}$ $V_2 = 60.0\ \text{mL}$ $c_2 = ?$
Calculate c_2, which is $[OH^-]$ after dilution, by transposing the formula: $c_1V_1 = c_2V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.02 \times 15.0}{60.0}$ $= 0.005\ \text{mol L}^{-1}$
Calculate the pOH using the expression: $\text{pOH} = -\log_{10}[OH^-]$	$\text{pOH} = -\log_{10}[OH^-]$ $= -\log_{10}(0.005)$ $= 2.3$
Calculate the pH using the expression: $\text{pH} = 14 - \text{pOH}$	$\text{pH} = 14 - \text{pOH}$ $= 14 - 2.3$ $= 11.7$

7.3 Review

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

$0.10 \times 3.0 = c_2 \times 4.0$

$c_2 = \frac{0.10 \times 3.0}{4.0} = 7.5 \times 10^{-2}\ \text{mol L}^{-1}$

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

$2.0 \times 10 = 0.50 \times V_2$

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

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

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3 $c_1V_1 = c_2V_2$, $c_1 = 0.600\,\text{mol L}^{-1}$, $V_1 = 20.0\,\text{mL}$, $V_2 = ?$, $c_2 = 0.100\,\text{mol L}^{-1}$

$0.600 \times 20.0 = 0.100 \times V_2$

$V_2 = \frac{0.600 \times 20.0}{0.100} = 120\,\text{mL}$

Final volume – initial volume = 120 – 20.0 = 100 mL so 100 mL of water needs to be added.

4 This increases the pH by one unit.

$[H_3O^+] = 10^{-\text{pH}} = 10^{-1.0} = 0.1\,\text{mol L}^{-1}$

$c_2 = \frac{0.1}{10} = 0.01\,\text{mol L}^{-1}$

new pH $= -\log_{10}[H_3O^+] = -\log_{10}(0.01) = 2.0$

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

$0.100 \times 20.0 = c_2 \times 50.0$

$c_2 = \frac{0.100 \times 20.0}{50.0} = 4.0 \times 10^{-2}\,\text{mol L}^{-1}$

NaOH dissociates completely to Na^+ and OH^-, $[NaOH] = [OH^-]$, so $[OH^-] = 0.0400\,\text{mol L}^{-1}$

$\text{pOH} = -\log_{10}[OH^-] = -\log_{10}(0.0400) = 1.400$

$\text{pH} = 14.0 - \text{pOH} = 14 - 1.400 = 12.600$

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

ii $[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.001} = 1 \times 10^{-11}\,\text{mol L}^{-1}$

iii $\text{pH} = -\log_{10}[H_3O^+] = -\log(0.001) = 3.0$

iv $\text{pOH} = 14 - \text{pH} = 14 - 3.0 = 11.0$

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

ii $[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.03} = 3 \times 10^{-13}\,\text{mol L}^{-1}$

iii $\text{pH} = -\log_{10}[H_3O^+] = -\log(0.03) = 1.5$

iv $\text{pOH} = 14 - \text{pH} = 14 - 1.5 = 12.5$

c **i** NaOH dissociates completely to Na^+ and OH^-, $[NaOH] = [OH^-]$, therefore $[OH^-] = 0.01\,\text{mol L}^{-1}$.

$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.01} = 1 \times 10^{-12}\,\text{mol L}^{-1}$

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

iii $\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(1 \times 10^{-12}) = 12.0$

iv $\text{pOH} = 14 - \text{pH} = 14 - 12.0 = 2.0$

d **i** $[H_3O^+] = 10^{-4.5} = 3 \times 10^{-5}\,\text{mol L}^{-1}$

ii $[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{3 \times 10^{-5}} = 3 \times 10^{-10}\,\text{mol L}^{-1}$

iii $\text{pH} = -\log_{10}[H_3O^+] = -\log(3 \times 10^{-5}) = 4.5$

iv $\text{pOH} = 14 - \text{pH} = 14 - 4.5 = 9.5$

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

$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.01} = 1 \times 10^{-12}\,\text{mol L}^{-1}$

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

iii $\text{pH} = -\log_{10}[H_3O^+] = -\log(1 \times 10^{-12}) = 12.0$

iv $\text{pOH} = 14 - \text{pH} = 14 - 12.0 = 2.0$

CHAPTER 7 **REVIEW**

1 $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$

2 $HClO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_3^-(aq)$

3 $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

4 $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$

5 $(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$

6 **a** $Ca(OH)_2(aq) \xrightarrow{H_2O(l)} Ca^{2+}(aq) + 2OH^-(aq)$

b As calcium hydroxide dissociates in water, it releases hydroxide ions, known for their strong basic properties.

7 At 25°C, $K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14}$

$\therefore [OH^-] = \frac{1.0\times10^{-14}}{[H_3O^+]}$

a 1×10^{-11} mol L^{-1}

b 10^{-9} mol L^{-1}

c 1.8×10^{-6} mol L^{-1}

d 2.9×10^{-3} mol L^{-1}

e 1.5×10^{-13} mol L^{-1}

f 4.5×10^{-2} mol L^{-1}

8 **a** $pOH = -\log_{10}[OH^-] = -\log_{10}[1 \times 10^{-11}] = 11.0$

b 9

c 5.74

d 2.54

e 12.82

f 1.35

9 **a** **i** $pH = -\log_{10}[H_3O^+]$

$$\begin{aligned}[H_3O^+] &= 10^{-pH} \\ &= 10^{-1} \\ &= 0.1 \text{ mol L}^{-1}\end{aligned}$$

ii At 25°C, $K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14}$

$\therefore [OH^-] = \frac{1.0\times10^{-14}}{[H_3O^+]} = \frac{1.0\times10^{-14}}{0.1} = 1 \times 10^{-13}$ mol L^{-1}

b **i** 10^{-3} mol L^{-1}

ii 10^{-11} mol L^{-1}

c **i** 10^{-7} mol L^{-1}

ii 10^{-7} mol L^{-1}

d **i** 2×10^{-12} mol L^{-1}

ii 5×10^{-3} mol L^{-1}

10 To determine $[H_3O^+]$ from pH, use:

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

minimum $[H_3O^+]$: $[H_3O^+] = 10^{-pH} = 10^{-7.45} = 3.5 \times 10^{-8}$ mol L^{-1}

maximum $[H_3O^+]$: $[H_3O^+] = 10^{-pH} = 10^{-7.35} = 4.5 \times 10^{-8}$ mol L^{-1}

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

pH = 3

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

pH = 5

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

∴ the difference is a factor of 100.

12 **a** $[H_3O^+] = 10^{-pH} = 10^{-3.0} = 0.001$ mol L^{-1}, $[OH^-] = \frac{1.0\times10^{-14}}{[H_3O^+]} = \frac{1.0\times10^{-14}}{0.001} = 1 \times 10^{-11}$ mol L^{-1}

b $[H_3O^+] = 1 \times 10^{-10}$ mol L^{-1}, $[OH^-] = 1 \times 10^{-4}$ mol L^{-1}

c $[H_3O^+] = 3 \times 10^{-9}$ mol L^{-1}, $[OH^-] = 3 \times 10^{-6}$ mol L^{-1}

d $[H_3O^+] = 2 \times 10^{-6}$ mol L^{-1}, $[OH^-] = 6 \times 10^{-9}$ mol L^{-1}

e $[H_3O^+] = 3 \times 10^{-10}$ mol L^{-1}, $[OH^-] = 4 \times 10^{-5}$ mol L^{-1}

f $[H_3O^+] = 3 \times 10^{-14}$ mol L^{-1}, $[OH^-] = 0.3$ mol L^{-1}

13 $[H_3O^+] = 10^{-pH} = 10^{-5.3} = 5 \times 10^{-6}$ mol L^{-1}

$[OH^-] = \frac{1.0\times10^{-14}}{[H_3O^+]} = \frac{1.0\times10^{-14}}{5\times10^{-6}} = 2 \times 10^{-9}$ mol L^{-1}

14 Remember to use $K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14}$ at 25°C and $pH = -\log_{10}[H_3O^+]$.

a pH = 2.0, $\therefore [H_3O^+] = 10^{-2.0}$ or 0.01 mol L^{-1}

b $n = c \times V = 0.01 \times 0.500 = 0.005$ mol

c pOH = 14.0 – pH = 14.0 – 2.0 = 12.0

15 These three questions have two steps.

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

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

a $c_2 = 0.025 \times \frac{10}{50} = 0.0050\ \text{mol L}^{-1}$

$\therefore [H_3O^+] = 0.0050\ \text{mol L}^{-1}$

$\text{pH} = -\log_{10}(0.0050) = 2.30$

$\text{pOH} = 14 - \text{pH} = 14 - 2.30 = 11.70$

b $c_2 = 0.0050 \times \frac{20}{500} = 2.0 \times 10^{-4}\ \text{mol L}^{-1}$

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

$[H_3O^+] = \frac{1.0\times10^{-14}}{[OH^-]} = \frac{1.0\times10^{-14}}{2.0\times10^{-4}} = 5.0 \times 10^{-11}\ \text{mol L}^{-1}$

$\text{pH} = -\log_{10}(5.0 \times 10^{-11}) = 10.30$

$\text{pOH} = 14 - \text{pH} = 14 - 10.30 = 3.70$

c $c_2 = 0.15 \times \frac{10}{1500} = 0.0010\ \text{mol L}^{-1}$

(1.5 L has been converted to mL to maintain identical units)

$\therefore [H_3O^+] = 0.0010\ \text{mol L}^{-1}$

$\therefore \text{pH} = -\log_{10}(0.0010) = 3.00$

$\text{pOH} = 14 - \text{pH} = 14 - 3.00 = 11.00$

16 $c_1V_1 = c_2V_2$, $c_1 = 18.0\ \text{mol L}^{-1}$, $V_1 = ?$, $c_2 = 2.00\ \text{mol L}^{-1}$, $V_2 = 1.00\ \text{L}$

$V_1 = \frac{2.00\times1.00}{18.0} = 0.111\ \text{L} = 111\ \text{mL}$

17 Initial pH = 2.00 $[H_3O^+] = 10^{-\text{pH}} = 10^{-2.00} = 0.010\ \text{mol L}^{-1}$

Final pH = 4.00 $[H_3O^+] = 10^{-\text{pH}} = 10^{-4.00} = 1.0 \times 10^{-4}\ \text{mol L}^{-1}$

$c_1V_1 = c_2V_2$, $c_1 = 0.010\ \text{mol L}^{-1}$, $V_1 = 10.0\ \text{mL}$, $c_2 = 1.0 \times 10^{-4}\ \text{mol L}^{-1}$, $V_2 = ?$

$V_2 = \frac{0.010\times10.0}{1.0\times10^{-4}} = 1000\ \text{mL}$

Volume of water added = final volume − initial volume = 1000 − 10.0 = 990 mL

18 $\text{pH}_{\text{initial}} = -\log_{10}[H_3O^+] = -\log_{10}(0.10) = 1.00$

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

$c_2 = \frac{0.10\times40.0}{500} = 8.0 \times 10^{-3}\ \text{mol L}^{-1}$

$\text{pH}_{\text{final}} = -\log_{10}(8.0 \times 10^{-3}) = 2.10$

Therefore the pH will increase. Note: conversely, the pOH will decrease

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

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

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

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

Solution E: weaker acid, few freely moving charged particles—ethanoic acid

20 **a** $NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$

b Sodium hydroxide is regarded as a strong base because sodium hydroxide completely dissociates within water producing hydroxide ions which are a strong base.

c $n(NaOH) = c \times V = 12 \times 0.500 = 6.0\ \text{mol}$

$m(NaOH) = n \times M = 6.0 \times 40.00 = 2.4 \times 10^2\ \text{g}$

d **i** $c_1V_1 = c_2V_2$, $c_1 = 12\ \text{mol L}^{-1}$, $V_1 = ?$, $c_2 = 0.020\ \text{mol L}^{-1}$, $V_2 = 250.0\ \text{mL}$

$V_1 = \frac{c_2 \times V_2}{c_1} = \frac{0.020\times250.0}{12} = 0.42\ \text{mL}$

ii As it is such a small volume, it would be very difficult to measure out before the dilution. It would be better to dilute the stock solution by, say, a factor of ten, and then from that dilution, further dilute it in subsequent steps.

e As it is a strong base, it undergoes complete dissolution. This means that $[OH^-] = [NaOH] = 0.020\ \text{mol L}^{-1}$

$\text{pOH} = -\log_{10}[OH^-] = -\log_{10}(0.020) = 1.70$

f $\text{pH} = 14 - \text{pOH}$

$= 14 - 1.70$

$= 12.30$

$[H_3O^+] = 10^{-\text{pH}} = 10^{-12.30} = 5.0 \times 10^{-13}\ \text{mol L}^{-1}$

21 Add equal amounts of red cabbage indicator to two test tubes. Then add equal amounts of the strong or weak acid into each test tube. The stronger acid, which contains a higher hydronium ion concentration, could cause the colour of the red cabbage indicator to change to a greater extent than the weak acid.

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Chapter 8 Quantitative analysis

8.1 Calculations involving acids and bases

Worked example: Try yourself 8.1.1

A SOLUTION VOLUME–VOLUME CALCULATION

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

Thinking	Working
Write a balanced full equation for the reaction.	$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$
Calculate the amount, in mol, of the substance with known volume and concentration.	The volume and concentration of calcium hydroxide solution are given, so use $n = c \times V$ (Remember that volume must be expressed in litres.) $n(Ca(OH)_2) = c \times V$ $= 0.100 \times 0.0250$ $= 0.00250$ mol
Use the mole ratio from the equation to calculate the amount, in mol, of the required substance.	The balanced equation shows that 2 mol of hydrochloric acid reacts with 1 mol of calcium hydroxide. $\frac{n(HCl)}{n(Ca(OH)_2)} = \frac{2}{1}$ $n(HCl) = 2 \times n(Ca(OH)_2)$ $= 2 \times 0.00250$ $= 0.00500$ mol
Calculate the volume or concentration required.	The volume of HCl is found by rearranging and using $n = c \times V$. $V(HCl) = \frac{n}{c}$ $= \frac{0.00500}{0.500}$ $= 0.0100$ L $= 10.0$ mL So 10.0 mL of 0.500 mol L^{-1} HCl reacts completely with 25.0 mL of 0.100 mol L^{-1} $Ca(OH)_2$ solution.

Worked example: Try yourself 8.1.2

SOLUTION STOICHIOMETRY: A LIMITING REACTANT PROBLEM

30.0 mL of a 0.100 mol L^{-1} H_2SO_4 solution is mixed with 40.0 mL of a 0.200 mol L^{-1} KOH solution. The equation for the reaction that occurs is:

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

a Which reactant is the limiting reactant?

Thinking	Working
Calculate the number of moles of each of the reactants using $n = c \times V$.	$n(H_2SO_4) = 0.100 \times 0.0300$ $= 0.00300$ mol $n(KOH) = 0.200 \times 0.0400$ $= 0.00800$ mol
Use the coefficients of the equation to find the limiting reactant.	The equation shows that 1 mol of H_2SO_4 reacts with 2 mol of KOH. So H_2SO_4 is the limiting reactant (it will be completely consumed).

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b What mass of K_2SO_4 is produced by this reaction?	
Thinking	**Working**
Find the mole ratio of the unknown substance to the limiting reactant from the equation coefficients: $\frac{\text{coefficient of unknown}}{\text{coefficient of limiting reactant}}$	From the equation coefficients: $\frac{n(K_2SO_4)}{n(H_2SO_4)} = \frac{\text{coefficient of } K_2SO_4}{\text{coefficient of } H_2SO_4} = \frac{1}{1} = 1$
Calculate the number of moles of the unknown substance using the limiting reactant: $n(\text{unknown}) = n(\text{limiting reactant}) \times \text{mole ratio}$	$n(K_2SO_4) = n(H_2SO_4) \times 1$ $= 0.00300 \times 1$ $= 0.00300\,\text{mol}$
Calculate the mass of the unknown substance using: $m(\text{limiting reactant}) = n(\text{unknown}) \times \text{molar mass}$	Molar mass of $K_2SO_4 = 174.27\,\text{g mol}^{-1}$ $m(K_2SO_4) = 0.00300 \times 174.27$ $= 0.523\,\text{g}$

8.1 Review

1 **a** $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

b $n(KOH) = c \times V = 0.300 \times 0.0100 = 0.00300\,\text{mol}$

$\frac{n(H_2SO_4)}{n(KOH)} = \frac{1}{2} = 0.5$

$n(H_2SO_4) = 0.5 \times n(KOH) = 0.5 \times 0.00300 = 0.00150\,\text{mol}$

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

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

b $n(Ca(OH)_2) = c \times V = 0.100 \times 0.010 = 0.00100\,\text{mol}$

$n(HNO_3) = 2 \times n(Ca(OH)_2) = 2 \times 0.00100 = 0.00200\,\text{mol}$

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

3 **a** $n(H_2SO_4) = c \times V = 0.200 \times 0.0100 = 0.00200\,\text{mol}$

b $n(Na_2CO_3) = c \times V = 0.100 \times 0.0160 = 0.00160\,\text{mol}$

c According to the reaction, $n(H_2SO_4) = n(Na_2CO_3)$, therefore Na_2CO_3 is the limiting reactant and H_2SO_4 is in excess.

d $n(H_2SO_4)$ reacts $= n(Na_2CO_3) = 0.00160\,\text{mol}$

$n(H_2SO_4)$ excess $= n(H_2SO_4)$ total $- n(H_2SO_4)$ reacts $= 0.00200 - 0.00160 = 0.00040\,\text{mol}$ in excess

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

b $n(KOH) = c \times V = 0.09927 \times 0.02000 = 0.001985\,\text{mol}$

c $n(HNO_3) = n(KOH) = 0.001985\,\text{mol}$

d $c(HNO_3) = \frac{n}{V} = \frac{0.001985}{0.01826} = 0.1087\,\text{mol L}^{-1}$

8.2 Volumetric analysis

8.2 Review

1 **a** A and D. Potassium hydroxide is a base so it must be titrated against solution of an acidic primary standard such as potassium hydrogen phthalate or hydrated oxalic acid.

b B and C. Hydrochloric acid is an acid is so it must be titrated against solution of a basic primary standard such as anhydrous sodium carbonate or sodium borate.

2 $n = \frac{m}{M} = \frac{13.25}{105.99} = 0.1250\,\text{mol}$

$c = \frac{n}{V} = \frac{0.01250}{0.05000} = 0.2500\,\text{mol L}^{-1}$

3 $n = c \times V = 0.200 \times 0.1000 = 0.02000\,\text{mol}$

$m = n \times M = 0.0200 \times 204.22 = 4.08\,\text{g}$

4 Trials 2, 3 and 5 provide concordant titres.

The average titre is $\frac{(25.46 + 25.38 + 25.42)}{3} = 25.42\,\text{mL}$

5 **a** A standard solution is a solution of accurately known concentration. A primary standard is a substance used to make a standard solution. It should be readily obtained in a pure form, have a known formula and can be stored without deteriorating or reacting with the atmosphere. It should also be cheap and have a high molar mass.

b The equivalence point in a titration occurs when the reactants have reacted in the mole ratio shown by the reaction equation. The end point occurs when the indicator changes colour.

c A burette is a piece of equipment capable of accurately delivering a range of volumes of a liquid (generally up to 50.00 mL). Pipettes usually deliver only a fixed volume of liquid (e.g. 20.00 mL).

d An aliquot is the volume of liquid delivered from a pipette. A titre is delivered by a burette.

8.3 Titration and conductivity curves

8.3 Review

1 **a** strong base added to a strong acid

b strong base added to a weak acid (a weak base is formed, which elevates the equivalence point to above pH 7)

c weak base added to a strong acid (a weak acid is formed, which lowers the equivalence point to below pH 7)

d weak base added to a weak acid

2 The strong acid will have the lowest intercept with the pH axis. The intercept shown on graphs **a** and **c** is at approximately pH = 1 which represents a monoprotic acid concentration = 0.1 mol L^{-1}.

3 7

4 Graph **c** represents the titration of a strong acid against a weak base. At the equivalence point the solution contains the conjugate base of the strong acid and the conjugate acid of the weak base. The conjugate acid of the weak base dissociates to form hydronium ions, thus lowering the pH.

5 The titration curve of a weak acid and a weak base is represented by graph **d**. There is no rapid change in pH at the equivalence point, making it difficult to accurately determine its exact location on the graph.

6 **a** phenolphthalein, methyl orange or bromothymol blue

b phenolphthalein, bromothymol blue

c methyl orange

7 Graph **a** is the pH curve of the titration of a strong base with a weak acid and indicates that the equivalence point occurred when a titre of 20.0 mL of acid has been added. A weak acid was added which reacts to produce a weak base. The weak base dissociates in water causing the pH of the equivalence point to be above 7.

Graph **b** is the conductivity curve for the titration of a strong acid and a strong base (e.g. NaOH) and indicates that a titre of 20.0 mL of base was required to reach the equivalence point. The conductivity initially decreases due to the replacement of H^+ ions with Na^+ ions. Conductivity drops to a minimum when all the H^+ ions have just reacted. Conductivity increases as excess NaOH is added to the mixture.

8 B. The conductivity decreases as H^+ ions react with OH^- ions and are replaced by NH_4^+ ions. Conductivity drops to a minimum when all the H^+ ions have just reacted. Conductivity remains constant as excess NH_3 is added to the mixture (NH_3 is a weak base so does not dissociate to a great extent so does not add more ions to the mixture).

9 **a** In a volumetric titration, a change in the colour of an indicator is used to determine the end point. In a conductimetric titration, the equivalence point is determined from the change in conductivity shown on a conductivity graph.

b Any two of the following situations:

- the analysis of a coloured solution where the colour change of an indicator cannot easily be detected.
- a turbid or cloudy solution where the colour of the indicator is masked.
- a very dilute solution.

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8.4 Calculations in volumetric analysis

Worked example: Try yourself 8.4.1

CALCULATING CONCENTRATION USING A SIMPLE TITRATION

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

A 10.00 mL aliquot of $Ba(OH)_2$ solution was titrated with a 0.125 mol L^{-1} solution of HCl. Titres of 17.23 mL, 17.28 mL and 17.21 mL of HCl were required to reach the end point. What is the concentration of the barium hydroxide solution?

Thinking	**Working**
Write a balanced chemical equation for the reaction.	An acid is reacting with a metal hydroxide, or base, so the products will be a salt and water. $2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$
Discard any titre that is not concordant (i.e. not within a 0.10 mL range), then determine the volume of the average titre.	All titres are concordant so none are discarded. average titre $= \frac{17.21+17.23+17.28}{3}$ $= 17.24$ mL
Calculate the amount, in mol, of the standard solution that was required to reach the end point.	$n(HCl) = c \times V$ $= 0.125 \times 0.01724$ $= 0.002155$ mol
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that would have reacted with the given amount, in mol, of the standard solution.	mole ratio $= \frac{n(Ba(OH)_2)}{n(HCl)} = \frac{1}{2} = 0.5$ $n(Ba(OH)_2) = 0.5 \times n(HCl)$ $= 0.5 \times 0.002155$ $= 0.001078$ mol
Determine the concentration of the unknown substance.	$c(Ba(OH)_2) = \frac{n}{V}$ $= \frac{0.001078}{0.01000}$ $= 0.108$ mol L^{-1}

Worked example: Try yourself 8.4.2

TITRATION THAT INVOLVES DILUTION

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

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

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Thinking	**Working**
Write a balanced chemical equation.	A dilute acid is reacting with a metal carbonate so the products will be a salt, water and carbon dioxide gas. $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
Using the concentration of the standard solution, calculate the amount, in mol, of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(Na_2CO_3) = c \times V$ $= 0.2406 \times 0.02000$ $= 0.004812$ mol

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Use the mole ratio in the equation to calculate the amount, in mol, of the diluted unknown solution that reacted in the titration.	$\frac{n(\text{HCl})}{n(\text{Na}_2(\text{CO})_3)}=\frac{2}{1}=2$ $n(\text{HCl}) = 2 \times n(\text{Na}_2\text{CO}_3)$ $= 2 \times 0.004812$ $= 0.009624\ \text{mol}$
Calculate the concentration of diluted unknown solution reacting in the titration.	$V(\text{diluted HCl}) = 0.01868\ \text{L}$ $c(\text{HCl}) = \frac{n}{V}$ $= \frac{0.009624}{0.01868}$ $= 0.5152\ \text{mol L}^{-1}$
Multiply by the dilution factor to determine the concentration of undiluted concrete cleaner.	dilution factor $= \frac{250.0}{10.00} = 25.00$ So undiluted $c(\text{HCl})$ = diluted $c(\text{HCl}) \times 25.00$ $= 0.5152 \times 25.00$ $= 12.88\ \text{mol L}^{-1}$

8.4 Review

1 $n(\text{KOH}) = c \times V = 1.34 \times 0.02298 = 0.03079\ \text{mol}$

$\frac{n(\text{H}_2\text{SO}_4)}{n(\text{KOH})}=\frac{1}{2}=0.5$

so $n(\text{H}_2\text{SO}_4) = n(\text{KOH}) \times 0.5 = 0.01540\ \text{mol}$

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

2 **a** $\text{CH}_3\text{COOH(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCH}_3\text{COO(aq)} + \text{H}_2\text{O(l)}$

b $n(\text{NaOH}) = c \times V = 0.995 \times 0.02156 = 0.02145\ \text{mol}$

c $n(\text{CH}_3\text{COOH}) = n(\text{NaOH}) = 0.02145\ \text{mol}$

d $c(\text{CH}_3\text{COOH}) = \frac{n}{V} = \frac{0.02145}{0.02500} = 0.858\ \text{mol L}^{-1}$

3 $n(\text{Na}_2\text{CO}_3) = c \times V = 0.5000 \times 0.02500 = 0.01250\ \text{mol}$

$n(\text{HCl}) = 2 \times n(\text{Na}_2\text{CO}_3)$

$= 2 \times 0.01250$

$= 0.02500\ \text{mol}$

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

dilution factor $= \frac{250.0}{25.00}=10.00$

concentration of undiluted acid $= 1.045 \times 10.00 = 10.45\ \text{mol L}^{-1}$

4 **a** $\text{HNO}_3\text{(aq)} + \text{KOH(aq)} \rightarrow \text{KNO}_3\text{(aq)} + \text{H}_2\text{O(l)}$

b $n(\text{KOH}) = c \times V = 0.995 \times 0.02156 = 0.02145\ \text{mol}$

c $n(\text{HNO}_3) = n(\text{KOH}) = 0.02145\ \text{mol}$

d $c(\text{HNO}_3) = \frac{n}{V} = \frac{0.021\,45}{0.02500} = 0.858\ \text{mol L}^{-1}$

e $c(\text{g L}^{-1}) = c(\text{M}) \times M = 0.858 \times 63.02 = 54.1\ \text{g L}^{-1}$

5 $n(\text{H}_2\text{SO}_4) = c \times V = 0.386 \times 0.02000 = 0.007720\ \text{mol}$

$n(\text{CH}_3\text{CH}_2\text{NH}_2) = 2 \times n(\text{H}_2\text{SO}_4) = 2 \times 0.007720 = 0.01544\ \text{mol}$

$c(\text{CH}_3\text{CH}_2\text{NH}_2) = \frac{n}{V} = \frac{0.01544}{0.02102} = 0.735\ \text{mol L}^{-1}$

6 The 22.06 mL titre is not included in the calculation because it is not concordant.

average titre $=\frac{21.06+21.00+21.08}{3}$

$=21.05$ mL

$n(\text{NaOH}) = c \times V = 1.25 \times 0.02105 = 0.02631\ \text{mol}$

Reaction equation: $\text{C}_2\text{H}_2\text{O}_4\text{(aq)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{C}_2\text{O}_4\text{(aq)} + 2\text{H}_2\text{O(l)}$

$n(\text{C}_2\text{H}_2\text{O}_4) = 0.5 \times n(\text{NaOH}) = 0.5 \times 0.02631 = 0.01316\ \text{mol}$

$c(\text{C}_2\text{H}_2\text{O}_4) = \frac{n}{V}=\frac{0.01316}{0.02000} = 0.658\ \text{mol L}^{-1}$

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8.5 Acid dissociation constants

Worked example: Try yourself 8.5.1

CALCULATING THE pK_a, pH AND % DISSOCIATION OF A SOLUTION OF A WEAK ACID

The K_a for hypochlorous acid (HOCl) is 3.0×10^{-8}. Given a 0.10 mol L^{-1} HOCl solution:

a calculate the pK_a

Thinking	**Working**
Write the expression for the relationship between K_a and pK_a.	$pK_a = -\log_{10}(K_a)$
Substitute the value of K_a into the formula and calculate pK_a.	$pK_a = -\log_{10}(3.0 \times 10^{-8})$ $= 7.52$

b calculate the pH

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Write the equation for the dissociation reaction.</td><td>$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$</td></tr>
<tr><td>Construct a reaction table, using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled I (initial), C (change) and E (equilibrium):
<table>
<tr><th></th><th colspan="2">Reactants $\rightleftharpoons$ Products</th></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table></td><td>Initially, the weak acid has not dissociated, so its concentration is 0.10 mol L^{-1}. The initial concentrations of both OCl^- and H_3O^+ are zero. As the acid dissociates, the OCl^- and H_3O^+ ions are produced in a 1:1 ratio. This can be represented by <i>s</i>.
<table>
<tr><th></th><th colspan="3">$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$</th></tr>
<tr><td>I</td><td>0.10</td><td>0</td><td>0</td></tr>
<tr><td>C</td><td>$-s$</td><td>$+s$</td><td>$+s$</td></tr>
<tr><td>E</td><td>$0.10 - s$</td><td>s</td><td>s</td></tr>
</table></td></tr>
<tr><td>Write an expression for K_a and substitute <i>s</i> for the equilibrium concentrations.</td><td>$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]}$
$3.0 \times 10^{-8} = \frac{s^2}{0.10 - s}$</td></tr>
<tr><td>What assumption can be made about the concentration of the weak undissociated acid at equilibrium?</td><td>Hypochlorus acid is a weak acid with a very small K_a, so it will only dissociate to a very small extent so the concentration of hypochlorus acid at equilibrium is approximately the same as the initial concentration of hypochlorus acid.
$0.10 - s \approx 0.10$</td></tr>
<tr><td>Rewrite the expression for K_a, taking into account any assumptions made.</td><td>$3.0 \times 10^{-8} = \frac{s^2}{0.10}$</td></tr>
<tr><td>Solve for $s = [H_3O^+]$.</td><td>$s^2 = 3.0 \times 10^{-8} \times 0.10$
$s = [H_3O^+]$
$= \sqrt{3.0 \times 10^{-8} \times 0.10}$
$= 5.5 \times 10^{-5}$ mol L^{-1}</td></tr>
<tr><td>Calculate the pH using:
$pH = -\log_{10}[H_3O^+]$</td><td>$pH = -\log_{10}[5.5 \times 10^{-5}]$
$= 4.26$</td></tr>
</table>

c calculate the percentage dissociation.	
Thinking	**Working**
Write the expression for % dissociation of a weak acid.	$\% \text{ dissociation} = \frac{[\text{OCl}^-]}{[\text{HOCl}]} \times 100$
Determine the concentration of the conjugate base of the weak acid.	From the dissociation equation: $[\text{OCl}^-] = [\text{H}_3\text{O}^+]$ $= 5.5 \times 10^{-5} \text{ mol L}^{-1}$
Substitute the values for the concentration of the weak acid and its conjugate base into the formula and calculate the % dissociation.	$\% \text{ dissociation} = \frac{[\text{OCl}^-]}{[\text{HOCl}]} \times 100$ $= \frac{5.5 \times 10^{-5}}{0.10} \times 100$ $= 0.055\%$

Worked example: Try yourself 8.5.2

CALCULATING VALUE OF K_a FROM THE pH OF A SOLUTION OF A WEAK ACID

Calculate the K_a value for a 0.05 mol L^{-1} solution of propanoic acid (CH_3CH_2COOH) which has a pH of 3.09.

<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>Write the equation for the dissociation reaction.</td><td>$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$</td></tr>
<tr><td>Determine $[H_3O^+]$ at equilibrium using the formula:
$[H_3O^+] = 10^{-pH}$</td><td>$[H_3O^+] = 10^{-pH}$
$= 10^{-3.09}$
$= 0.00081 \text{ mol L}^{-1}$</td></tr>
<tr><td>Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled I (initial), C (change) and E (equilibrium):
<table>
<tr><th></th><th colspan="2">Reactants ⇌ Products</th></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table></td><td>Initially, the weak acid has not dissociated, so its concentration is 0.05 mol L^{-1}. The initial concentrations of both $CH_3CH_2COO^-$ and H_3O^+ are zero. As the acid dissociates, the $CH_3CH_2COO^-$ and H_3O^+ ions are produced in a 1:1 ratio. This can be represented by *s*.
<table>
<tr><th></th><th colspan="3">$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$</th></tr>
<tr><td>I</td><td>0.05</td><td>0</td><td>0</td></tr>
<tr><td>C</td><td>$-s$</td><td>$+s$</td><td>$+s$</td></tr>
<tr><td>E</td><td>$0.05 - s$</td><td>s</td><td>s</td></tr>
</table></td></tr>
<tr><td>Using the coefficients from the equation, calculate the concentration of all species at equilibrium.</td><td>Initially no H_3O^+ was present. Since 0.00081 mol L^{-1} is present at equilibrium:
$s = 0.00081 \text{ mol L}^{-1}$
So the table becomes:
<table>
<tr><th></th><th colspan="3">$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$</th></tr>
<tr><td>I</td><td>0.05</td><td>0</td><td>0</td></tr>
<tr><td>C</td><td>−0.00081</td><td>+0.00081</td><td>+0.00081</td></tr>
<tr><td>E</td><td>0.05 − 0.00081 = 0.04919</td><td>0.00081</td><td>0.00081</td></tr>
</table></td></tr>
<tr><td>Write the expression for K_a and substitute the equilibrium concentrations.
Calculate the K_a value.</td><td>$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$
$= \frac{0.00081^2}{0.04919}$
$= 1.3 \times 10^{-5}$</td></tr>
</table>

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8.5 Review

1 **a** $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$K_a = \frac{[NH_3]\ H_3O^+]}{[NH_4^+]}$

b $HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$

$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$

c $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

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

2 A. The reaction for the dissociation of H_3PO_4 has the largest K_a.

3

Acid	**Formula**	**K_a**	**pK_a**
nitrous acid	HNO_2	7.1×10^{-4}	3.15
methanoic acid	HCOOH	1.8×10^{-4}	3.74
hydrogen cyanide	HCN	6.2×10^{-10}	9.21
hypochlorous acid	HOCl	3.0×10^{-8}	7.52

4 **a** Step 1. Write the equation for the dissociation of $CH_2ClCOOH$.

$CH_2ClCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_2ClCOO^-(aq)$

Step 2. Write the K_a expression.

$K_a = \frac{[CH_2ClCOO^-][H_3O^+]}{[CH_2ClCOOH]}$

Step 3. Because $CH_2ClCOOH$ is a weak acid, assume that the extent of dissociation is very small, so $[CH_2ClCOOH]$ is the same as it was initially.

$[CH_2ClCOOH] = 1.0\ mol\ L^{-1}$

Step 4. From the equation, for every mole of H_3O^+ formed there is 1 mol CH_2ClCOO^- formed.

$[H_3O^+] = [CH_2ClCOO^-]$

Step 5. Substitute into the K_a expression and calculate $[H_3O^+]$

$K_a = 1.3 \times 10^{-3} = \frac{[H_3O^+]^2}{1.0}$

$[H_3O^+]^2 = 1.3 \times 10^{-3}$

$[H_3O^+] = \sqrt{1.3 \times 10^{-3}}$

$= 0.036\ mol\ L^{-1}$

Step 6. Calculate the pH.

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

$= -\log_{10}(0.036)$

$= 1.44$

b $\%\ dissociation = \frac{[CH_2ClCOO^-]}{[CH_2ClCOOH]} \times 100$

$= \frac{0.036}{1.0} \times 100$

$= 3.6\%$

5 Step 1. Write the expression for K_a.

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

Step 2. This is a weak monoprotic acid, so for every 1 mol of H_3O^+ ions formed there is 1 mol CH_3COO^- formed. Calculate $[H_3O^+]$.

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

$= 10^{-3.0}\ mol\ L^{-1}$

$= 1 \times 10^{-3}\ mol\ L^{-1} = [CH_3COO^-]$

Step 3. Substitute into the K_a expression to calculate $[CH_3COOH]$.

$$[CH_3COOH] = \frac{[H_3O^+]\, CH_3COO^-]}{K_a}$$
$$= \frac{(1 \times 10^{-3})\, 1 \times 10^{-3})}{1.74 \times 10^{-5}}$$
$$= 0.06 \text{ mol L}^{-1}$$

6 Hydrofluoric acid dissociates in water according to the equation:

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

Converting pK_a to K_a:

$K_a = 10^{-pK_a} = 10^{-3.17} = 6.8 \times 10^{-4}$

The equilibrium expression for the dissociation of hydrofluoric acid is:

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = 6.8 \times 10^{-4}$$

From the equation $[H_3O^+] = [F^-]$. If the concentration of HF decreases by $s \text{ mol L}^{-1}$ as equilibrium is attained then at equilibrium $[H_3O^+] = [F^-] = s \text{ mol L}^{-1}$. The equilibrium concentration of HF is $0.5 - s$.

The change in concentration before and after equilibrium is established can be summarised in the following ICE table.

	$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$		
I	0.5	0	0
C	$-s$	$+s$	$+s$
E	$0.5 - s$	s	s

Substituting equilibrium concentrations into the equilibrium expression gives

$$\frac{s^2}{0.5 - s} = 6.8 \times 10^{-4}$$

Since HF is a weak acid, as demonstrated by its pK_a value, it can be assumed that very few HF molecules dissociate and the HF concentration at equilibrium is unchanged, i.e. $0.5 - s \approx 0.5 \text{ mol L}^{-1}$. The above expression then simplifies to:

$$\frac{s^2}{0.5} = 6.8 \times 10^{-4}$$
$$s^2 = 6.8 \times 10^{-4} \times 0.5 = 3.4 \times 10^{-4}$$
$$s = \sqrt{3.4 \times 10^{-4}} = 1.8 \times 10^{-2}$$

So $[H_3O^+] = 1.8 \times 10^{-2} \text{ mol L}^{-1}$

$pH = -\log_{10}[H_3O^+] = 1.73$

$$\%\text{ dissociation} = \frac{[F^-]}{[HF]}$$
$$= \frac{1.8 \times 10^{-2}}{0.5} \times 100$$
$$= 4\%$$

7 **a** $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+]\, OH^-]}{[NH_3]}$$

b $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

c $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

8.6 Buffers

8.6 Review

1 D. An appropriate buffer made from a weak acid and its conjugate base will maintain the pH of the water within the desired range.

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

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

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

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3 **a** basic buffer

b basic buffer

c basic buffer

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

5 **a** The addition of a small amount of HCl to the ethanoic acid buffer system will disturb the equilibrium. As equilibrium is re-established, the added H_3O^+ from HCl reacts with CH_3COO^-. The position of the equilibrium shifts to the left. Because the buffer contains a relatively large amount of CH_3COO^-, most of the added H_3O^+ is consumed and there is a small change in the concentration of H_3O^+.

b When a small amount of OH^- is added to the buffer system, the OH^- reacts with CH_3COOH. The excess OH^- is consumed without any large change in the concentration of H_3O^+.

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

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

b When acid is added, the concentration of H_3O^+ increases and the equilibrium is disturbed. In accordance with Le Châtelier's principle, the position of equilibrium moves to the left to re-establish equilibrium

8 $H_6C_8O_7(aq) + H_2O(l) \rightleftharpoons H_5C_8O_7^-(aq) + H_3O^+(aq)$

CHAPTER 8 **REVIEW**

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

2 Molar mass of $H_2C_2O_4.2H_2O$ = 126.07 g mol^{-1}

$n = \frac{m}{M} = \frac{25.21}{126.07} = 0.19997\ \text{mol}$

$c = \frac{n}{V} = \frac{0.19997}{0.2500} = 0.7999\ \text{mol L}^{-1}$

3 $n = c \times V = 0.400 \times 0.500 = 0.200\ \text{mol}$

$m = n \times M = 0.200 \times 105.99 = 21.2\ \text{g}$

4 $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$

$n(HNO_3) = c \times V = 0.100 \times 0.0300 = 0.00300\ \text{mol}$

$n(HNO_3) = n(KOH) = 0.00300\ \text{mol}$

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

5 **a** $n(HCl) = c \times V = 1.00 \times 0.0200 = 0.0200\ \text{mol}$

b $n(K_2CO_3) = c \times V = 1.00 \times 0.0160 = 0.0160\ \text{mol}$

c $2HCl(aq) + K_2CO_3(aq) \rightarrow 2KCl(aq) + CO_2(g) + H_2O(l)$

$n(K_2CO_3\ \text{reacts}) = \frac{n(HCl)}{2} = \frac{0.0200}{2} = 0.0100$ mol, total $n(K_2CO_3)$ = 0.0160 mol

Therefore K_2CO_3 is in excess, so HCl is the limiting reactant.

d $n(K_2CO_3\ \text{total}) - n(K_2CO_3\ \text{reacts}) = 0.0160 - 0.0100 = 0.0060$ mol in excess

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

$n(HCl) = c \times V = 0.200 \times 0.02000 = 0.00400\ \text{mol}$

$n(HCl) = n(NaOH) = 0.00400\ \text{mol}$

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

7 **a** $n(LiOH) = c \times V = 2.00 \times 0.0150 = 0.0300\ \text{mol}$

$n(HNO_3) = c \times V = 0.400 \times 0.0250 = 0.0100\ \text{mol}$

According to the reaction equation, $n(LiOH) = n(HNO_3)$, therefore HNO_3 is the limiting reactant.

b $n(LiNO_3) = n(HNO_3) = 0.0100\ \text{mol}$

$M(LiNO_3) = 68.95\ \text{g mol}^{-1}$

$m(LiNO_3) = n \times M = 0.0100 \times 68.95 = 0.690\ \text{g}$

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8 **a** A burette delivers a precise variable volume of solution.

b A pipette delivers a precise set volume of solution.

c A standard flask is used to prepare a solution of known concentration.

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

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

b $c(K_2CO_3) = \frac{n}{V} = \frac{m}{M \times V} = \frac{1.227}{138.21 \times 0.2500}$

$= 0.03551\ mol\ L^{-1}$

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

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

$n(K_2CO_3) = c \times V = 0.03551 \times 0.02000 = 0.0007102\ mol$

$\therefore\ c(H_2SO_4) = \frac{n}{V} = \frac{0.0007102}{0.02256} = 0.03148\ mol\ L^{-1}$

11 **a** $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

b $c(Na_2CO_3) = \frac{n}{V} = \frac{m}{M \times V} = \frac{1.358}{105.99 \times 0.2500} = 0.05125\ mol\ L^{-1}$

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

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

$n(Na_2CO_3) = c \times V = 0.05125 \times 0.02000 = 0.001025\ mol$

$n(HCl) = 2 \times n(Na_2CO_3) = 2 \times 0.001025 = 0.002050\ mol$

$\therefore\ c(HCl) = \frac{n}{V} = \frac{0.002050}{0.02024} = 0.1013\ mol\ L^{-1}$

d Sulfuric acid is a diprotic acid so only half as much acid would be required to neutralise an equivalent amount of sodium carbonate. Since the two acids have the same concentration, half the volume of sulfuric acid is required.

12 $2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$

a $c(Na_2CO_3) = \frac{n}{V} = \frac{m}{M \times V} = \frac{1.104}{105.99 \times 0.2500}$

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

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

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

$n(Na_2CO_3) = c \times V = 0.04166 \times 0.02000 = 0.0008332\ mol$

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

$c(HNO_3) = \frac{n}{V} = \frac{0.001666}{0.02347} = 0.07100\ mol\ L^{-1}$

13 **a** $HOI(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OI^-(aq)$

b $K_a = \frac{[OI^-][H_3O^+]}{[HOI]}$

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

$= 10^{-5.80}$

$= 1.6 \times 10^{-6}\ mol\ L^{-1}$

d Step 1. Because HOI is a weak acid, we assume that the extent of dissociation is very small so [HOI] is the same as it was initially.

$[HOI] = 0.100\ mol\ L^{-1}$

Step 2. From the equation, for every mole of H_3O^+ formed there is 1 mol OI^- is formed.

$[OI^-] = [H_3O^+] = 1.6 \times 10^{-6}\ mol\ L^{-1}$

Step 3. Substitute these values in the expression for K_a in part b and calculate.

$K_a = \frac{[O]^-\ H_3O^+]}{[HOI]}$

$= \frac{(1.6 \times 10^{-6})\ 1.6 \times 10^{-6})}{0.100}$

$= 2.6 \times 10^{-11}$

14 Step 1. Calculate $[H_3O^+]$.

$[H_3O^+] = 10^{-pH}$
$= 10^{-2.40}$
$= 4.0 \times 10^{-3}\ mol\ L^{-1}$

Step 2. As this is a weak monoprotic acid, for every mole of H_3O^+ ions formed there is 1 mol $HCOO^-$ formed.

$[HCOO^-] = [H_3O^+] = 4 \times 10^{-3}\ mol\ L^{-1}$

Step 3. Because HCOOH is a weak acid, it can be assumed that the extent of dissociation is very small, so [HCOOH] is the same as it was initially.

$[HCOOH] = 0.10\ mol\ L^{-1}$

Step 4. Calculate K_a.

$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$
$$= \frac{(4.0\times10^{-3})\ 4.0\times10^{-3})}{0.10}$$
$$= 1.6 \times 10^{-4}\ mol\ L^{-1}$$

15 **a** Step 1. As the solution is a weak acid, the $[C_6H_5COOH]$ initially will be assumed to be the same as the concentration after hydrolysis, due to the very small extent of hydrolysis.

% hydrolysis = 1.4%

$$1.4 = \frac{C_6H_5COO^-}{[C_6H_5COOH\ ]} \times 100$$
$$= \frac{C_6H_5COO^-}{1.0} \times 100$$
$$[C_6H_5COO^-] = \frac{1.4\times1.0}{100}$$
$$= 1\ 4\times10^{-2}\ mol L^{-1}$$
$$= 0.014\ mol\ L^{-1}$$

Step 2. As this is a weak monoprotic acid, for every 1 mol of H_3O^+ ions formed there is 1 mol of $C_6H_5COO^-$ ions formed.

$[H_3O^+] = [C_6H_5COO^-] = 0.014\ mol\ L^{-1}$

Step 3. Write the expression for K_a.

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5OOH]}$$

Step 4. Calculate K_a.

$$K_a = \frac{(0.014)(0.014)}{1.0}$$
$$= 2.0 \times 10^{-4}\ mol\ L^{-1}$$

Step 5. Calculate pK_a.

$pK_a = -\log_{10}(K_a)$
$= -\log_{10}(2.0 \times 10^{-4})$
$= 3.70$

b Step 1. K_a will be the same for this solution. As this is a weak monoprotic acid, for every 1 mol of H_3O^+ ions formed there is 1 mol of $C_6H_5COO^-$ ions formed.

$[C_6H_5COOH^-] = [H_3O^+]$

$$K_a = 2.0 \times 10^{-4}$$
$$= \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5OOH]}$$
$$= \frac{[C_6H_5COO^-]^2}{[0.10]}$$
$$[C_6H_5COO^-]^2 = 2.0 \times 10^{-4} \times 0.10$$
$$[C_6H_5COO^-] = \sqrt{2.0 \times 10^{-5}}$$
$$= 4.4 \times 10^{-3}\ mol\ L^{-1}$$

Step 2. To determine $[C_6H_5COOH]$, make the assumption that the extent of dissociation is very small. Hence $[C_6H_5COOH]$ is approximately the same as it was initially.

$[C_6H_5COOH] = 0.10\ mol\ L^{-1}$

Step 3. Write the expression for % hydrolysis.

$$\% \text{ hydrolysis} = \frac{[C_6H_5COO^-]}{[C_6H_5OOH]} \times 100$$

Step 4. Calculate % hydrolysis.

$$\% \text{ hydrolysis} = \frac{4.4 \times 10^{-3}}{0.10} \times 100$$

$$= 4.4\%$$

16 An acidic buffer is made from a weak *acid* and its conjugate *base*, producing a solution of pH *less than* 7.

A basic buffer is made from a weak *base* and its conjugate *acid*, producing a solution of pH *greater than* 7.

17 $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$

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

$$= \frac{(8.4 \times 10^{-3})\ 8.4 \times 10^{-3})}{(9.8 \times 10^{-2})}$$

$$= 7.2 \times 10^{-4}$$

$pK_a = -\log_{10}(K_a) = -\log_{10}(7.2 \times 10^{-4}) = 3.14$

18 K_a of HCN $= 10^{-pK_a} = 10^{-9.21} = 6.2 \times 10^{-10}$

$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

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

$$= 6.2 \times 10^{-10}$$

The ICE table for this equilibrium system is where *s* represents the decrease in HCN concentration.

	$HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$		
I	0.10	0	0
C	$-s$	$+s$	$+s$
E	$0.10 - s$	s	s

Substituting into the equilibrium expression gives:

$$\frac{s^2}{0.10 - s} = 6.2 \times 10^{-10}$$

Since HNO_2 is a weak acid and only dissociates to a slight extent it can be assumed that $0.10 - s \approx 0.10$ and the above expression simplifies to

$$\frac{s^2}{0.10} = 6.2 \times 10^{-10}$$

$s^2 = 6.2 \times 10^{-10} \times 0.10 = 6.2 \times 10^{-11}$

$s = \sqrt{6.2 \times 10^{-11}} = 7.9 \times 10^{-6}$

The concentration of CN^- and H_3O^+ is 7.9×10^{-6} mol L^{-1}. The concentration of HCN is 0.10 – 0.0000079 = 0.0999 = 0.10 mol L^{-1} to 2 significant figures.

19 It is incorrect to assume that 0.10 mol L^{-1} solutions of HBr and HOBr have the same pH.

HBr dissociates according to the equation

$HBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Br^-(aq)$

$K_a = 1.0 \times 10^9$

The dissociation constant of HBr is very large indicating that HBr is a strong acid. It can be assumed that HBr is completely dissociated in water. So:

$[H_3O^+] = [HBr] = 0.10$ mol L^{-1}

$pH = -\log_{10}[H_3O^+] = -\log_{10}(0.10) = 1.0$

The pH of a 0.10 mol L^{-1} solution of hypobromic acid is 1.0

HOBr dissociates according to the equation

$HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OBr^-(aq)$

$K_a = 2.4 \times 10^{-9}$

The dissociation constant of HOCl is very small indicating that the HOCl is a weak acid and dissociates to a limited extent in water. The equilibrium expression for the dissociation reaction is

$$K_a = \frac{[OBr^-][H_3O^+]}{[HOBr]}$$

$$= 2.4 \times 10^{-9}$$

If the change in concentration be represented by s then the equibilbrium concentrations can be determined using the following ICE table.

	$HOBr(aq) + H_2O(l) \rightleftharpoons$	$OBr^-(aq) +$	$H_3O^+(aq)$
I	0.10	0	0
C	$-s$	$+s$	$+s$
E	$0.10 - s$	s	s

Substituting into the equilibrium expression gives:

$$\frac{s^2}{0.10 - s} = 2.4 \times 10^{-9}$$

Since hypobromous acid is a weak acid and dissociates to a very small, extent the concentration of hypobromous acid at equilibrium is approximately the same as its initial concentration.

So $0.10 - s \approx 0.10$ and the above expression simplifies to

$$\frac{s^2}{0.10} = 2.4 \times 10^{-9}$$

$$s^2 = 2.4 \times 10^{-10}$$

$$s = \sqrt{2.4 \times 10^{-10}} = 1.55 \times 10^{-5}$$

$[H_3O^+] = 1.55 \times 10^{-5}\ mol\ L^{-1}$

$pH = -\log_{10}[H_3O^+] = -\log_{10}(1.55 \times 10^{-5}) = 4.81$

The pH of $0.10\ mol\ L^{-1}$ solution of hypobromous acid is 4.81.

20 **a**

Base	**Formula**	K_b	pK_b
butanoate	$CH_3(CH_2)_2COO^-$	6.6×10^{-10}	9.18
fluoride	F^-	1.5×10^{-11}	10.83
chlorate	ClO_3^-	3.4×10^{-7}	6.47

b Chlorate (ClO_3^-) is the strongest base because it has the highest K_b value or the lowest pK_b value.

21 **a** Both solutions contain the same amount of acid since they have the same volume and concentration. The perchloric acid and hypochlorous acid solutions require the same amount, in mol, and consequently volume, of sodium hydroxide to reach the equivalence point.

b Perchloric acid has a large K_a indicating that it is a strong acid. At the equivalence point the solution contains Na^+ and ClO_4^- ions. Na^+ is neither acid nor basic, and ClO_4^- is a very weak conjugate base of a strong acid, so the pH at the equivalence point will be 7.

The small K_a value of hypochlorous acid indicates that it is a weak acid. The solution at the equivalence point contains ClO^- and Na^+ ions. ClO^- ions are the conjugate base of a weak acid and will react with water to form OH^- ions. Na^+ ions will not react with water.

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

The pH at the equivalence point will therefore be greater than 7.

22 Substance B contains ethanoate ion and its conjugate acid, ethanoic acid. This would make an effective buffer system that is able to counteract the effect of added acid or base. Substance A would not make a buffer because NaOH is a strong base. The conjugate acid of the hydroxide ion is water. Water is a very weak acid. This solution would only counteract the effect of added acid but not added base.

23 The addition of a small amount of HCl to the phosphate buffer system will disturb the equilibrium. As equilibrium is re-established, the added H_3O^+ reacts with *HPO_4^{2-}*. The position of the equilibrium in the equation given above shifts to the *left*. Since the buffer contains a relatively large amount of HPO_4^{2-}, most of the added *H_3O^+* is consumed and there is a *small* change in the concentration of H_3O^+.

When a small amount of base is added to the buffer system the OH^- reacts with *$H_2PO_4^-$*. The excess OH^- is consumed without any large change in the concentration of *H_3O^+*.

24 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. An increase in the pH of blood indicates a decrease in $[H_3O^+]$. The buffer equilibrium responds by shifting to the right to increase $[H_3O^+]$. Overall, $[H_2CO_3]$ decreases, $[HCO_3^-]$ increases, $[H_3O^+]$ slightly decreases.

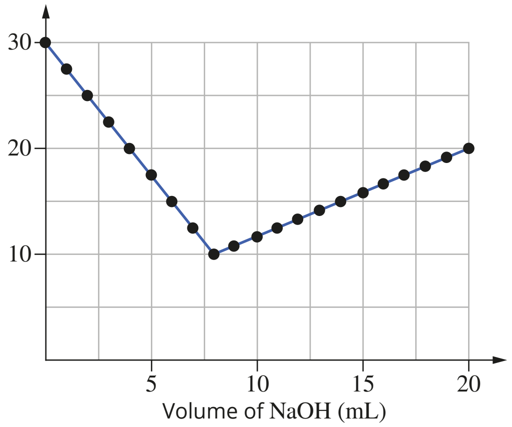
25 The buffer can be summarised as:

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

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

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

27 **a**



b The equivalence point occurs at the point where there is a change in the gradient of the conductivity graph, i.e. when 8 mL of NaOH has been added.

The equation for the neutralisation reaction is:

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

From the equation:

$$\begin{aligned} n(HCl) &= n(NaOH) \\ &= c \times V \\ &= 0.50 \times 0.008 \\ &= 4 \times 10^{-3}\ \text{mol} \end{aligned}$$

$$\begin{aligned} c(HCl) &= \frac{n}{V} = \frac{4 \times 10^{-3}}{0.010} \\ &= 0.4\ \text{mol L}^{-1} \end{aligned}$$

c The conductivity of a solution is determined by the:

- degree of ionisation or dissociation of the electrolyte
- identity of ions
- charge of the ions
- concentration of ions
- mobility of the ions
- temperature of the solution.

28 **a** The equation for the neutralisation reaction is:

$$HCOOH(aq) + NaOH(aq) \rightarrow NaHCOO(aq) + H_2O(l)$$

The equivalence point occurs when there is a sudden change in gradient in the graph, i.e at 25.0 mL of NaOH added. From the equation:

$$\begin{aligned} n(HCOOH) &= n(NaOH) \\ &= c \times V \\ &= 0.15 \times 0.0250 \\ &= 3.75 \times 10^{-3}\ \text{mol} \end{aligned}$$

$$\begin{aligned} [HCOOH] &= \frac{n}{V} = \frac{3.75 \times 10^{-3}}{0.010} \\ &= 0.375\ \text{mol L}^{-1} \end{aligned}$$

b As indicated by its pK_a, methanoic acid is a weak acid and is only dissociated to a slight extent. Consequently a solution of methanoic acid has a low conductivity. As NaOH is added the conductivity increases due to the presence of Na^+ ions and the formation of methanoate ions ($HCOO^-$) produced when OH^- ions reacts with the HCOOH molecules.

$$HCOOH(aq) + Na^+(aq) + OH^-(aq) \rightarrow HCOO^-(aq) + Na^+(aq) + H_2O(l)$$

The equivalence point occurs when 25.0 mL of NaOH solution has been added.

As additional NaOH solution is added the conductivity increases dramatically due to the increasing concentration of Na^+ ions and the highly mobile OH^- ions.

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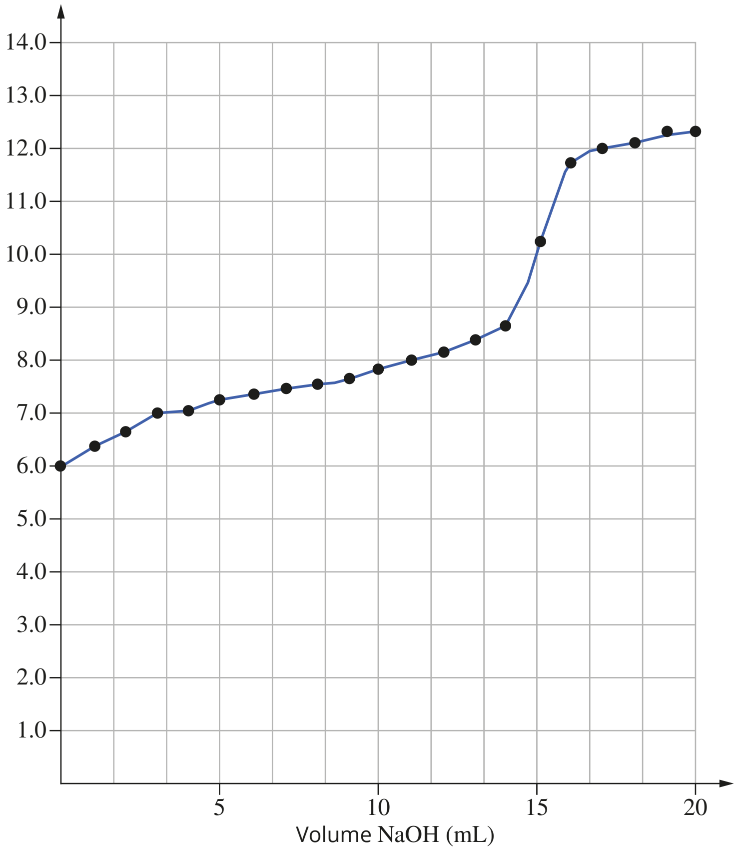
29 **a**



b The equivalence point is taken from the midpoint of the steep section of the graph. This occurs when the volume of NaOH is 15 mL.

$$HNO_2(aq) + NaOH(l) \rightarrow NaNO_2(aq) + H_2O(l)$$

$$\begin{aligned} n(HNO_2) &= n(NaOH) \\ &= c \times V \\ &= 0.25 \times 0.015 \\ &= 3.75 \times 10^{-3} \text{ mol} \\ [HNO_2] &= \frac{n}{V} = \frac{3.75 \times 10^{-3}}{0.020} \\ &= 0.19 \text{ mol L}^{-1} \end{aligned}$$

30 **a** a strong base added to a weak acid

b a strong acid added to a weak base

c strong base added to a strong acid

d weak base added to a strong acid

31 The equivalence point = 15.0 mL

$$\begin{aligned} n(CH_3COOH) = n(NaOH) &= c \times V \\ &= 0.10 \times 0.0200 \\ &= 0.0020 \text{ mol} \end{aligned}$$

$$\begin{aligned} c(CH_3COOH) &= \frac{n}{V} = \frac{0.0020}{0.0150} \\ &= 0.13 \text{ mol L}^{-1} \end{aligned}$$

32 **a** Anhydrous sodium carbonate meets the following criteria for a primary standard:

- is readily obtainable in a pure form
- has a known chemical formula
- is easy to store without deteriorating or reacting with the atmosphere
- has a high molar mass to minimise the effect of errors in weighing
- is inexpensive.

b Use an analytical balance to accurately weigh an amount of Na_2CO_3 in a clean, dry weighing bottle or beaker. Transfer the solid into a volumetric flask using a dry funnel. Wash any solid particles from the bottle or beaker using deionised water. Half fill the volumetric flask with deionised water, stopper and swirl the flask vigorously to dissolve the solid Na_2CO_3. Add deionsied water up to the calibration line on the neck of the volumetric flask. The bottom of the meniscus should be level with the calibration mark. Stopper and shake the flask to ensure an even concentration throughout.

c The final rinse of a burrette and a pipette must be with the acid or base they are to be filled with to avoid dilution of the solution. The volumetric flask and conical flask must only be rinsed with deionised water.

33 Lactic acid ($C_3H_6O_3$) is a monoprotic acid. It dissociates according to the following equation:

$C_3H_6O_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_3H_5O_3^-(aq)$

This causes a rise in $[H_3O^+]$ in the blood which affects the H_2CO_3/HCO_3^- buffer:

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

In accordance with Le Châtelier's principle, the rise in $[H_3O^+(aq)]$ causes the buffer to move to the left side of the equation and absorb the excess H_3O^+.

34 **a** With no removal of carbon dioxide the blood pH will fall as concentration of carbon dioxide increases.

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

The reaction between the basic HCO_3^- and hydronium ions reduces the concentration of H_3O^+.

35 **a** $H_5C_8O_7^-(aq)$

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

c Citric acid solution when mixed with approximately equimolar solution of its conjugate base (citrate) will form a buffer with a pH below 7.

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

If the hydronium ion concentration rises, the equilibrium is disturbed. In accordance with Le Châtelier's principle the position of equilibrium moves to the left to re-establish equilibrium. In a more alkaline environment, some of the citric acid molecules will be consumed. This minimises the impact on hydronium ion concentration, so pH is minimally affected.

36 This experiment is a crude form of volumetric analysis. The design of the experiment can be improved to produce a more accurate result by adding the vinegar in smaller portions, such as 1 mL, using an indicator to detect when all the bicarbonate of soda has been consumed, and using a different base to react with the vinegar.

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Chapter 9 Structure and nomenclature of organic compounds

9.1 Diversity of carbon compounds

9.1 Review

1 B. The C–F bond requires the most energy to break.

2 **a** A structural formula is a graphic representation of the molecular structure, showing how the atoms are arranged.

b A condensed structural formula shows the connections in the structure of a molecule without showing single bonds (but double and triple bonds may be shown).

c A saturated orgnaic compound contains all single bonds between carbon atoms.

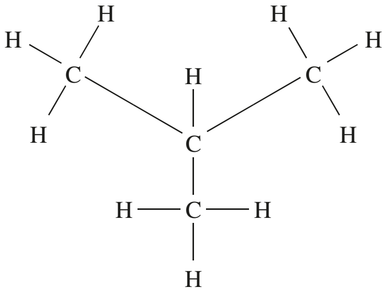
d An unsaturated organic compound contains one or more double or triple bonds between carbon atoms.

e Position isomers have the same molecular formula but have the functional group on a different carbon in the chain.

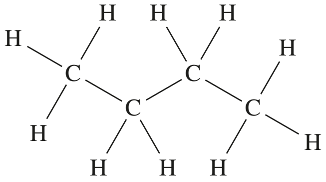
3 A and C are alkanes. Their molecular formulae follow the general formula for an alkane: C_nH_{2n+2}.

4 **a** 2-methylpropane and butane

b



2-methylpropane (C_4H_{10})



butane (C_4H_{10})

5 The carbon atoms in alkanes have four bonds to other atoms. According to the valence shell electron repulsion theory, the angle around between each bond is 109.5° and the geometry around each carbon is tetrahedral. This means that carbon–carbon bonds are much less than 180° and so the chain is zig-zag shaped. The carbon chains are commonly drawn as straight chains for clarity and convenience.

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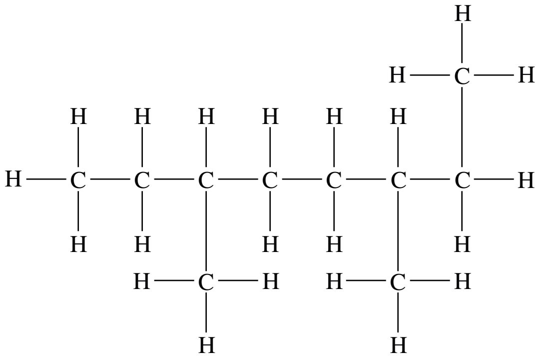
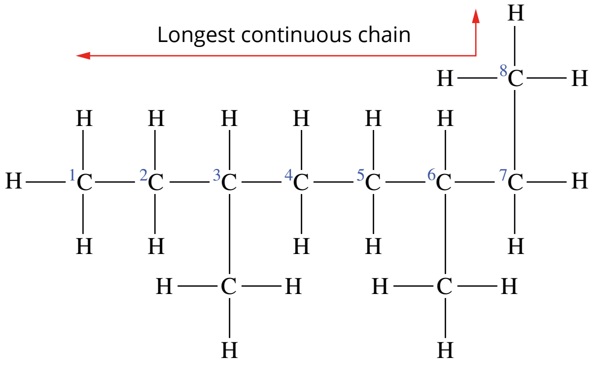
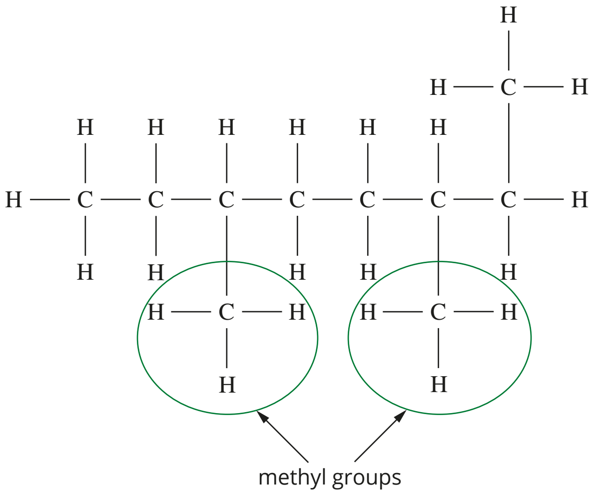
9.2 Hydrocarbons

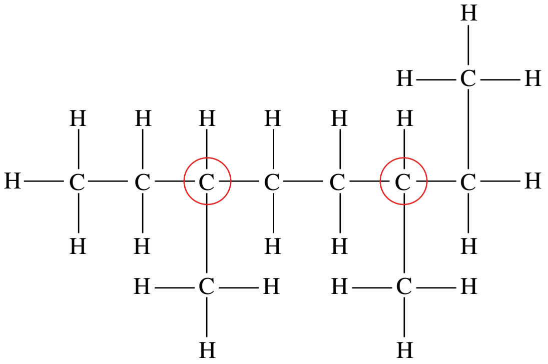
Worked example: Try yourself 9.2.1

NAMING AN ISOMER OF AN ALKANE WITH MORE THAN ONE ALKYL BRANCH

Write the systematic name of the molecule with the following structure.



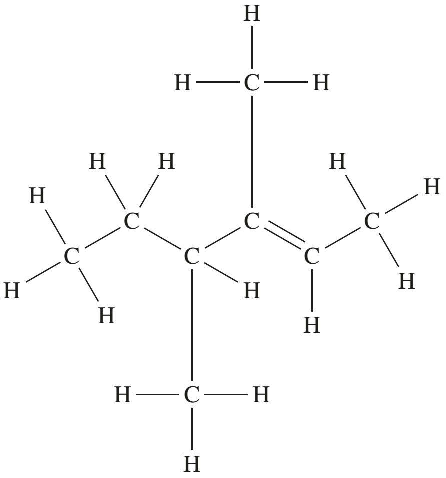
Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	 There are eight carbon atoms in the longest continuous chain, so the parent name is octane.
Identify any alkyl side chains by counting the number of carbon atoms in any branches.	 There is one carbon atom in each of the alkyl groups, so they are methyl groups.

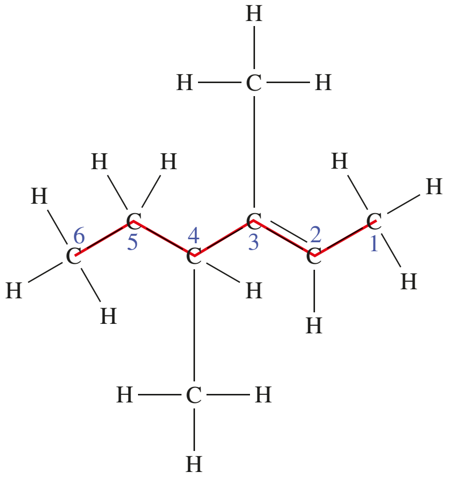
Identify the number(s) of the carbon atom(s) to which any alkyl group is attached. Count from the end that will give the lowest possible number to the carbons the groups are attached to.	 Each methyl group is attached to the third carbon from an end so it does not matter which end to count from. This will give numbers 3 and 6 to the methyl groups.
Assemble the name of the isomer, listing alkyl groups in alphabetic order with the number of the carbon atom before each group.	The name of the isomer is 3,6-dimethyloctane.

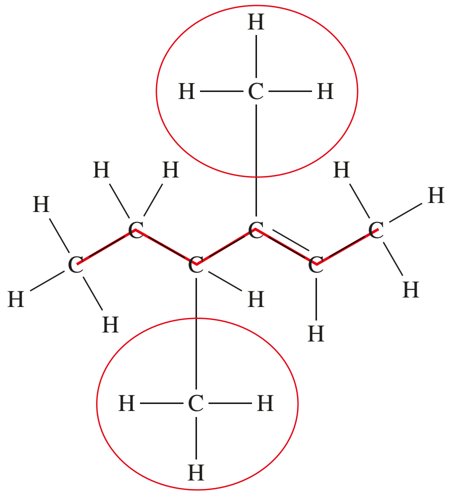
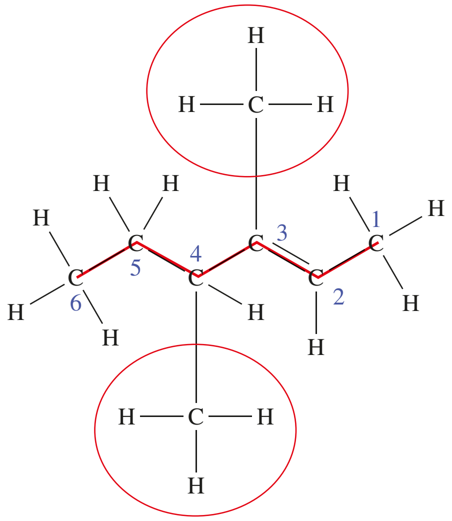
Worked example: Try yourself 9.2.2

NAMING AN ISOMER OF AN ALKENE

Write the systematic name of the following alkene.



Thinking	**Working**
Identify the parent name by counting the longest continuous chain of carbon atoms that contains the carbon-carbon double bond.	 There are six carbon atoms in the longest continuous chain, so the parent name is hexene.

Identify any alkyl side chains by counting the number of carbon atoms in any branches.	 There are two methyl groups.
Number the chain from the end closest to the double bond and identify the lowest numbered carbon atom in the double bond.	The lowest numbered carbon atom in the double bond is 2, so the parent name becomes hex-2-ene.
Number any alkyl side chains using the numbers of the carbon atoms to which they are attached.	 A methyl group is attached to the third carbon. A second methyl is attached to the fourth carbon.
Name the isomer.	The name of the isomer is 3,4-dimethylhex-2-ene.

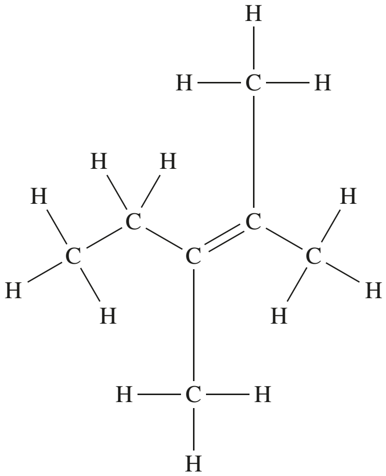
9.2 Review

1 **a** 3,3-dimethylhex-1-yne

b 2-methylbut-2-ene

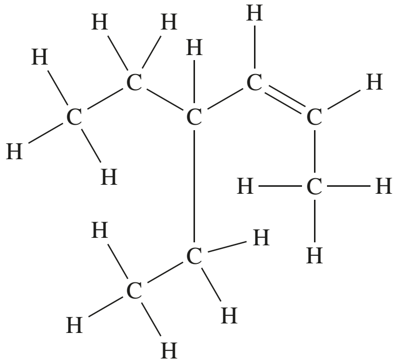
c 4-ethylhex-2-ene

2 **a**



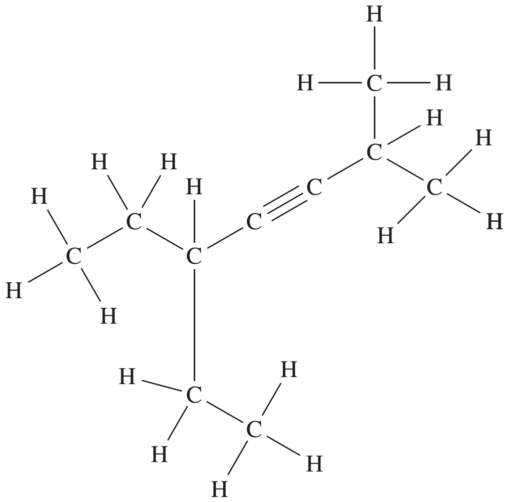
2,3-dimethylpent-2-ene

b



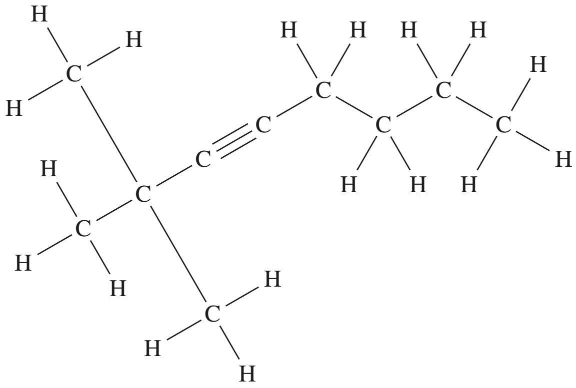
4-ethylhex-2-ene

c



5-ethyl-2-methylhept-3-yne

d



2,2-dimethyloct-3-yne

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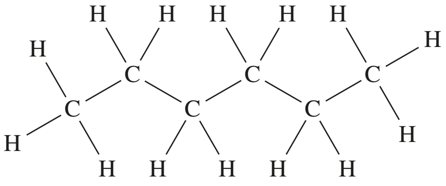
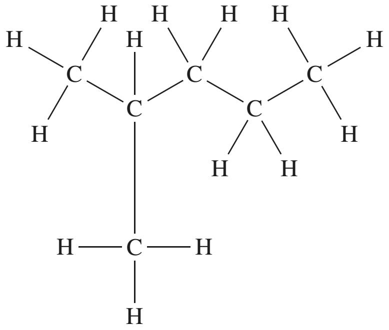
3 C and D

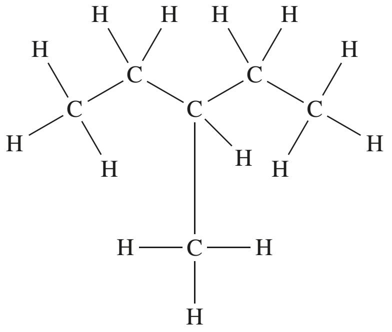
4 There are five possible isomers.



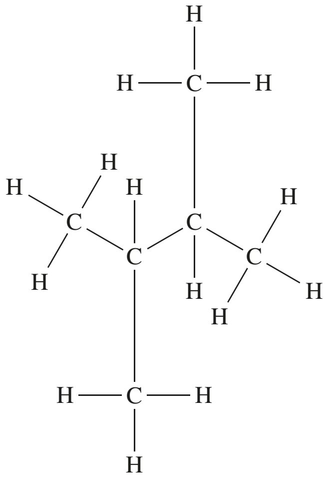
hexane (C_6H_{14})



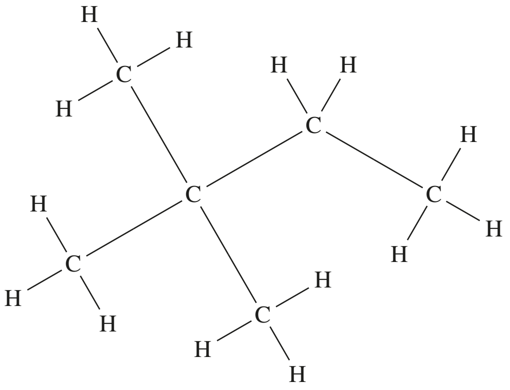
2-methylpentane



3-methylpentane



2,3-dimethylbutane



2,2-dimethylbutane

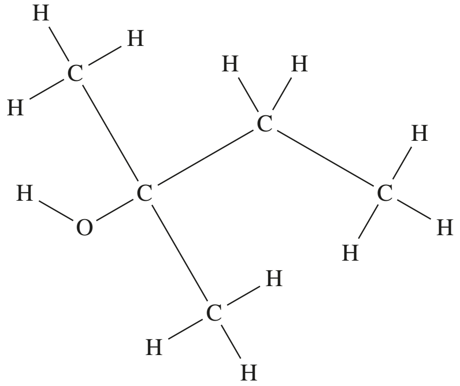
9.3 Functional groups—Part 1

9.3 Review

1 3-bromo-2-fluoropentane

2 $CH_3CHIFCHClCH_2CH_2CH_3$

3



2-methylbutan-2-ol

4
- **a** 1-bromopropane
- **b** 2-chloro-4-methylpentane
- **c** pentan-1-ol
- **d** octan-4-amine

5 Chloroethane has no isomers and so numbers are not needed. In propan-3-amine, the carbons should be numbered from the carbon atom closest to the amino functional group. Thus the amino group is located on the first carbon instead of the third carbon. Hence, the correct name is propan-1-amine.

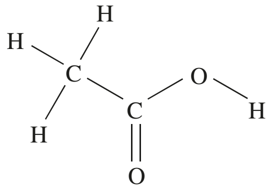
9.4 Functional groups—Part 2

9.4 Review

1
- **a** ketone
- **b** aldehyde
- **c** amide
- **d** ester

2
- **a** methyl methanoate
- **b** methanoic acid
- **c** propyl butanoate
- **d** methyl ethanoate
- **e** ethyl hexanoate

3



ethanoic acid

4
- **a** propanamide
- **b** butanamide
- **c** propanone
- **d** butanal

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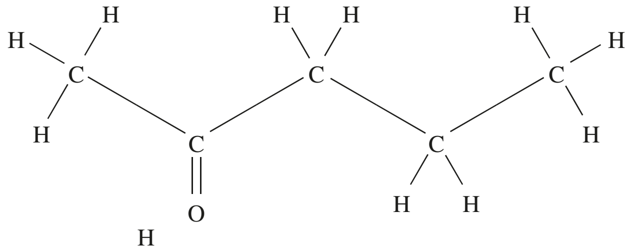
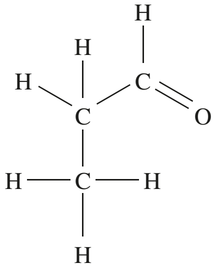
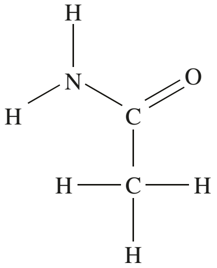
5 a



b



c

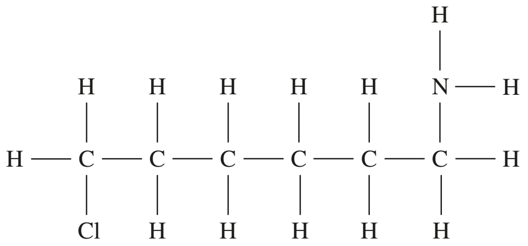


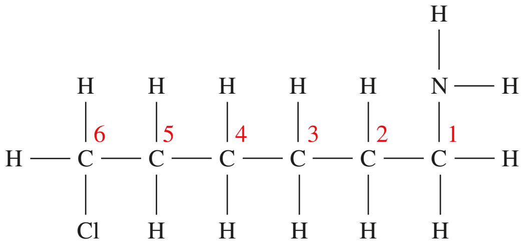
9.5 An overview of IUPAC nomenclature

Worked example: Try yourself 9.5.1

NAMING AN ORGANIC MOLECULE WITH TWO FUNCTIONAL GROUPS

Name this molecule according to IUPAC rules.

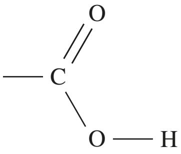


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	There are six carbons in the longest chain, so the parent name is hexane.
Identify the functional groups present.	The two functional groups present are chloro and amino.
Determine which functional group has the higher priority and determine the prefixes and suffixes to use.	The amino group has the higher priority, so the molecule will end in -amine. The chloro group has lower priority and so the prefix chloro- will be used.
Number the carbon chain, giving the highest priority group the lowest number possible.	
Determine the number of the carbon each functional group is attached to.	The $–NH_2$ is attached to carbon 1 and the –Cl is attached to carbon 6.
Use the functional group names and carbon numbers to construct the full name.	The name of the molecule is 6-chlorohexan-1-amine.

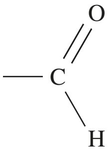
9.5 Review

1 **a** $-C{\equiv}C-$

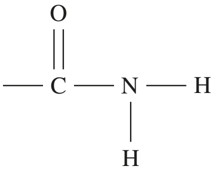
b



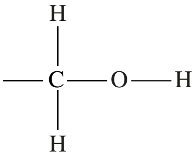
c



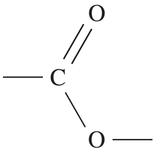
d



e



f



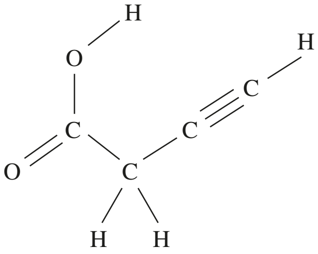
2 **a** 3-hydroxybutanoic acid

b 3-methylpentan-2-amine

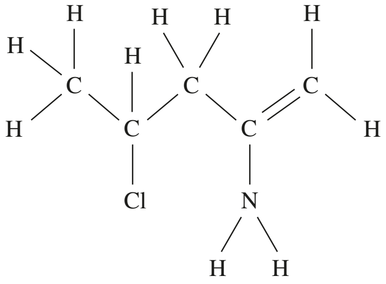
c 4-chloro-3-ethylpenan-2-ol

d 5-fluoropent-2-yne

3 **a**



b



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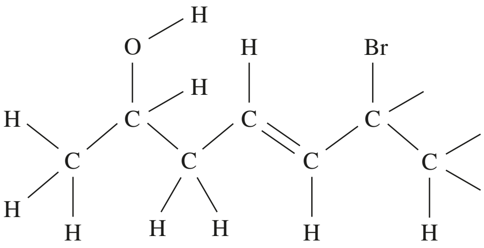

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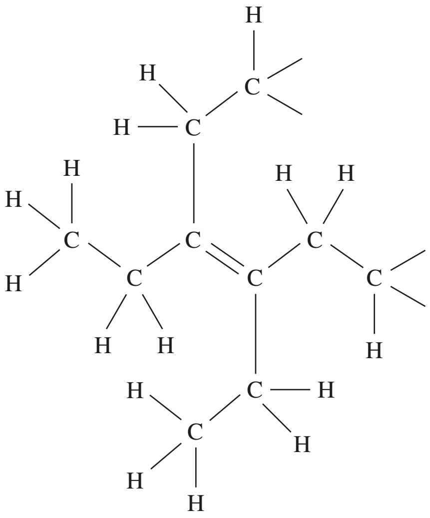


4 **a** **i** $CH_2{=}CHCH_2NH_2$

ii $CH_3CHClCH_2CH_2COOH$

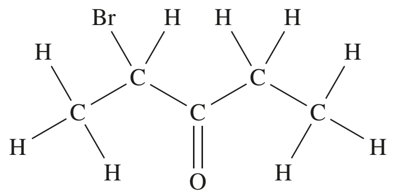
iii $CH_2{=}CHCHOHCH_2CH_3$

b **i** Amino groups have priority over alkenes, so -amine should go at the end of the name and have the lowest number. The correct name is prop-2-en-1-amine.

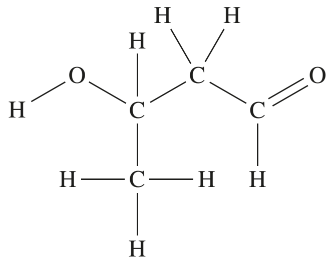
ii Carboxylic acid groups always go at the end of the chain and contain carbon 1. The correct name is 4-chloropentanoic acid.

iii The ethyl chain is a part of the longest carbon chain. Hydroxyl groups have priority over alkenes and so –ol should go at the end of the name. Numbering of the longest carbon chain should aim to minimise the number of the hydroxyl and alkene functional groups. Therefore the carbon-carbon double bond is at carbon number 1 and the hydroxyl group is at carbon number 3. The correct name is pent-1-en-3-ol.

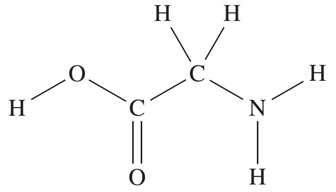
5 **a** **i**



ii



iii



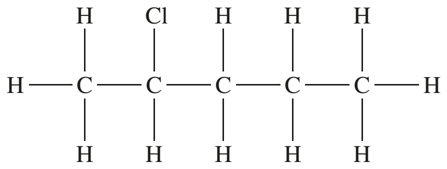
b **i** 2-chlorobutanamide

ii dichlorodifluoromethane

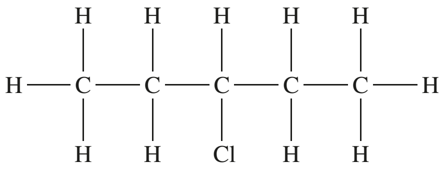
iii methanal

CHAPTER 9 REVIEW

1



2-chloropentane



3-chloropentane

2 Chain isomers have different configurations of alkyl groups whereas position isomers refer to isomers where one or more functional groups are in a different position.

3 Position isomers have the functional group on different carbon atoms. Whereas functional group isomers will have different functional groups but maintain a common molecular formula.

4 Position isomers: $CH_2{=}CHCH_2CH_3$ (but-1-ene) and $CH_3CH{=}CHCH_3$ (but-2-ene). These are position isomers because the location of the carbon-carbon double bond is different.

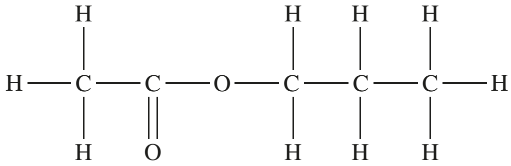
Chain isomers: $CH_2{=}C(CH_3)_2$ (2-methylpropene) and $CH_2{=}CHCH_2CH_3$ (but-1-ene). These are chain isomers because the longest carbon chain and position of alkyl groups are different.

5 **a** 2,4-dimethylhexane

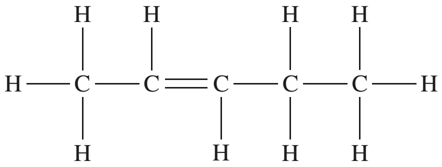
b 4,4-dimethylhex-1-ene

c ethyl butanoate

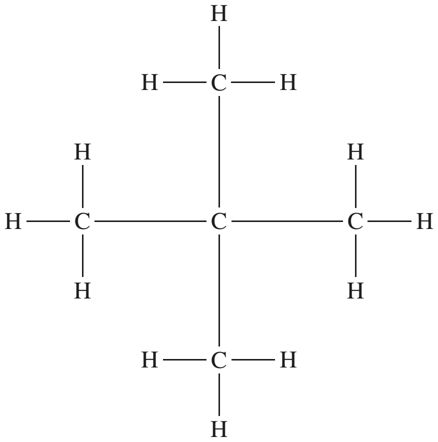
6 **a**



b



c



7 **a** The general formula for an alkane is C_nH_{2n+2}.

$n = \frac{72-2}{(12+2)} = 5$

$\therefore C_5H_{12}$

b The general formula for an alkene is C_nH_{2n}.

$n = \frac{84}{(12+2)} = 6$

$\therefore C_6H_{12}$

c The general formula for an alkyne is C_nH_{2n-2}.

$n = \frac{54+2}{(12+2)} = 4$

$\therefore C_4H_6$

d By trial and error, only one formula produces an integer result. The general formula for an alkene is C_nH_{2n}.

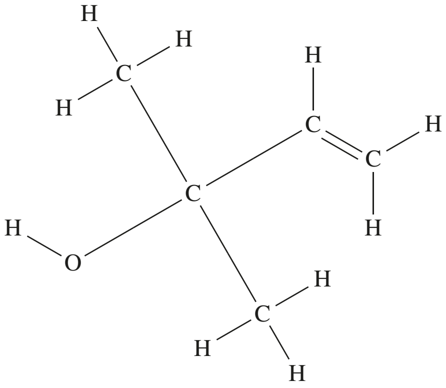
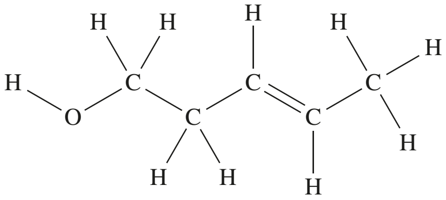
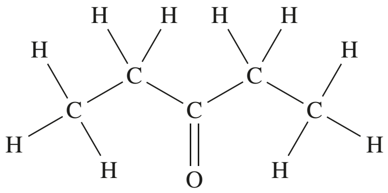
$n = \frac{98}{(12+2)} = 7$

$\therefore C_7H_{14}$

8 Three: pentane, 2-methylbutane, 2,2-dimethylpropane.

9 If an ethyl group is on the second carbon, then the longest chain is 6 carbons long and the correct name would be 2-methylhexane.

10

chain, e.g.		2-methylbut-3-en-2-ol
position, e.g.		pent-3-en-1-ol
functional group, e.g.		pentan-3-one

11 **a** nitrogen, hydrogen

b chlorine

c oxygen, hydrogen

12 In a primary alcohol, the hydroxyl group is attached to a carbon atom which is attached to one other carbon atom, e.g. propan-1-ol. Whereas in a secondary alcohol, the hydroxyl group is attached to a carbon which is attached to two other carbon atoms e.g. propan-2-ol.

13 **a** 2-aminopropan-1-ol

b 8-chlorooctan-2-ol

c 2-iodoheptan-3-amine

14 Aldehyde: terminal carbonyl group. Ketone: secondary carbonyl group. Carboxylic acid: terminal carbonyl with hydroxyl attached to the same carbon. Amide: terminal carbonyl group with amino attached to the same carbon.

15 Carboxyl and amide carbons have three bonds to the carbon atom within the functional group. The carbon atom in these functional groups can only make one more additional bond to connect to a carbon chain and so can never be within a chain.

16 **a** but-3-en-oic acid

b 4-aminobutan-2-ol

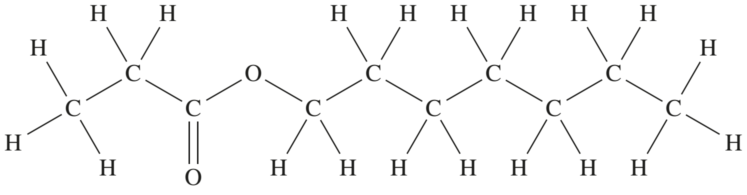
c butyl ethanoate

d 2-methylhex-3-ene

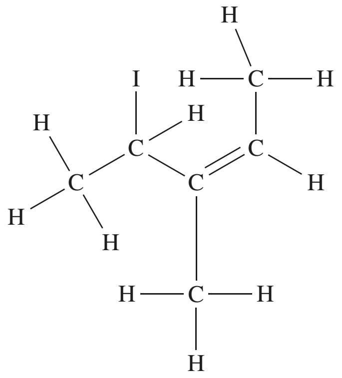
e 4-fluorobut-1-yne

f 1-bromobut-2-ene

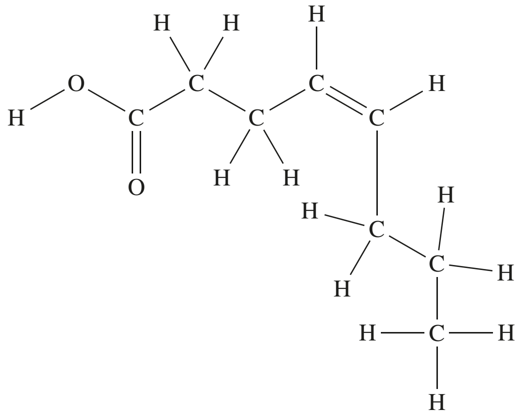
17 **a** heptyl propanoate



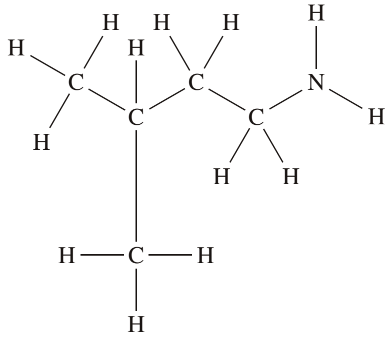
b 4-iodo-3-methylpent-2-ene



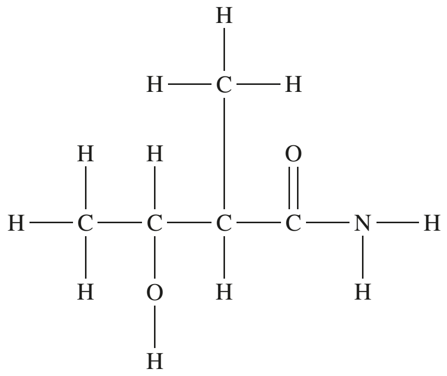
c oct-4-enoic acid



d 3-methylbutan-1-amine.



e 3-hydroxy-2-methylbutanamide



18 **a** $CH_3CH_2CH{=}CHCH_2CH_2CH_2CH_3$

b $CH_3OOC(CH_2)_4CH_3$

c $CH_2FCH_2CH_2OH$

d $HOCH_2CH_2CH_2COOH$

e $H_2NCH_2CH(CH_3)CH(CH_3)CH_2CH_3$

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19 **a** $CH_3CH_2CH_2COCH_3$

b $CH_3CH(CH_3)CH_2CH_2OH$ or $(CH_3)_2CHCH_2CH_2OH$

c $CH_3CH_2CONH_2$

d $CH_3CHClCH_2C{\equiv}CH$

e $CH_3CH_2COOCH_2CH_3$

20 **a** but-1-ene

b 2-aminoethan-1-ol

c 3-chloro-hex-1-yne

d 2-chloro-3-methylpentane

e 4,4-dimethylpent-1-ene

f 4-bromoheptane

21 **a** alcohol; heptan-1-ol

b haloalkane; 4-chloroheptane

c alcohol; hexan-2-ol

d carboxylic acid; pentanoic acid

e amine; butan-2-amine

f alkane; 2-methyloctane

g alkene; 2-methylprop-1-ene

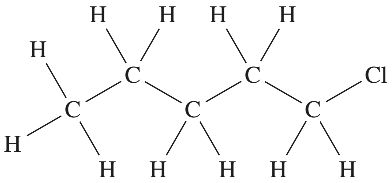
h ketone; propanone

i aldehyde; propanal

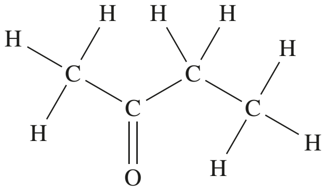
j amide; pentanamide

22 For each formula, more than one structure is possible.

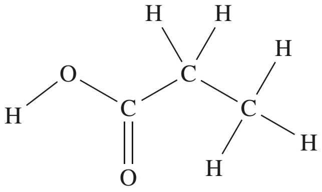
a $C_5H_{11}Cl$, 1-chloropentane



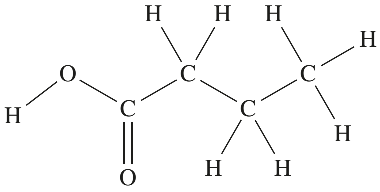
b C_4H_8O, butanone



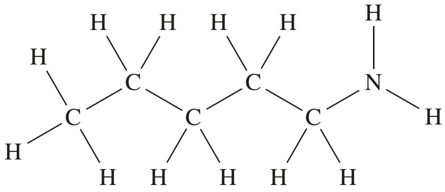
c $C_3H_6O_2$, propanoic acid



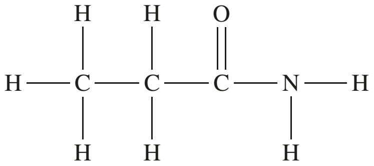
d $C_4H_8O_2$, butanoic acid



e $C_5H_{13}N$, pentan-1-amine



f C_3H_7NO, propanamide



23 Student responses will vary.

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Chapter 10 Properties of hydrocarbons and haloalkanes

10.1 Boiling points, melting points and solubilities of organic compounds

10.1 Review

1 Butane is a member of the *alkane* homologous series. The forces of attraction holding butane molecules to each other are *dispersion forces.* As the chain length of alkanes increases, the boiling point *increases.* Alkanes are *insoluble* in water. This is because the forces of attraction between water molecules and alkane molecules are *weaker* than the *hydrogen bonding* between water molecules.

2 $CH_3CH(CH_3)CH_3$ $CH_3CH_2CH_2CH_3$ $CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$ $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Boiling point increases with molecular size. The presence of branching within the molecule will result in a lower boiling point compared to a molecule of the same size with a straight chain structure.

3 CHCH CH_3CHCH_2 $CH_3CH_2CH_2CH_3$ $CH_3CH_2CH_2CH_2Cl$
Boiling point increases with molecular size. Ethyne, an alkyne, is the smallest molecule and has the lowest boiling point. Propene with three carbons is next, followed by butane with four carbons. The only haloalkane in the group, 1-chlorobutane ($CH_3CH_2CH_2CH_2Cl$), has the highest boiling point because the chlorine–carbon bond is polar and creates a dipole–dipole attraction between molecules. This attraction is stronger than the dispersion forces experienced by the straight-chained butane. Therefore 1-chlorobutane has a higher boiling point.

4 **a** Miscible. Both are non-polar hydrocarbons and liquids, so they can mix together.
  b Miscible. Both are non-polar hydrocarbons and liquids, so they can mix together.
  c Immiscible. Pent-1-yne is non-polar but water is polar, so they cannot mix together.
  d Miscible. Both are haloalkanes with similar polarity, so they can mix together.

10.2 Impacts of uses of organic substances

10.2 Review

1 The three fossil fuels used today are coal, natural gas and oil.

2 Organic chemists have the skills needed to synthesise many modern drugs that are made from small organic molecules.

3 Information on how to dispose of organic substances can be found on the Safety Data Sheets (SDS).

4 In January 2017, New South Wales adopted the Globally Harmonized System of Classification and Labelling of Chemicals.

CHAPTER 10 REVIEW

1 The forces that exist between molecules in both liquid and solid alkanes are dispersion forces. These are weak forces of attraction between non-polar molecules, such as hydrocarbons. As the chain length of the hydrocarbon molecule increases the strength of dispersion forces increases because of greater surface area between molecules.

2

Property	Hydrocarbon
intramolecular bond type	covalent
intermolecular bond type	dispersion forces
melting point, high or low?	low
boiling point, high or low?	low
solubility in water	insoluble
solubility in organic solvents	soluble

3

Name	Formula	Condensed structural formula	Physical state at room temperature
methane	CH_4	CH_4	gas
ethane	C_2H_6	CH_3CH_3	gas
propane	C_3H_8	$CH_3CH_2CH_3$	gas
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	gas
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	liquid
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	liquid

4 The boiling points of haloalkanes are higher than those of the parent hydrocarbon because the addition of a halogen atom introduces polarity. The carbon-halogen bond allows dipole-dipole attractions to occur. Dipole-dipole attractions are stronger than the dispersion forces of hydrocarbons so the haloalkane molecules are more strongly attracted to each other. This stronger attraction requires more energy to overcome making the boiling point higher.

5 2-methylpropane and butane have the lowest boiling points because alkanes are non-polar, so dispersion forces are the only intermolecular forces between molecules. Dispersion forces are not as strong as other intermolecular forces so the boiling points of alkanes are low. Butane has a higher boiling point because its molecules have a greater surface area and can fit more closely together than molecules of 2-methylpropane, forming stronger intermolecular bonds. Methyl methanoate has the next highest boiling point because there is dipole-dipole attraction between its molecules. This is due to the presence of an ester functional group (–COO–) in the molecules. Propan-1-ol has the highest boiling point because hydrogen bonds exist between the propan-1-ol molecules. This is due to the presence of a hydroxyl group (–OH) in the molecules. These bonds are stronger than the dispersion forces between 2-methylpropane and butane molecules and dipole–dipole attraction between methyl methanoate molecules.

6 Boiling points of compounds are determined by the strength of the intermolecular forces. Weak dispersion forces are present in all molecules, whether polar or non-polar, so the masses must be as close to constant as possible when making comparisons on the effect of changing functional groups. Because dispersion forces increase with molecular size, it is important to select compounds of a similar molar mass.

7 **a** $CH_3CH(CH_3)CH(CH_3)CH_2CH_3$ $CH_3CH(CH_3)CH_2CH_2CH_2CH_3$ $CH_3(CH_2)_5CH_3$

All compounds have seven carbon atoms. However, the more branched the hydrocarbon chain is, the more difficult it is for the molecules to pack together. Conversely, the non-branched alkane, in this case hexane, can pack together with other hexane molecules very tightly. Efficient packing together increases boiling point as more energy is needed to separate the molecules to move from a liquid to a gaseous state. Therefore, generally the more branches that a molecule has, the lower its boiling point will be as less energy is needed to cause the phase change.

b These alkanes are non-polar so they would have greater solubility in octane because octane is a non-polar solvent.

8 Intramolecular bonds: Covalent bonds between atoms in octane molecules.

Intermolecular bonds: Octane is a hydrocarbon so its molecules are non-polar. This means there are only dispersion forces between molecules.

9 Water is a very polar molecule, and the main intermolecular force between the molecules is produced by hydrogen bonds. This force is too strong to be overcome by mixing the water with non-polar molecules such as hydrocarbons.

10 Chloromethane (CH_3Cl) would be the most soluble in water. The C–Cl bond is polar so chloromethane molecules are polar, allowing them to form dipole-dipole attractions with water molecules. The other molecules, chloroethane (CH_3CH_2Cl) and 1-chloropropane ($CH_3CH_2CH_2Cl$), also contain polar C–Cl bonds but their longer non-polar hydrocarbon chains reduce the solubility of the molecules in water.

11 Smog, acid rain, the destruction of natural ecosystems and climate change are all examples of the negative environmental effects due to the combustion of fossil fuels.

12 **a** Oct-1-ene is an alkene and is non-polar. Therefore, in a polar solvent such as water it is immiscible and will not dissolve. It will sit on the surface of the water in a less dense layer.

b 7-methyloct-1-yne is an alkyne and (like the alkene oct-1-ene) is non-polar. When the two substances are added they will mix together completely.

13 Coal, oil and natural gas are denser than wood, so more enery can be prduced per unit of fuel.

14 Laboratory technicians use online resources to search for Safety Data Sheets, experimental methods and hazard labels, and to generate risk assessments.

15 **a** Hexane is a clear, colourless, volatile liquid with a petrol-like odour. It is less dense than water.

b Place hexane in a shallow vessel in an operating fume cupboard and allow the solvent to evaporate.

c Move the patient to fresh air and keep at rest in a position comfortable for breathing. Get medical advice or attention if they feel unwell.

16 Vegetable oil represents a hydrocarbon. It was chosen because, like hydrocarbons, it is non-polar, less dense than water and insoluble in water.

Chapter 11 Products of reactions involving hydrocarbons

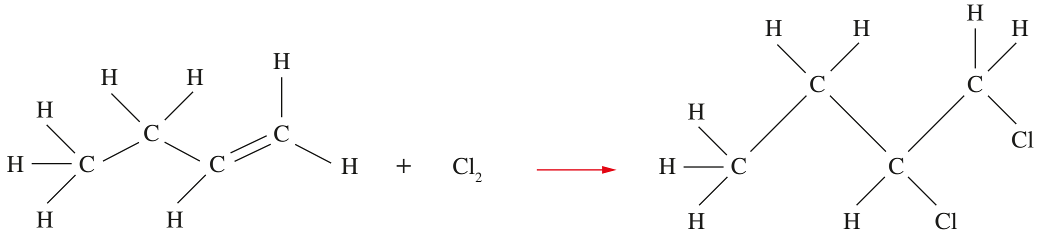
11.1 Chemical properties of hydrocarbons

11.1 Review

1 $CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$
$CH_3Cl(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_2Cl_2(g) + HCl(g)$
$CH_2Cl_2(g) + Cl_2(g) \xrightarrow{\text{UV light}} CHCl_3(g) + HCl(g)$
$CHCl_3(g) + Cl_2(g) \xrightarrow{\text{UV light}} CCl_4(g) + HCl(g)$

2 **a** chloroethane
  b 1,2-dichloroethane
  c ethanol
  d ethane.

3 **a**



but-1-ene 1,2-dichlorobutane

b

but-2-ene 2-bromobutane

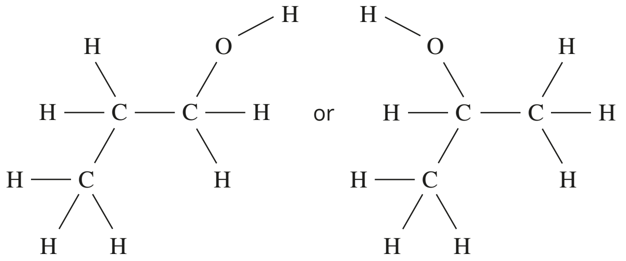
4 **a** but-1-ene or but-2-ene
  b 2-methylprop-1-ene
  c pent-2-ene.

CHAPTER 11 REVIEW

1

Reactants	Type of reaction	Product
alkene and hydrogen	addition (hydrogenation)	alkane
alkene and hydrogen bromide	addition	bromoalkane
alkene and water (with a catalyst)	addition (hydration)	alcohol
alkene and bromine	addition	dibromoalkane

2



3 **a** $CH_3CH_2CH_2CH_3(l) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3CH_2CH_2CH_2Cl(l) + HCl(g)$ (other chloroalkane products are possible)

b $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$

4 **a** $CH_3CH_2CH_2CH_3(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3CH_2CHClCH_3(g) + HCl(g)$ (other chloroalkane products are possible)

b $CH_3CH_2CH_2CH_2CH_3(l) + 7O_2(g) \rightarrow 5CO_2(g) + 4H_2O(g)$

c $CH_2CHCH_3(g) + 3O_2(g) \rightarrow 3CO(g) + 3H_2O(g)$

5 By reaction of the alkene with hydrogen gas in the presence of a metal catalyst such as nickel.

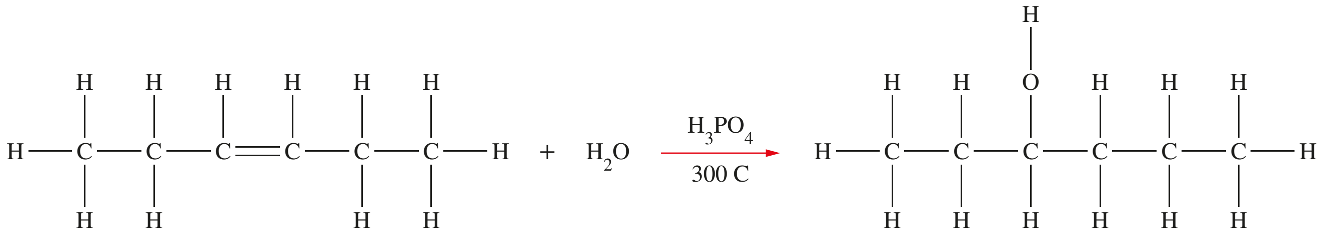
6 Fluorine would be the most reactive. This is because reactivity decreases down the halogen group as the electronegativity decreases.

7 Bromine solution. In the presence of ethane the bromine solution stays orange/brown. When ethene is present, the bromine solution becomes colourless.

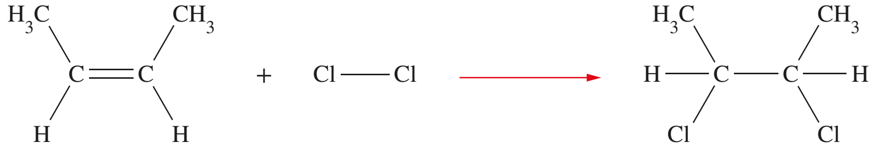
8 B.

9 C.

10



11 **a** but-2-ene



b chlorine (Cl_2)

12 **a** propane: $CH_2CHCH_3(g) + H_2(g) \xrightarrow{Ni} CH_3CH_2CH_3(g)$

b 1-bromopropane and 2-bromopropane: $CH_2CHCH_3(g) + HBr(g) \rightarrow CH_2BrCH_2CH_3(g)$ or $CH_3CHBrCH_3(g)$

c 1,2-dibromopropane: $CH_2CHCH_3(g) + Br_2(g) \rightarrow CH_2BrCHBrCH_3(g)$

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

b $C_4H_8 + HCl \rightarrow C_4H_9Cl$

c $C_5H_{10} + Br_2 \rightarrow C_5H_{10}Br_2$

d $C_5H_{12} + Br_2 \xrightarrow{\text{UV light}} C_5H_{11}Br + HBr$ (other bromoalkane products are possible)

14 C. This is a hydrogenation reaction, i.e. the addition of hydrogen.

15 **a** ethanol

b $C_2H_4(g) + H_2O(g) \xrightarrow[300°C]{\text{H PO}} C_2H_5OH(g)$

16 The vegetable oil is the most spreadable because it is a liquid at room temperature. This is because it contains polyunsaturated molecules, i.e. molecules that contain multiple C=C double bonds. These cause ‘kinks’ in the molecules, so they are not able to pack closely together and the dispersion forces between molecules are therefore weaker.

Margarine and dairy blend contain partially hydrogenated vegetable oils. What this means is that the vegetable oil molecules undergo an addition reaction with hydrogen gas, which reduces their degree of unsaturation. This reduces the number of ‘kinks’ in the molecules, so they are able to pack more closely together and the dispersion forces between molecules are therefore stronger. This causes the oils to turn into a solid fat, which reduces their spreadability.

Butter is the least spreadable because it contains saturated molecules, which are straight-chained, resulting in strong dispersion forces between molecules.

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Chapter 12 Alcohols

12.1 Physical and chemical properties of alcohols

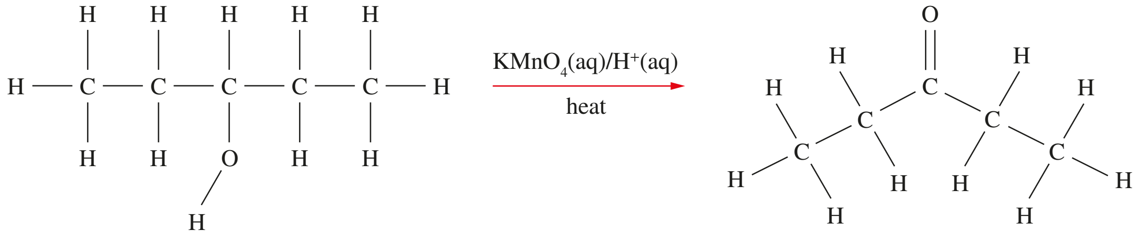
12.1 Review

1 (lowest) $CH_3CHOHCH_3$ $CH_3CH_2CH_2OH$ $CH_3CH_2CH_2CH_2OHCH_3CH_3CH_3$ $CH_3CH_2CH_2CH_2CH_2CH_2OH$ (highest)
Boiling point increases with molecular size. When comparing primary and secondary alcohols, secondary alcohols have a poorer ability to form hydrogen bonds than a primary alcohol with the same molecular formula. The secondary alcohol will have a lower boiling point.

2 The non-polar hexane molecules form stable interactions with the non-polar hydrocarbon chains of propan-1-ol molecules. The hydrogen bonding between methanol molecules is too strong to be overcome by the very weak dispersion forces that would form between hexane molecules and the very short hydrocarbon chains of methanol molecules.

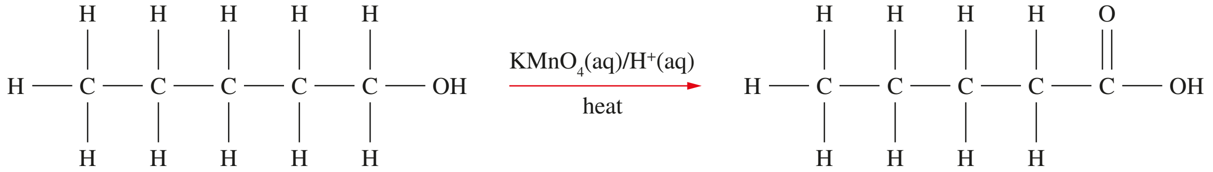
3 **a** tertiary
  b secondary
  c secondary

4 **a** $2C_5H_{12}O(l) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(g)$
  b Pentan-3-ol, secondary; 2-methylbutan-2-ol, tertiary; pentan-1-ol, primary.
  c Pentan-3-ol will be oxidised to pentan-3-one.



2-Methylbutan-2-ol is a tertiary alcohol so will not react under the conditions described.

Pentan-1-ol will be oxidised to the carboxylic acid.



The propanal will be produced first but because there is no mention of how harsh the reaction conditions are, it is assumed that pentan-1-ol is oxidised completely to pentanoic acid.

  d The heat required to change the temperature of water is calculated using $q = mc\Delta T$
  c is the specific heat capacity of water, $4.18\,J\,g^{-1}\,K^{-1}$, m is the mass of water (500 g) and the change in temperature (ΔT) is the difference between the boiling point of water and 20.0°C, so $\Delta T = 100 - 20.0 = 80.0°C = 80.0\,K$

$$q = mc\Delta T$$
$$= 500 \times 4.18 \times 80.0$$
$$= 167\,200\,J$$
$$= 167.2\,kJ$$
$$\Delta H = \frac{q}{n}$$
$$n = \frac{q}{\Delta H} = \frac{-167.2}{-3324} = 0.0503\,mol$$

5 **a** butan-2-ol
  b pentan-2-ol
  c butan-1-ol

6 **a** $CH_3Cl \xrightarrow{OH^- \text{ or } H_2O \text{ with catalyst}} CH_3OH$
  b $CH_3CH_2CH_2Cl \xrightarrow{OH^- \text{ or } H_2O \text{ with catalyst}} CH_3CH_2CH_2OH$

7 Yeast and bacteria do not survive in ethanol concentrations that are greater than about 15%, so the concentration of ethanol must be increased by distilling the mixture.

12.2 Fossil fuels and biofuels

12.2 Review

1 A non-renewable fuel cannot be replenished at the rate at which it is consumed. A renewable fuel can be replenished at a rate at which it is consumed.

2 For a fuel to be sustainable, the starting material must be produced at least as quickly as it is consumed, and it must be possible for the environment to absorb or process all of the wastes produced in making and using the fuel.

3 Renewable: bioethanol, biogas, biodiesel

Non-renewable: coal, oil, LPG, natural gas, coal seam gas

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

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

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

6 **a** advantage

b disadvantage

c advantage

d advantage

e disadvantage.

CHAPTER 12 REVIEW

1 D. Hydrogen bonds between molecules of propan-1-ol are much stronger than the dispersion forces between propane molecules, so the boiling point is higher.

2 **a** $CH_3CH(CH_3)CH(CH_3)CH_2CH_2OH$, $CH_3CH(CH_3)CH_2CH_2CH_2CH_2OH$, $CH_3(CH_2)_5CH_2OH$.

Alcohols with fewer branches have higher boiling points than those with more branches with the same molar mass, because they are more able to form hydrogen bonds.

b They would have greater solubility in hexane because hexane is a non-polar solvent. The presence of the single polar hydroxyl group would not be enough to overcome the non-polar characteristic of the large hydrocarbon chains.

3 **a** ethanol + sodium bromide

b pentan-1-ol + hydrogen iodide

c hexan-2-ol + potassium chloride

4 **a** There are many different fermentation processes and these are caused by many different microorganisms. Most fermentation reactions are catalysed by more than one organism. Different species can produce different products, or different mixtures of products. The reactions depend strongly on temperatures and concentrations.

b

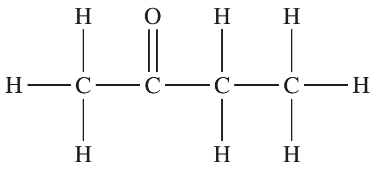
Advantages of haloalkane reactions	**Advantages of fermentation**
faster reaction	lower cost
produces a pure product	lower temperature required
produces a higher yield	can be performed by low-skilled operators
	more likely to produce a renewable resource
Disadvantages of haloalkane reactions	**Disadvantages of fermentation**
chloroethane is suspected to cause cancer; other haloalkanes are toxic	slower
haloalkanes are more flammable than ethanol-water mixtures	produces a mixture

5 **a** aldehyde (mild conditions, lower temperatures) or carboxylic acid (higher temperatures, longer reaction times)

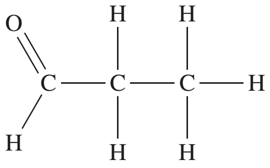
b ketone

c no reaction.

6 **a**



b



c no reaction.

7 **a** No reaction between a tertiary alcohol and $H^+/MnO^{-}{}_{4}$.

b Ethanoic acid is formed if the reaction time is long and the temperature is high.

c The ketone pentan-3-one is formed from a secondary alcohol

d The aldehyde butanal is formed when the temperature is mild and the product is removed as it is formed.

8 **a** $CH_3CH_2CH_2OH \xrightarrow[\text{or conc. acid}]{Al_2O_3} CH_3CH{=}CH_2$

b $CH_3CH_2CH_2CH_2Cl \xrightarrow{OH^-} CH_3CH_2CH_2CH_2OH$

c $CH_3CH_2CH_2OH \xrightarrow{HBr} CH_3CH_2CH_2Br$

9 **a** $2C_5H_{11}OH(l) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(l/g)$

b $2CH_3CHOHCH_3(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l/g)$

10 **a** $\Delta T = 77.04 - 22.72$

$= 54.32°C = 54.32\,K$

$n(\text{2-methylbutan-2-ol}) = \frac{m}{M}$

$= \frac{0.793}{88.15}$

$= 9.00 \times 10^{-3}\,\text{mol}$

$q = mc\Delta T$

$= 100.0 \times 4.18 \times 54.32$

$= 22.7 \times 10^3\,J$

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

$= \frac{-22.7 \times 10^3}{9 \times 10^{-3}}$

$= -2.52 \times 10^6\,J\,mol^{-1}$

$= -2.52 \times 10^3\,kJ\,mol^{-1}$

b It is assumed that all of the energy released from the combustion of 2-methylbutan-2-ol is used to heat the water. However, some of the energy will heat the metal and some will be lost to the surroundings.

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

12 D

13 They are separated by fractional distillation. The crude oil is heated and introduced into a fractionating column, which separates the components on the basis of their boiling point.

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

15 soybean, canola and palm oil

16 C. Petrodiesel contains alkanes ranging from $C_{10}H_{22}$ to $C_{15}H_{32}$.

17 The rate of production of the starting material for the fuel's production and the ability of the environment to absorb or convert the waste products from its use are important factors in determining a fuel's sustainability.

18 **a** petrol, bioethanol, biogas

b B

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

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

Fermentation of glucose produces ethanol and two molecules of CO_2:

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

Combustion of ethanol releases heat and two molecules of CO_2:

$$C_2H_6O(aq) + 3O_2(g) \rightarrow 3H_2O(g) + 2CO_2(g)$$

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

20 **a**, **b**, **d**, **e** and **f** are all advantages; **c** is a disadvantage

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

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

22 All of the points are interrelated. Sample answers are given here; many other valid answers are possible.

a Polar ice caps are shrinking, contributing to sea level rise and affecting wildlife that depend on the ice caps. Melting ice adds cold, fresh water to the ocean, which could alter the major ocean currents, resulting in unexpected climate changes, e.g. in western Europe.

b Changed weather patterns may cause more droughts and floods and more intense storms, and may change growth patterns in plants that might lead to both plant and animal extinctions.

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

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

23 **a** Biochemical fuels are derived from renewable resources such as plants. Ethene, the raw material used for most of the industrial production of ethanol, is derived from crude oil, which is a non-renewable resource.

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

24 Student answers may vary according to the information sources used, but the usual countries cited are China, USA, Russia, India, Japan, Canada, Germany, Brazil, South Korea and France.

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

b Biofuels could potentially be carbon neutral—the carbon dioxide produced from the combustion of the fuels is offset by the carbon dioxide absorbed to grow the crops which are used to make the fuels. This would help Australia meet its Paris Agreement obligations.

26 Ethanol is insoluble in vegetable oil because the hydrogen bonds between ethanol molecules and the dispersion forces between vegetable oil molecules are stronger than intermolecular forces formed between the molecules of the two different substances.

Chapter 13 Reactions of organic acids and bases

13.1 Physical properties of organic acids and bases

13.1 Review

1 $CH_3CH_2CH_2CH_3$ $CH_3CH_2CH_2NH_2$ $CH_3CH_2CH_2OH$ CH_3CH_2COOH $CH_3CH_2CONH_2$
The strength and extent of hydrogen bonding increases from none for butane to very extensive hydrogen bonding in propanamide. Stronger intermolecular forces between molecules mean that the boiling point will be higher.

2 CH_3NH_2 $CH_3CH_2NH_2$ $CH_3CH_2CH_2NH_2$ $CH_3CH_2CH_2CH_2NH_2$ $CH_3CH_2CH_2CH_2CH_2CH_2NH_2$
Longer-chain amines have stronger dispersion forces between molecules and a higher melting point than shorter-chain amines.

3 Octanoic acid, octan-2-one and heptan-1-amine will be more soluble in hexane. Their longer hydrocarbon chains have better interactions with non-polar hexane.

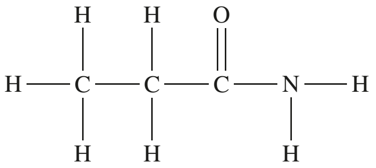
4 Amides have much more extensive hydrogen bonding than amines. There are two parts of an amide involved in hydrogen bonding (the C=O and the $-NH_2$ parts of the functional group) but only one part of an amine (the $-NH_2$) participates in hydrogen bonding.

5 Octan-1-ol. This is the only one of the three molecules that can participate in hydrogen bonding. The intermolecular forces between the other molecules are dipole–dipole attractions.

13.2 Chemical properties of organic acids and bases

13.2 Review

1 **a**



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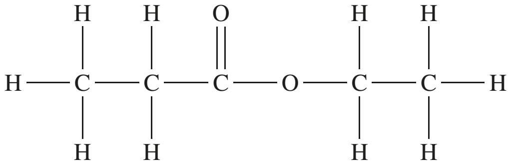
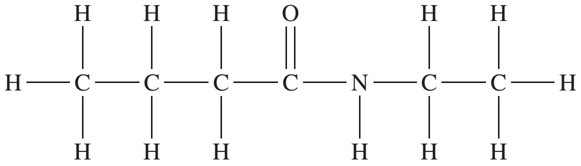


c



2 **a** $CH_3(CH_2)_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3(CH_2)_3COO^-(aq) + H_3O^+(aq)$

b $CH_3CH_2CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + OH^-(aq)$

c no reaction

3 **a** The molecule needs to be boiled with a strong base.

b $CH_2OHCHOHCH_2OH$ and $CH_3(CH_2)_3CH{=}CH(CH_2)_2CH{=}CH(CH_2)_3COO^-$

4 The non-polar hydrocarbon tails of stearate ions are unable to overcome the hydrogen bonding between water molecules. Instead, the non-polar tails of the stearate ions are attracted to each other, forming a micelle. This leaves the charged heads of the stearate ions facing the water.

5 The non-polar oil droplet is unable to overcome the hydrogen bonding between water molecules so it will remain surrounded by hydrocarbon tails in a non-polar environment.

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13.3 Organic reaction pathways

13.3 Review

1 **a** ethene $\xrightarrow[H_3PO_4]{H_2O}$ ethanol $\xrightarrow{NH_3}$ ethanamine

b butane $\xrightarrow[UV]{Cl_2}$ 1-chlorobutane $\xrightarrow{OH^-}$ butan-1-ol

c 1-chloropentane $\xrightarrow{OH^-}$ pentan-1-ol $\xrightarrow{K_2Cr_2O_7/H^+}$ pentanoic acid

2 **a** methane $\xrightarrow[UV]{Cl_2}$ chloromethane $\xrightarrow{OH^-}$ methanol $\xrightarrow{K_2Cr_2O_7/H^+}$ methanoic acid

b ethene $\xrightarrow[H_3PO_4]{H_2O}$ ethanol

c This synthesis can be carried out in three stages: (1) synthesis of propan-1-ol, (2) synthesis of methanoic acid, and (3) synthesis of propyl methanoate

Stage 1: propane $\xrightarrow[UV]{Cl_2}$ 1-chloropropane $\xrightarrow{OH^-}$ propan-1-ol
Stage 2: methane $\xrightarrow[UV]{Cl_2}$ chloromethane $\xrightarrow{OH^-}$ methanol $\xrightarrow{H^+/Cr_2O_7^{2-}}$ methanoic acid
Stage 3: propan-1-ol + methanoic acid $\xrightarrow{H^+}$ propyl methanoate + water

3 **a** pentan-1-ol

b sodium hydroxide or potassium hydroxide

c pentanoic acid

d acidified potassium dichromate or potassium permanganate and heat

e ammonia

4 This synthesis is carried out in three parts: (1) synthesis of butan-1-ol, (2) synthesis of ethanoic acid, and (3) synthesis of butyl ethanoate. Other reaction pathways are possible.

Stage 1: butane $\xrightarrow[UV]{Cl_2}$ 1-chlorobutane $\xrightarrow{OH^-}$ butan-1-ol
Stage 2: ethene $\xrightarrow[H_3PO_4]{H_2O}$ ethanol $\xrightarrow{H^+/Cr_2O_7^{2-}}$ ethanoic acid
Stage 3: ethanoic acid + butan-1-ol $\xrightarrow{H^+}$ butyl ethanoate + water

CHAPTER 13 REVIEW

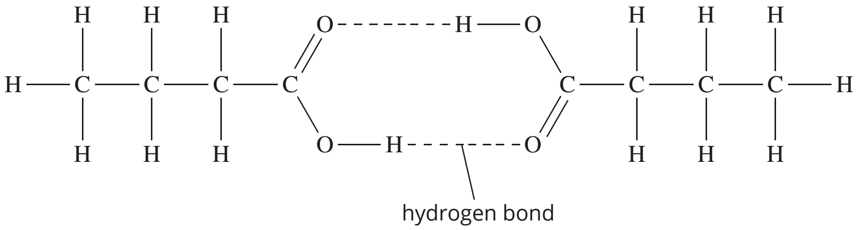
1 Butane has the lowest boiling point because alkanes are non-polar, so dispersion forces are the only intermolecular forces between molecules. Dispersion forces are not as strong as other intermolecular forces so the boiling points of alkanes are low. Dipole–dipole attractions exist between the polar regions of methyl methanoate, propan-1-ol and ethanamide molecules. Hydrogen bonds exist between propan-1-ol and ethanamide molecules because their molecules contain hydrogen atoms bonded to oxygen and nitrogen atoms respectively. These bonds are stronger than the dispersion forces between butane molecules and dipole–dipole forces in methyl methanoate molecules. Ethanamide has the highest boiling point because there are more atoms capable of forming hydrogen bonds in its molecules than in molecules of propan-1-ol.

2 Boiling points of compounds are determined by the strength of the intermolecular forces. Weak dispersion forces are present in all molecules, whether polar or non-polar, so they must be kept as close to constant as possible when making comparisons about the effect of changing functional groups. Because the strength of dispersion forces increases with molecular size, it is important to select compounds that have a similar molar mass.

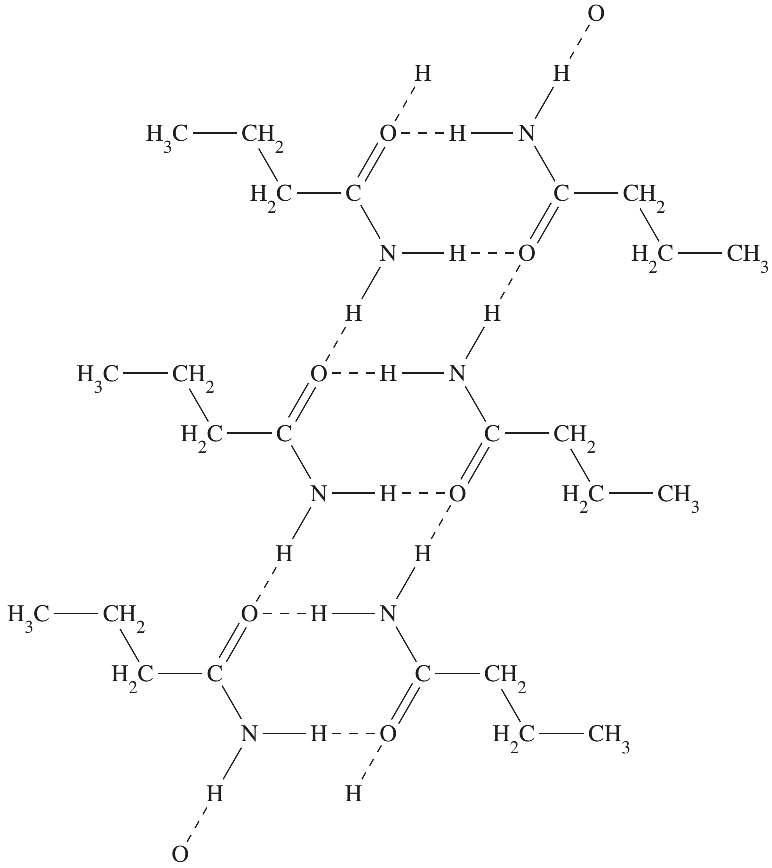
3 **a** CH_3CHO, CH_3COOH, $CH_3(CH_2)_6CHO$, $CH_3(CH_2)_5COOH$. Aldehydes have a lower boiling point than carboxylic acids of a similar molar mass because of weaker intermolecular forces. Boiling points of aldehydes and carboxylic acids increase as molar mass increases.

b The molecules with longer hydrocarbon chains, $CH_3(CH_2)_6CHO$ and $CH_3(CH_2)_5COOH$, would have greater solubility in hexane because hexane is a non-polar solvent.

4 **a**

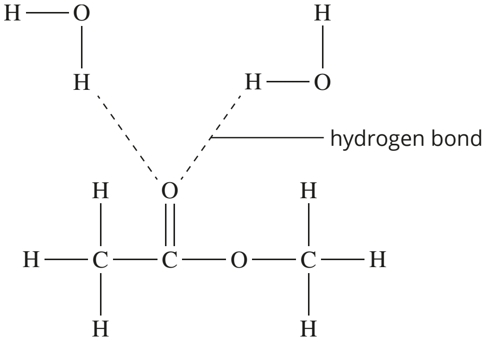


b



c Butanamide has a higher boiling point because the molecules have more extensive hydrogen bonding.

5 Methyl ethanoate can hydrogen bond with one or more water molecules. The answer shown here has the molecule forming two hydrogen bonds with water.



6 **a** $CH_3CH_2COOCH_3 + H_2O$

b $CH_3COO(CH_2)_4CH_3 + H_2O$

c $HCOOCH(CH_3)_2 + H_2O$

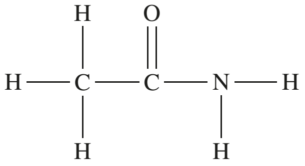
7 **a** ethanol, propanoic acid and a strong acid, such as sulfuric acid, to catalyse the reaction

b propanoic acid and ammonia

c butanoic acid and ammonia

d methanoic acid, methanol, and a strong acid, such as sulfuric acid, to catalyse the reaction

8 **a**



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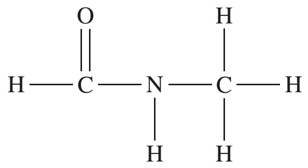
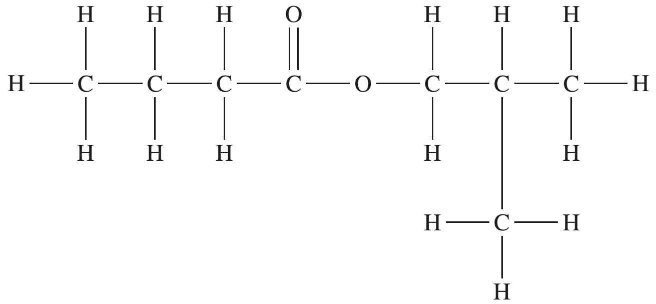


c



9 **a** $CH_3(CH_2)_3NH_3^+ + OH^-$

b Butanamide does not dissociate in water.

10 The electronegative oxygen atom of an amide draws electron density away from the nitrogen atom, reducing its ability to hold a positive charge after accepting a H^+ ion. The nitrogen atom is the most electronegative atom in an amine, so it draws electron density from the rest of the molecule. This extra electron density means that an amine is better at holding the positive charge when it acts as a base and accepts H^+.

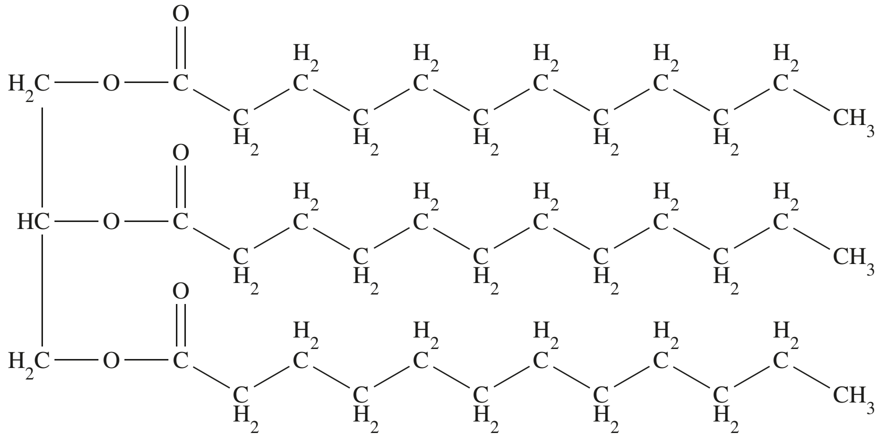
11 **a** The hydrocarbon chain is hydrophobic and the COONa section is hydrophilic.

b The hydrocarbon chain (hydrophobic end) of the molecule will be in the centre of the micelle.

12 Soap molecules can be described as surfactant molecules. They act as surface active agents. The hydrophobic section of the surfactant molecule adsorbs onto the oil stain and the charged heads of the molecules provide a hydrophilic coating for the oil. Surfactant molecules move between the oil and the fabric to completely surround the oil in a ball-like structure called a micelle, and this micelle is carried off into the solution. A solution of oil-containing micelles in water is called an emulsion.

13 **a** $CH_3(CH_2)_{10}COONa$

b

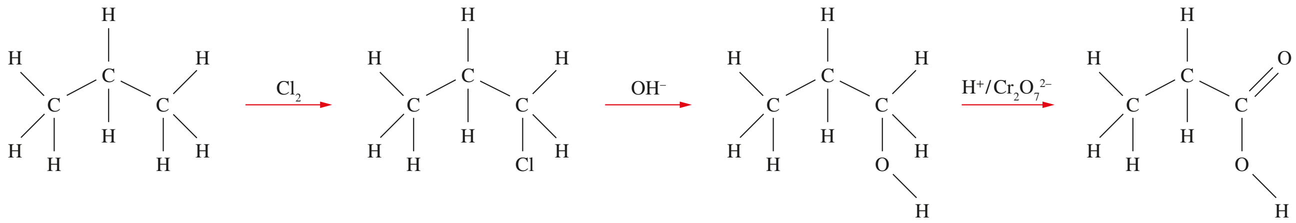


14 C is most likely to be found in shampoo. Potassium salts of shorter-chain surfactant molecules form softer liquid soaps, while sodium salts of longer chain surfactants form harder soaps.

15 **a** Cl_2 and UV

b propan-2-ol

16 **a**



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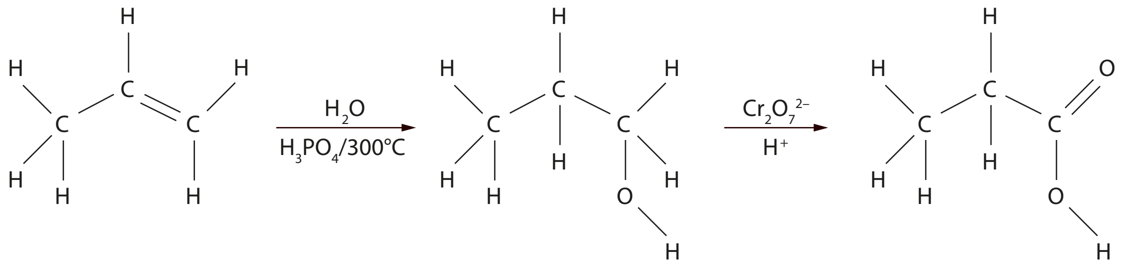


17 **a** Step 1. ethene $\xrightarrow[H_3PO_4]{H_2O}$ ethanol

Step 2. 1-chloropropane $\xrightarrow{OH^-}$ propan-1-ol $\xrightarrow{H^+/Cr_2O_7^{2-}}$ propanoic acid

Step 3. ethanol + propanoic acid $\xrightarrow{H_2SO_4}$ ethyl propanoate

b ethane $\xrightarrow[UV]{Cl_2}$ chloroethane $\xrightarrow{OH^-}$ ethanol $\xrightarrow{H^+/Cr_2O_7^{2-}}$ ethanoic acid $\xrightarrow{ethanol, H_2SO_4}$ ethyl ethanoate

18 **a** **i** $CH_3CH_3 \xrightarrow[UV]{Cl_2} CH_3CH_2Cl$

ii $CH_2CH_2 \xrightarrow[H_3PO_4]{H_2O} CH_3CH_2OH$

iii $CH_3CH_2Cl \xrightarrow{OH^-} CH_3CH_2OH$

iv $CH_3CH_2OH \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3COOH$

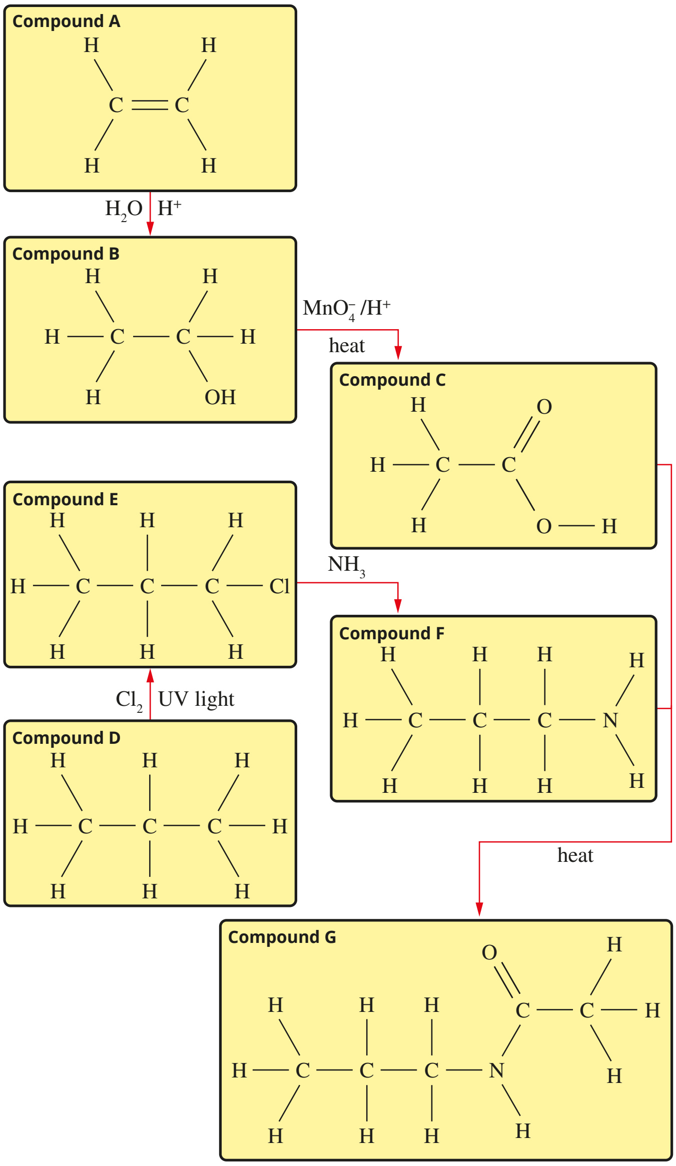
b **i** substitution

ii addition

iii substitution

iv oxidation

19



N-propylethanamide

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b The bromine test for unsaturated hydrocarbons. When aqueous Br_2 is added to A, an addition reaction will occur and the solution will turn from orange to colourless. If aqueous Br_2 is added to D, no reaction will occur and the solution will remain orange.

c B. Although both compounds can form hydrogen bonds with water, the larger size of the hydrocarbon chain of propan-1-amine (F) results in lower solubility.

20 Bicarbonate of soda reacts with vinegar in an acid and metal carbonate reaction. This reaction produces carbon dioxide gas, which is trapped in the washing detergent.

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Chapter 14 Polymers

14.1 Addition polymers

14.1 Review

1 C. Polymers are long chains formed from a smaller, repeated monomer.

2 A and D. They both have carbon–carbon double bonds that can break and allow new bonds to form that join the monomers together.

3 **a** CH_2 (An empirical formula shows only the ratio of atoms in the molecule. It does not necessarily show the actual number of atoms.)
  b CH_2
  c CH
  d C_2H_3Cl

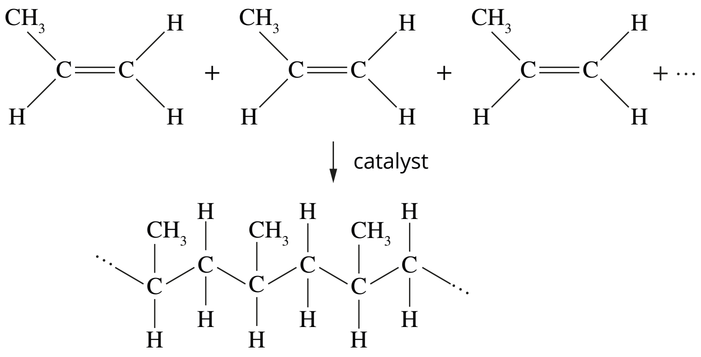
4 **a** monomer formula C_3H_6. $3 \times C_3H_6 = C_9H_{18}$
  b monomer formula C_2H_3Cl. $6 \times C_2H_3Cl = C_{12}H_{18}Cl_6$
  c monomer formula C_2H_4. $65 \times C_2H_4 = C_{130}H_{260}$

5 The repeating unit is $–CH_2CF_2–$ so there are three full units in this segment. Half a repeating unit starts and ends this polymer segment.

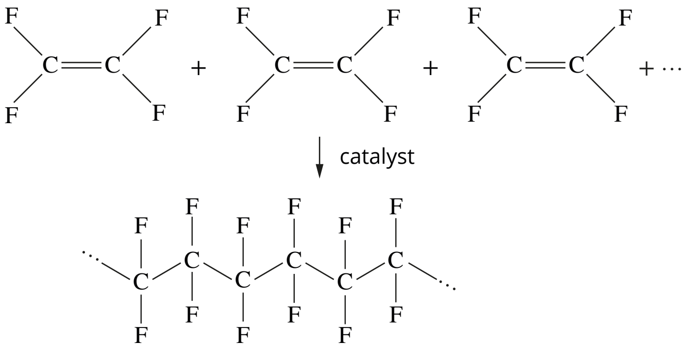
6 Polymers usually consist of thousands to millions of monomer repeating units, so this would not be considered a polymer.

7 **a** High-density polyethene (HDPE) is made of relatively unbranched chains of polyethene, which can pack more closely together than the chains of low-density polyethene (LDPE). LDPE contains branched chains of polyethene that cannot pack together as closely. HDPE is therefore stronger and slightly less flexible than LDPE. Both HDPE and LDPE are chemically unreactive, waterproof, non-conductors and only slightly permeable to gases.
  b **i** LDPE
    ii HDPE
    iii LDPE

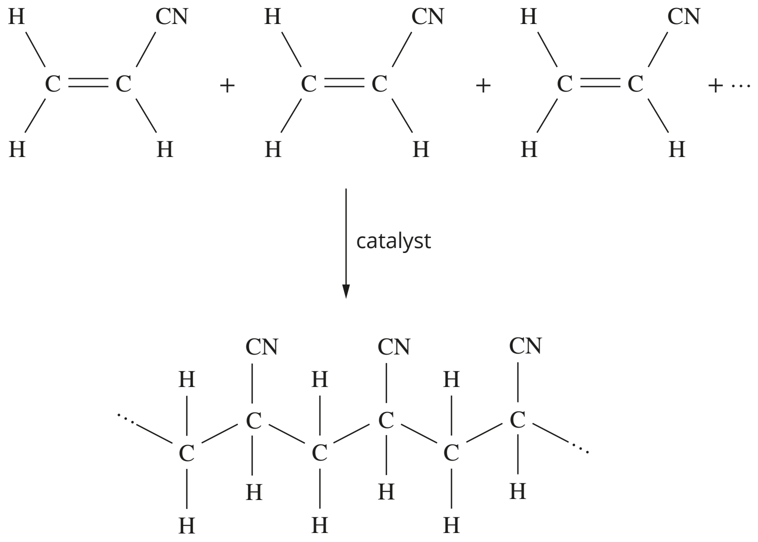
8 **a**



b



c

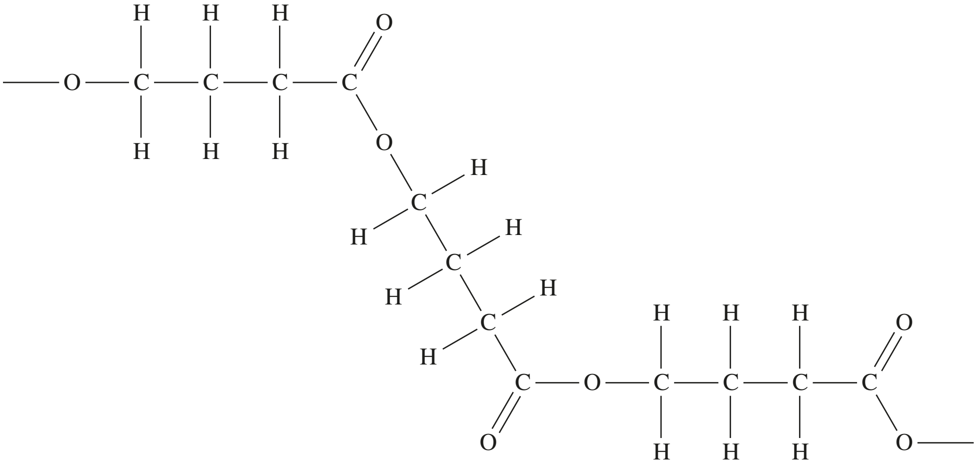


14.2 Condensation polymerisation

14.2 Review

1 D. When functional groups on the monomers react, a different functional group is formed.

2 **a**

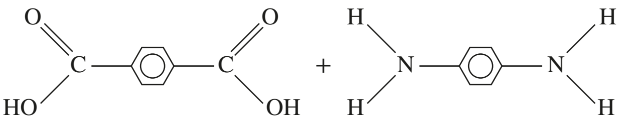


b water

c polyester

3 A and D. Monomers for condensation reactions need functional groups on each end.

4 **a**



b To be used in bullet proof vests, Kevlar must be very tough yet relatively light.

c The presence of C=O and –N–H bonds allows for hydrogen bonding between neighbouring polymer chains. The polymer chains will pack together tightly as there are few, if any, side-chains.

5 **a** Both made from monomers, both contain very long polymer molecules.

b Addition polymers are made from monomers that contain carbon-carbon double bonds while condensation polymers are made from monomers that contain a functional group at either end of the molecule. Condensation polymerisation produces a small molecule but addition polymerisation does not.

6 dispersion forces dipole–dipole attractions covalent bonds

7 **a** The polymer used in the handle will have cross-links while the polymer used for the coating will not.

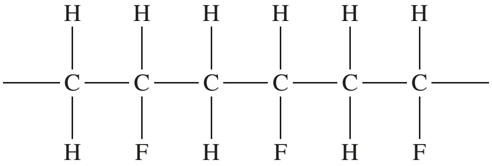
b The coating needs to have a relatively high melting point and low friction, and to be durable and non-toxic.

c The handle needs to have a high melting point and be tough, and to be non-flammable in case it is exposed to a flame.

CHAPTER 14 REVIEW

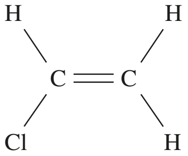
1 C. Crystalline regions are due to polymer chains that are regularly arranged and closer together. The intermolecular forces between the closely packed chains are stronger and the presence of crystalline regions strengthens the material overall.

2 **a**



b The melting point should be higher due to the presence of highly electronegative fluorine atoms. The fluorine atoms will cause dipole attractions between neighbouring molecules.

3 **a**



b 6

c dipole–dipole attractions

4 **a** Monomers are small molecules that are able to react to form long chains of repeating units, called polymers.

b When the material is heated, it softens, allowing it to be reshaped. This is because the bonds between molecules are broken and the polymer chains become free to move.

c When the material is heated it does not melt, but at high temperatures, covalent bonds are broken and the material decomposes or burns. It cannot be moulded into a different shape.

d One or more covalent bonds that connect neighbouring polymer chains.

e A chemical added to plastics to make them more flexible.

5 **a** False. Polymer chains are similar in length.

b False. Chains in thermoplastic polymers are held together by hydrogen bonds, dipole–dipole bonds or weak dispersion forces.

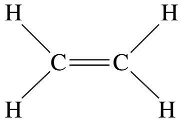
c False. HDPE has very few branches.

d True.

6 A, C, and D can act as monomers in addition polymerisation; B, propane, cannot as it does not contain a carbon–carbon double bond.

7 **a** The ethene molecule has a carbon–carbon double bond.

b



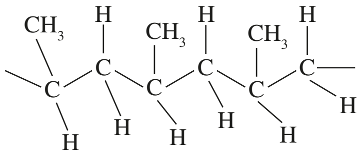
c Ethane cannot undergo addition polymerisation because it is a saturated compound.

8 **a** Several thousand ethene monomers undergo an addition polymerisation reaction to make one molecule of polyethene.

b Ethene ($CH_2{=}CH_2$) is unsaturated because it contains a carbon-carbon double bond. Polyethene is saturated because it contains only single bonds between carbon atoms.

c The empirical formula is the simplest whole-number ratio of elements in a compound. The empirical formula of ethene ($CH_2{=}CH_2$) is CH_2.

9 **a**



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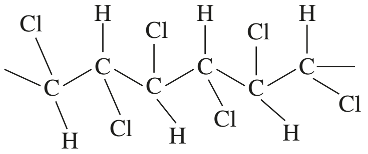
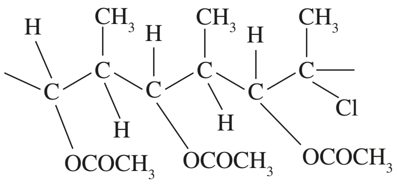


c



10 **a** weak dispersion forces
b dipole–dipole attractions
c weak dispersion forces
d weak dispersion forces
e dipole–dipole attractions

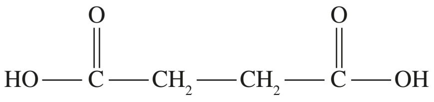
11 –H (in polyethene)
–F (in Teflon)
–Cl (in polyvinyl chloride)
–C_6H_5 (in polystyrene)
–$NC_{12}H_8$ (in polyvinyl carbazole)

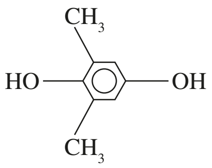
12 **a** will have *more* branches
b will have *fewer* crystalline regions
c will have a *lower* density
d will have a *lower* melting point
e will be *less* brittle.

13 C. A polyamide could be formed.

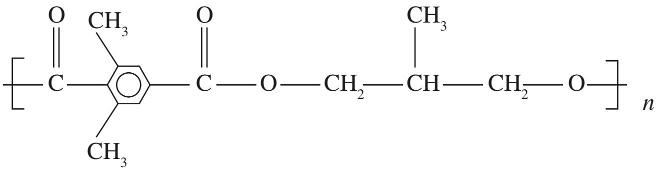
14 **a** polyamide
b polyamide
c polyester
d polyester.

15





16 **a**



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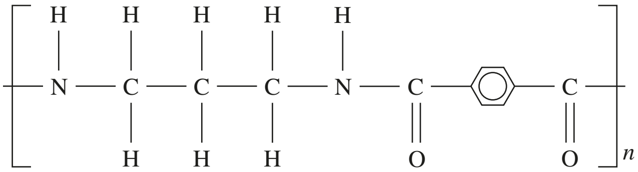
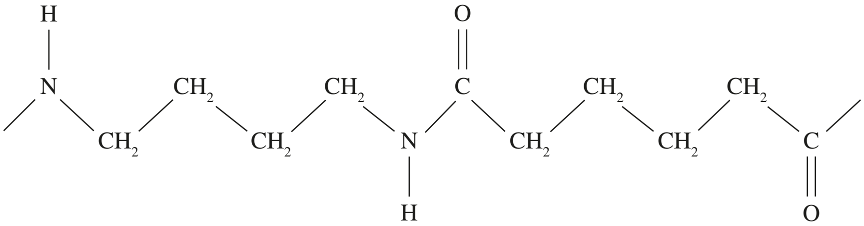


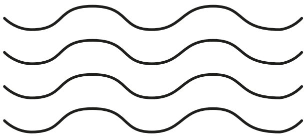
17 **a** amide

b 99. 100 monomers combine, therefore 99 amide bonds are formed.

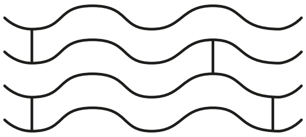
18



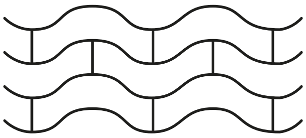
19 **a** **i**



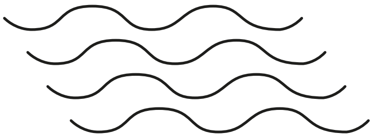
ii



iii

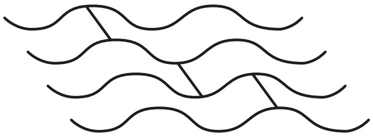


b **i**



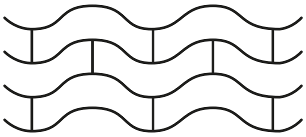
polymer easily stretched

ii



Some stretching but polymer tends to return to its original shape.

iii



no stretching possible

20 Thermosetting polymers have much stronger inter-chain bonds than thermoplastic polymers.

21 The inter-chain bonds in thermosetting polymers have about the same strength as the covalent bonds within chains. When heated strongly both the inter-chain and within-chain bonds break.

22 Distinguishing between thermoplastic and thermosetting polymers is important. The former get soft when heated, whereas the latter remain rigid and will char if heating continues.

a thermosetting

b thermoplastic

c thermosetting

d thermoplastic

e thermoplastic.

23 **a** the polymer used in saucepan handles

b Elastic bands have the least amount of cross-linking, because they are extremely flexible. The polymer on the outside of the golf ball is hard, but it is still somewhat elastic. The inside of a golf ball consists of a much more flexible polymer, allowing it to deform considerably when it is struck. Saucepan handles are much harder and more resistant to the effect of heat than elastic bands and golf balls.

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24 The relative molecular mass would have increased. The melting point of the polymer would have increased because there are stronger intermolecular forces between the longer polymer molecules. The overall strength of inter-chain forces would have increased due to longer polymer molecules. The electrical conductivity of the polymer would have remained the same.

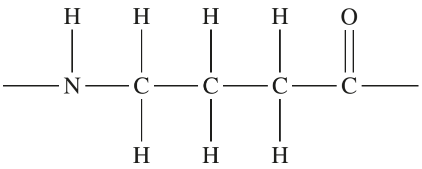
25 A. This will be an addition polymer, because the backbone consists entirely of carbon atoms. The relatively high melting point suggests an electronegative element such as fluorine is present in the monomer.

26 **a** HCl

b 4999

c amide

d



$-\text{N(H)}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C(=O)}-$

27 It would be impractical to produce polymers from milk. The monomers used to make polymers are products of the petrochemical industry and at the moment are relatively inexpensive. It would be much more costly to produce a polymer from milk. Also, a polymer from milk would have limited applications due to its limited properties. Polymers derived from a range of petrochemicals have a range of useful properties.

Chapter 15 Analysis of inorganic substances

15.1 The source of salts in the environment

15.1 Review

1 A. Caves are likely to form in regions where there is limestone ($CaCO_3$).

2 A heavy metal is a metal with a relatively high density that has a toxic effect on living organisms. Examples are cadmium, lead, chromium, copper and mercury, and the metalloid arsenic.

3 Toxic heavy metal levels are increased in our waterways indirectly by combustion of fuels and wastes and directly by improper disposal of batteries, natural deposits in the Earth, and leaching from landfill.

4 **a** ammonium nitrate, superphosphate or ammonium sulfate
  b The use of fertilisers leads to run-off into water supplies.

5 **a** Hard water contains relatively high levels of metal ions.
  b Ca^{2+}, Mg^{2+}
  c It limits the effectiveness of soaps and detergents and it causes deposits to form in kettles and pipes, reducing their efficiency.

15.2 Qualitative techniques for detecting salts

Worked example: Try yourself 15.2.1

IDENTIFYING THE PRESENCE OF A PARTICULAR METAL ION USING A PRECIPITATION REACTION

How can a precipitation reaction be used to confirm the presence of Ca^{2+} ions in a colourless solution?

Thinking	**Working**
Use solubility tables to select a compound containing Ca^{2+} ions that is insoluble.	$CaSO_4$ will be insoluble.
Use the solubility tables to select a soluble substance that contains the necessary anion to form the insoluble calcium compound.	Na_2SO_4 can be used to provide the SO_4^{2-} ions.
Write an ionic equation for the reaction occurring.	$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$
What do you know about the appearance of the precipitate?	$CaSO_4$ is white. The formation of a white solid indicates Ca^{2+} ions might be present.

Worked example: Try yourself 15.2.2

IDENTIFYING THE PRESENCE OF AN UNKNOWN METAL ION

HCl added to a solution causes no change nor does the addition of NH_3. A flame test produces a red flame. Identify the metal ion present.

Thinking	**Working**
What does the response to HCl tell you about the metal ion present?	The ion is not Pb^{2+} or Ag^{+}.
What does the response to NH_3 tell you about the metal ion?	The ion is either NH_4^{+}, Ca^{2+} or Ba^{2+}.
Identify the metal ion present.	The red flame suggests Ca^{2+}.

15.2 Review

1 B. Detecting the presence of a chemical is a qualitative test. The other alternatives are all quantitative tests.

2

Compound	**Flame colour**
strontium chloride	scarlet
strontium carbonate	scarlet
copper chloride	green
potassium sulfate	lilac
sodium nitrate	yellow

3 **a** Both barium compounds produce the same colour flame but the flames from the two compounds containing sulfate ions are different. Therefore the metal ion is causing the visible flame colour.

b Not all metals produce a visible flame colour. It can be difficult to distinguish one flame colour from another. The presence of several metal ions will cause confusion.

4 **a** PbI_2

b $Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s)$

5 **a** $Cu(OH)_2$ (or $[Cu(H_2O)_4(OH)_2]$ if the water molecules are shown)

b Several metals could produce a precipitate with OH^{-} ions, but Cu^{2+} is one of the few that will be blue.

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

6 **a** The metal ion is most likely to be Ag^{+} or Pb^{2+}.

b The metal ion is Ag^{+}.

7 $[CoCl_4]^{2-}$

8 **a** Fe^{3+}

b H_2O

c The metal ion is positively charged. The water molecules are orientated so that their oxygen atoms, through their lone pairs, form bonds with the metal ion.

15.3 Gravimetric analysis of a salt

Worked example: Try yourself 15.3.1

CALCULATING MASS–MASS STOICHIOMETRIC PROBLEMS

A reaction between solutions of sodium sulfate and barium nitrate produces a precipitate of barium sulfate (molar mass 233.39 g) with a mass of 2.440 g. Calculate the mass of sodium sulfate required to produce this precipitate.

Thinking	**Working**
Write a balanced equation for the reaction.	$Na_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$
Calculate the number of moles of the known substance (the precipitate): $n = \frac{\text{mass } (m)}{\text{molar mass } (M)}$	$n(BaSO_4) = \frac{2.440}{233.39}$ $= 0.01045 \text{ mol}$
Calculate the mole ratio: $\text{mole ratio} = \frac{\text{coefficient of unknown}}{\text{coefficient of known}}$	$\text{mole ratio} = \frac{\text{coefficient of } Na_2SO_4}{\text{coefficient of } BaSO_4} = \frac{1}{1} = 1$
Calculate the number of moles of the unknown substance: $n(\text{unknown}) = n(\text{known}) \times \text{mole ratio}$	$n(Na_2SO_4) = 0.01045 \times 1$ $= 0.01045 \text{ mol}$
Calculate the mass of the unknown substance: $m = n(\text{unknown}) \times \text{molar mass}$	$m(Na_2SO_4) = 0.01045 \times 142.06$ $= 1.485 \text{ g}$

Worked example: Try yourself 15.3.2

USING GRAVIMETRIC ANALYSIS

Water discharged from a mining plant contains silver ions present as silver nitrate ($AgNO_3$). Excess potassium chromate (K_2CrO_4) solution is added to a 50.0 g sample of the water to precipitate the silver as silver chromate (Ag_2CrO_4). The precipitate is heated to remove any water, producing 1.32 g of silver chromate.

Calculate the percentage mass of silver in the water sample. (The molar mass of Ag_2CrO_4 is 331.74 g mol^{-1}.)

Thinking	**Working**
Write a balanced equation for the precipitation reaction.	$2AgNO_3(aq) + K_2CrO_4(aq) \rightarrow Ag_2CrO_4(s) + 2KNO_3(aq)$
Calculate the number of moles of precipitate using: $n = \frac{m}{M}$	$n(Ag_2CrO_4) = \frac{m}{M}$ $= \frac{1.32}{331.74}$ $= 3.98 \times 10^{-3}$ mol
Use the balanced equation to find the mole ratio of the known and unknown substances. The known substance is the one you know the mass of the unknown substance is the one whose mass you are required to calculate.	mole ratio $= \frac{\text{coefficient of } AgNO_3}{\text{coefficient of } Ag_2CrO_4} = \frac{2}{1} = 2$
Calculate the number of moles of unknown substance.	$n(AgNO_3) = n(Ag_2CrO_4) \times 2$ $= 3.98 \times 10^{-3} \times 2$ $= 7\ 96 \times 10^{-3}$ mol
Calculate the mass of unknown substance in the sample.	The question asks for % of silver not silver nitrate, so using mole ratios: $n(Ag) = n(AgNO_3) = 7.96 \times 10^{-3}$ mol $m(Ag) = n \times M$ $= 7.96 \times 10^{-3} \times 107.87$ $= 0.858$ g
Calculate the percentage mass of the unknown substance in the 50.0 g of sample.	$\%\, Ag = \frac{0.858}{50.0} \times 100$ $= 1.72\%$

Worked example: Try yourself 15.3.3

USING A PRECIPITATION TITRATION TO DETERMINE THE CONCENTRATION OF METAL IONS IN A SAMPLE

The concentration of Zn^{2+} ions in a solution was determined by a precipitation titration with 15.00 mL aliquots of a 0.100 mol L^{-1} solution of NaOH. A few drops of ferric cyanide ($Fe(CN)_6{}^{3-}$) containing indicator are added to the NaOH. The mean titre of Zn^{2+} solution required was 23.40 mL. What was the molar concentration of zinc ions?

Thinking	**Working**
Write an ionic equation for the precipitation reaction.	$Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s)$
Calculate the amount of NaOH, in mol, in the aliquot.	$n(NaOH) = c \times V = 0.100 \times 0.01500 = 0.00150$ mol
Use the balanced equation to calculate the amount of Zn^{2+} ions, in mol, that reacted.	$n(Zn^{2+}) = \frac{1}{2} \times n(OH^-) = \frac{1}{2} \times n(NaOH)$ $= \frac{1}{2} \times 0.00150$ $= 0.000750$ mol
Determine the concentration of Zn^{2+} ions in the solution.	$c(Zn^{2+}) = \frac{n}{V}$ $= \frac{0.000750}{0.02340}$ $= 0.0321$ mol L^{-1}

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Worked example: Try yourself 15.3.4

USING A CONDUCTOMETRIC TITRATION TO DETERMINE THE CONCENTRATION OF METAL IONS IN A SAMPLE

The concentration of Ag^+ ions in a solution was determined by a conductometric precipitation titration with 20.00 mL aliquots of a 0.0500 mol L^{-1} solution of NaCl.

The mean titre of Ag^+ solution required was 11.60 mL. What was the molar concentration of silver ions?

Thinking	**Working**
Write an ionic equation for the precipitation reaction.	$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
Calculate the amount of NaCl, in mol, in the aliquot.	$n(\text{NaCl}) = c \times V = 0.0500 \times 0.02000 = 0.00100$ mol
Use the balanced equation to calculate the amount of Ag^+ ions, in mol, that reacted.	$n(Ag^+) = n(Cl^-) = n(\text{NaCl}) = 0.00100$ mol
Determine the concentration of Ag^+ ions in the solution.	$c(Ag^+) = \frac{n}{V}$ $= \frac{0.00100}{0.01160}$ $= 0.0862$ mol L^{-1}

15.3 Review

1 C. This equation shows silver bromide precipitating from the mixture of solutions of silver nitrate and lithium bromide. To be used for gravimetric analysis the chemical reaction must form a solid (precipitation reaction).

2
- **a** false
- **b** true
- **c** true
- **d** true (as long as the precipitate is stable when heated)
- **e** true
- **f** true
- **g** true

Gravimetric analysis cannot be used if the salt of interest is insoluble. Even if the salt is soluble, the technique still requires at least one of the ions in the salt to form insoluble substances when other reactants are added. For accurate results, the precipitate should be washed carefully and then dried thoroughly. The precipitate must be relatively stable so that its composition does not change during heating.

3

Poor practice	**Impact**
Precipitate is not dried to constant mass.	Mass of the precipitate is too high because of the presence of water.
Precipitate is not washed with deionised water.	Mass of the precipitate is too high because of the presence of impurities.
Precipitate is left on the sides of the flask.	Precipitate is pure but due to sample loss its measured mass is lower than it should be.
Precipitate decomposes when heated.	The composition of the precipitate is not known.

4
- **a** Silver nitrate. All nitrate salts are highly soluble.
- **b** $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
- **c** The mass of the precipitate will be used to initially calculate the number of moles of silver chloride.

  mole ratio $= \frac{\text{coefficient of NaCl}}{\text{coefficient of AgCl}} = \frac{1}{1} = 1$

5 $n(Ca_3(PO_4)_2) = \frac{m}{M} = \frac{5.64}{310.18} = 0.0182$ mol

$n(Ca(NO_3)_2) = 3 \times n(Ca_3(PO_4)_2) = 0.0182 \times 3 = 0.0546$ mol

$m(Ca(NO_3)_2) = n \times M = 0.0546 \times 164.10 = 8.96$ g

6
- **a** $n(Al_2(CO_3)_3) = \frac{m}{M} = \frac{4.68}{233.99} = 0.0200$ mol
- **b** mole ratio $= \frac{\text{coefficient of Al(NO}_3)_3}{\text{coefficient of Al}_2\text{(CO}_3)_3} = \frac{2}{1} = 2$

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c $n(\text{Al(NO}_3)_3) = 2 \times n(\text{Al}_2(\text{CO}_3)_3) = 2 \times 0.0200 = 0.0400\,\text{mol}$

$m(\text{Al(NO}_3)_3) = n \times M = 0.0400 \times 213.01 = 8.52\,\text{g}$

7 $n(\text{HgI}_2) = \frac{m}{M} = \frac{4.82}{454.39} = 0.0106\,\text{mol}$

mole ratio $= \frac{\text{coefficient of Hg(CH}_3\text{COO}\ _2}{\text{coefficient of HgI}_2} = \frac{1}{1} = 1$

$n(\text{Hg(CH}_3\text{COO)}_2) = n(\text{HgI}_2) = 0.0106\,\text{mol}$

$m(\text{Hg(CH}_3\text{COO)}_2) = n \times M = 0.0106 \times 318.70 = 3.38\,\text{g}$

8 **a** $2\text{KI(aq)} + \text{Pb(NO}_3)_2\text{(aq)} \rightarrow \text{PbI}_2\text{(s)} + 2\text{KNO}_3\text{(aq)}$

b $n(\text{Pb}^{2+}) = 0.5 \times n(\text{K}^+)$

c The conductance drops because the precipitation of PbI_2 leads to the total number of ions in the solution decreasing.

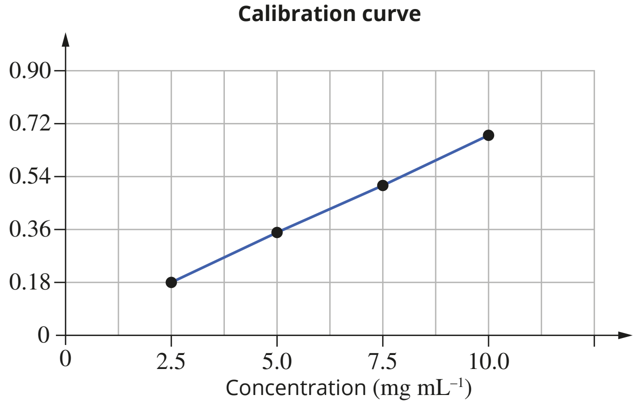
15.4 Determining salt concentration by colorimetry and UV–visible spectroscopy

Worked example: Try yourself 15.4.1

USING A CALIBRATION CURVE

Determine the lead level in a solution using the following colorimetry data.

Concentration of Pb^{2+} (mg mL^{-1})	Absorbance
2.5	0.18
5.0	0.35
7.5	0.51
10.0	0.68
sample	0.60

Thinking	**Working**
Construct a calibration curve from the data above. Concentration will be on the horizontal axis.	

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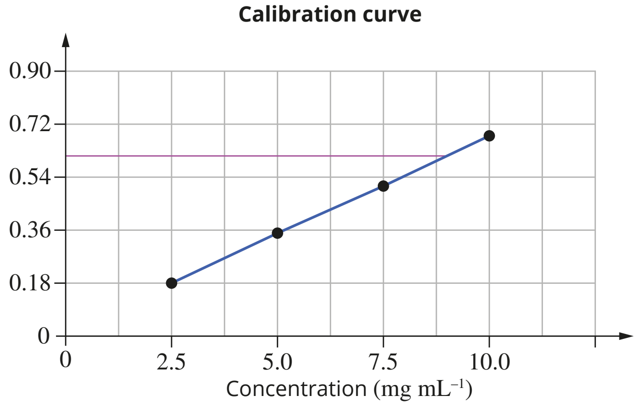
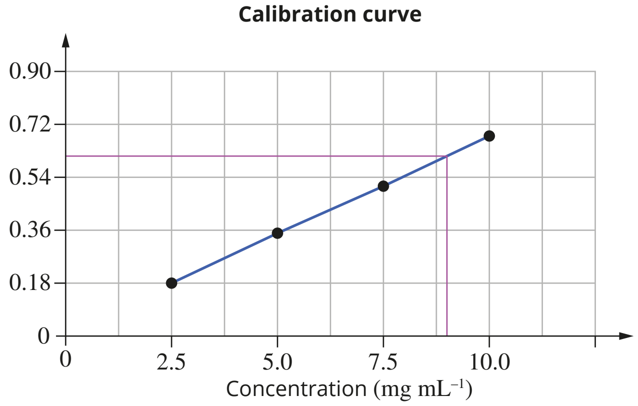
Mark where the absorbance of the sample lies on the calibration curve by tracing a horizontal line to the curve.	
Draw a vertical line from the absorbance value to the *x*-axis.	
Determine the concentration of the sample by reading the concentration value for the unknown solution from the *x*-axis.	The concentration of Pb^{2+} in the sample can be determined from the graph as 8.8 mg mL^{-1}.

15.4 Review

1 a 0.080 mol L^{-1} solution
  b 0.30 mol L^{-1} solution

2 Copper(II) sulfate is blue because it transmits blue light and absorbs light of other frequencies. Since a colorimeter measures the amount of light absorbed by a sample, light of a colour other than blue must be used when measuring the concentration of a copper(II) sulfate solution.

3 Blue. The sample is absorbing light with wavelengths of 600–700 nm. This means that the sample is absorbing red and yellow light but not blue light. If the sample is not absorbing blue light, the dye will be observed to be blue. Blue is the complement of red and yellow light.

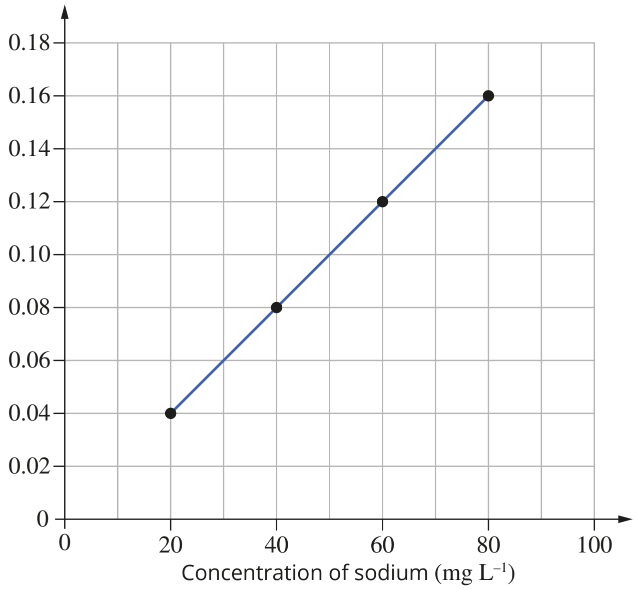
4 a From the calibration graph, an absorbance of 0.24 corresponds to a concentration of 0.15 mol L^{-1} Fe^{2+}.
  b The original solution was diluted by a factor of 4, so the concentration of Fe^{2+} ions in the tank water was $0.15 \times 4 = 0.60$ mol L^{-1}.
  c Fe^{2+} ions are oxidised to Fe^{3+} with acidified permanganate (H^+/MnO_4^-) before the addition of KSCN. The reaction of KSCN with Fe^{3+} forms the highly coloured red metal complex $FeSCN^{2+}$. The concentration of the complex can then be determined using spectrophotometry.

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

5

Solution colour	Complementary colour
green	purple
purple	green
orange	blue
green–yellow	violet
blue–green	red

6 **a** **AAS calibration curve for sodium analysis**



b Mark where the absorption of 0.42 of the sample lies on the calibration curve by tracing a horizontal line to the curve. Then drawing a vertical line from the curve to the horizontal axis. Read the concentration from the *x*-axis: concentration = 175 mg L^{-1}.

7 Blue is the complementary colour of orange. If potassium dichromate solutions are analysed in a colorimeter, a blue filter should be used. The sample will be placed in a glass or plastic cell and light directed at it. The higher the concentration of the solution, the more light is absorbed and the lower the intensity of the light arriving at the detector. A series of potassium dichromate solutions of different concentrations should be prepared and tested. The absorbances obtained allow a calibration curve to be prepared.

8 **a** There are two strong absorption peaks at 450 nm and 660 nm.

b Either 660 nm or 450 nm could be used, because chlorophyll absorbs strongly at both these wavelengths.

15.5 Determining concentration by atomic absorption spectroscopy

Worked example: Try yourself 15.5.1

USING A CALIBRATION CURVE TO DETERMINE CONCENTRATION

Determine the concentration of sodium in a sample given the data in the following table.

Concentration of sodium (μg mL^{-1})	Absorbance
20	0.041
40	0.080
60	0.121
80	0.159
sample	0.104

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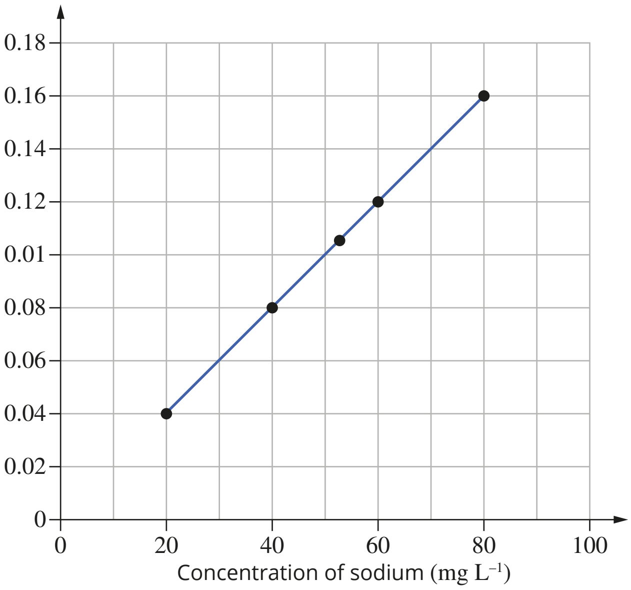
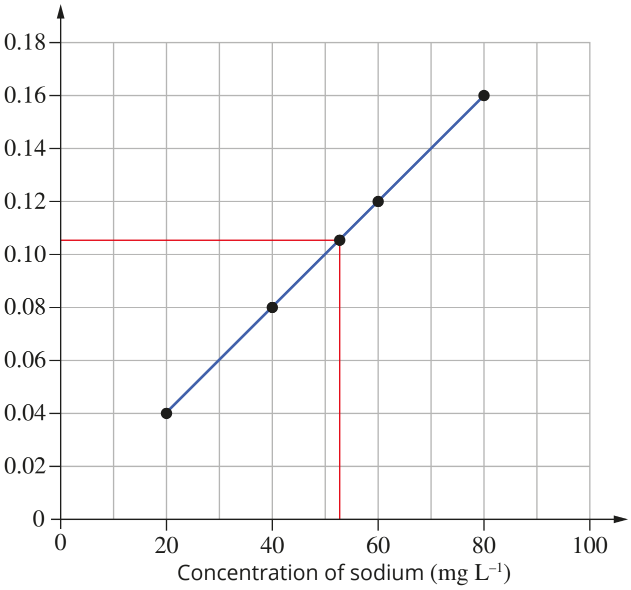
Thinking	Working
Construct a calibration curve using the concentrations of the standard solutions and their absorbance.	AAS calibration curve for sodium analysis 
Mark where the absorbance of the sample lies on the calibration curve. This can be done by finding the absorbance of the sample on the vertical axis and moving horizontally right until you reach the calibration curve and marking that point.	AAS calibration curve for sodium analysis 
Determine the concentration of the sample by reading off the graph on the horizontal axis at the point where the sample's absorbance lies on the calibration curve.	From the graph it can be determined that the concentration of sodium in the sample is $52\,mg\,L^{-1}$.

15.5 Review

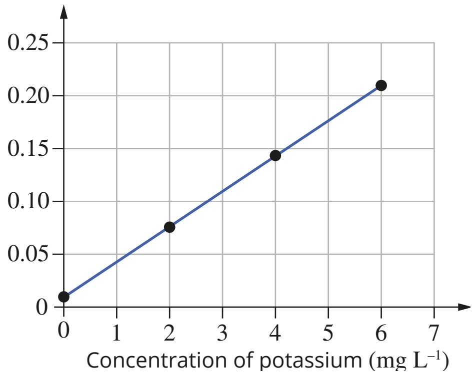
1. When a sample containing copper is heated in the flame of a Bunsen burner, the flame turns a green colour. This is because the *electrons* in the copper atoms absorb energy and move to *higher* energy levels and then *emit* light that corresponds to a green colour as they return to *lower* energy levels.
2. An emission spectrum is the spectrum of the light emitted by an element when it is heated. Atoms must be heated so that electrons move to higher energy levels, before returning to lower levels and emitting light.

3

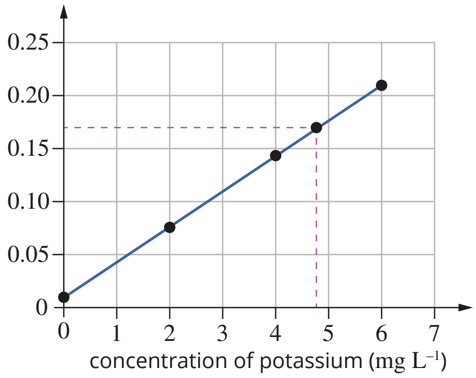
Component	Description
flame	where the sample is sprayed and light is absorbed
hollow-cathode lamp	produces light with wavelengths that are absorbed by the metal being analysed
computer	converts the amount of light detected into the amount of light absorbed by the sample
monochromator	selects a specific wavelength of light
detector	measures the amount of light

4 C. AAS does not heat a sample to a sufficient temperature to analyse all elements. It can, however, be used to analyse most metals but not non-metals.

5 **a** **AAS calibration curve for potassium analysis**



b **AAS calibration curve for potassium analysis**



concentration = 4.7 mg L^{-1}

6 **a** true

b false

c false

d true

e false

7 The absorbance of the sample increases as the concentration increases. The absorbance is directly proportional to the concentration.

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CHAPTER 15 REVIEW

1 **a** Any three of the following human activities lead to an increase in salts in our waterways: mining and industry lead to an increase of mercury and other heavy metals in the water system, and other sources are the burning of fuels containing trace amounts of mercury, leaching from landfill, incorrect disposal of batteries and fluorescent light bulbs. Run off from agriculture increases ammonium and phosphate levels because of their presence in fertilisers. Sewage treatment and domestic grey water increase levels of phosphate.

b They can be removed by precipitation reactions. Addition of calcium hydroxide will result in the precipitation of insoluble heavy metal hydroxides.

2 Many possible answers. Some regions are high in limestone, some high in particular minerals, Broken Hill being an obvious example.

3 **a** AgBr

b $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

c There are other metals ions such as Pb^{2+} that will form a precipitate with Br^- ions but the yellow colour would make Ag^+ highly likely.

4 **a** Copper gives a green flame.

b It is necessary to vaporise traces of other substances that could lead to a false result.

c Copper wire would give the flame a green colour, and so interfere with the test. The wire must be made of an element that does not change the colour of the Bunsen burner flame.

d Flame tests are rarely used for analysis by today's chemists because relatively few elements may be analysed in this way and the presence of one element (sodium, for example) may mask the presence of another. Also colours emitted by some elements are similar and difficult to distinguish, and a relatively large amount of sample is needed to give a clear colour.

5 **a** metal complex or complex ion

b Cl^-

c $Cu^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq)$

d HCl solution could be added to a solution containing copper(II) ions. If Cu^{2+} is present, this complex should form and it is likely to have a green colour.

6 No reaction with Cl^- rules out Pb^{2+} and Ag^+. A white precipitate suggests a main group metal, probably Al^{3+}.

7

$Ca(NO_3)_2$	Na_3PO_4	$Ca_3(PO_4)_2$	$NaNO_3$
27 mol	18	9.0	54
0.72	0.48 mol	0.24	1.44
0.54	0.36	0.18 mol	1.1
1.2	0.80	0.40	2.4 mol

8 **a** lead(II) chloride, lead(II) hydroxide, copper(II) hydroxide

b $Pb(NO_3)_2(aq) + CuCl_2(aq) \rightarrow PbCl_2(s) + Cu(NO_3)_2(aq)$

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

$Pb(NO_3)_2(aq) + Ba(OH)_2(aq) \rightarrow Pb(OH)_2(s) + Ba(NO_3)_2(aq)$

$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$

$CuCl_2(aq) + Ba(OH)_2(aq) \rightarrow Cu(OH)_2(s) + BaCl_2(aq)$

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

9 $n(AgCl) = \frac{m}{M} = \frac{0.169}{143.32} = 0.00118\,mol$

$n(Ag) = n(AgCl) = 0.00118\,mol$

$m(Ag) = n \times M = 0.00118 \times 107.87 = 0.127\,g$

$\%(Ag) = \frac{0.127}{0.693} \times 100 = 18.4\%$

10 Step 1. Write a balanced equation.

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

Step 2. Calculate the amount of AgCl.

$n(AgCl) = \frac{0.636}{143.32} = 0.004438\,mol$

Step 3. From the equation, 1 mol of NaCl produces 1 mol of AgCl.

$\frac{n(\text{NaCl})}{n(\text{AgCl})} = \frac{1}{1}$

$n(\text{NaCl}) = n(\text{AgCl}) = 0.004438\,\text{mol}$

Step 4. Calculate the mass of salt.

$m(\text{NaCl}) = n \times M = 0.004438 \times 58.44 = 0.2593\,\text{g}$

Step 5. Convert to percentage.

$\%(\text{NaCl}) = \frac{0.2593}{8.45} \times 100 = 3.0686\%$

Step 6. Express the answer with the correct number of significant figures.

$\%(\text{NaCl}) = 3.07\%$

11 Step 1. Find the percentage of P in $Mg_2P_2O_7$.

$\%(\text{P}) = \frac{2 \times 30.97}{222.56} \times 100 = 27.83\%$

Step 2. Using the %(P) in $Mg_2P_2O_7$, calculate the mass of P in the precipitate.

$m(\text{P}) = 27.83\%$ of 0.085

$\frac{27.83}{100} \times 0.085 = 0.02366\,\text{g}$

Step 3. Calculate the percentage (P) in 2.0 g of washing powder.

$\%(\text{P}) = \frac{0.02366}{2.0} \times 100 = 1.183\%$

Step 4. Express the answer with the correct number of significant figures.

$\%(\text{P}) = 1.2\%$

12 The mass of the precipitate is higher than it should be. The experimental errors that could lead to a high result include: the precipitate was not dried completely, the precipitate was not washed, the presence in the solution of other metal ions that form precipitates.

13 **a** $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

b $2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$

c $n(Ag^+) = c \times V = 0.084 \times 0.01420 = 0.0012\,\text{mol}$

$n(\text{NaCl}) = n(Ag^+) = 0.0012\,\text{mol}$

$c(Na^+) = \frac{n}{V} = \frac{0.0012}{0.02000}$

$= 0.060\,\text{mol}\,\text{L}^{-1}$

14 **a** $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

b The formation of precipitate is lowering the concentration of ions in the solution. Conductivity depends upon the ion concentration.

c No further precipitate can form so each time more ions are added the conductivity increases.

d The two lines can be drawn from two readings of conductivity before equivalence point and two after. The value of the equivalence point is the intersection of the two lines.

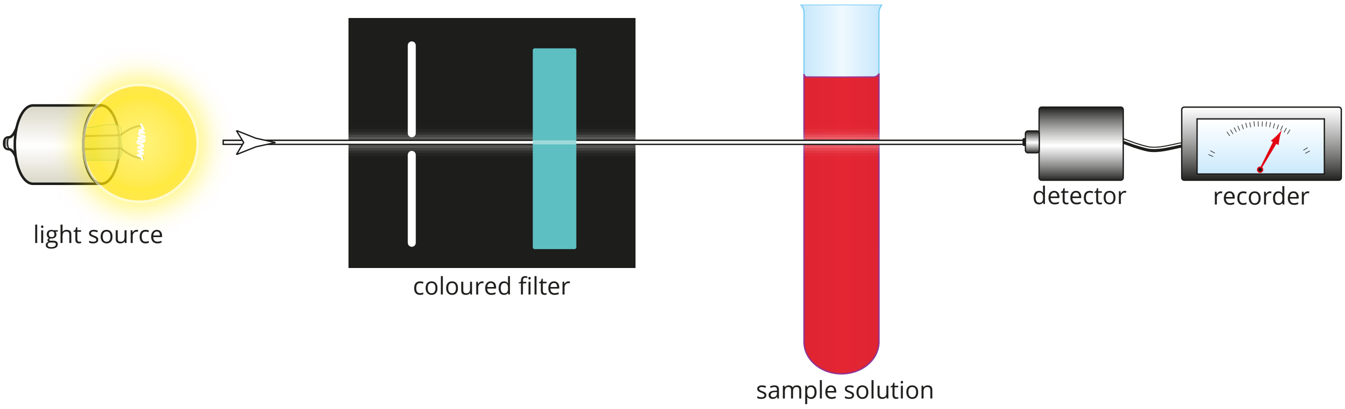
e $n(SO_4^{2-}) = c \times V = 0.02000 \times 0.14 = 0.0028\,\text{mol}$

$n(Ba^{2+}) = n(SO_4^{2-}) = 0.0028\,\text{mol}$

$c(Ba^{2+}) = \frac{n}{V} = \frac{0.0028}{0.012}$

$= 023\ \text{mol}\,\text{L}^{-1}$

15



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16 **a** 700 nm

b Light is absorbed in the orange/red region.

c The solution would be blue.

17

Component	**Function**
detector	measures the intensity of light
filter	selects a range of wavelengths of light
light source	provides ultraviolet and visible light of all wavelengths
monochromator	allows selection of light of a particular wavelength
sample cell	transparent container that holds the sample
recorder	displays the absorbance measurement

18 **a** $0.10\,\text{mol}\,\text{L}^{-1}$

b $n(\text{phosphorous}) = c \times V = 0.10 \times 0.25 = 0.025\,\text{mol}$

$m(\text{phosphorous}) = n \times M = 0.025 \times 30.97 = 0.774\,\text{g}$

$$\%\text{phosphorus} = \frac{0.774}{2.5} \times 100 = 30.97\%$$

$= 31\%$ to 2 significant figures

c Orange light of wavelength 600 nm is strongly absorbed by a blue solution.

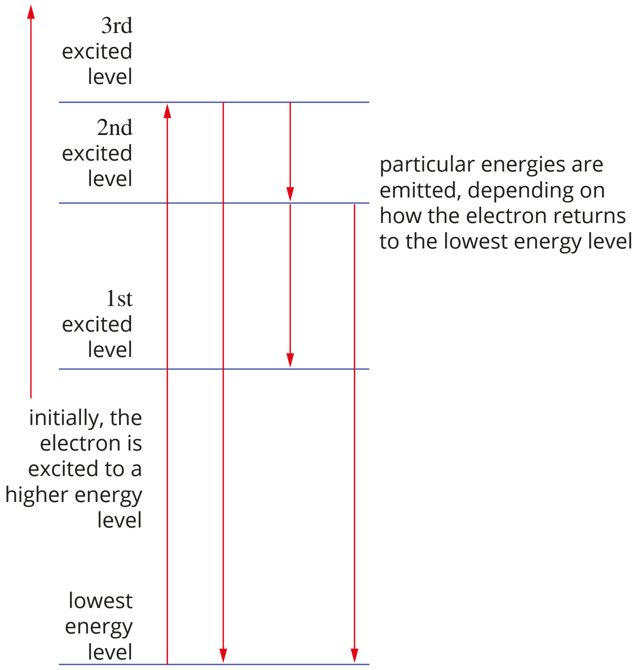
19 **a** false

b false

c true

d false

20 When atoms absorb energy, it is often possible for electrons to be promoted to various higher energy levels. Electrons can return to the ground state from these excited states by undergoing a number of transitions of different energy. (This is shown in the diagram.) Each transition results in a line of specific energy in the emission spectrum.

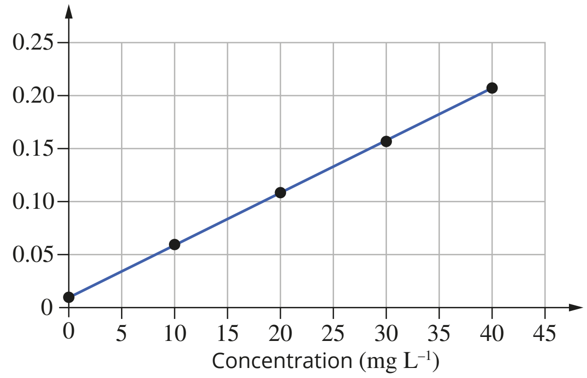


21 The absorption of light occurs in the flame of the spectrometer.

22 **a** Both involve the absorption of electromagnetic radiation of particular wavelengths characteristic of the substance under investigation. The amount of radiation absorbed is measured by a detector. The amount of light absorbed is proportional to the amount of the light-absorbing substance in the sample.

b In AAS, the sample is sprayed into a flame and light of a particular wavelength is passed through the flame. Atoms of the element being analysed absorb some of the radiation and the amount of light absorbed indicates the amount of the element present in the sample. AAS can be used to detect most metals. In UV–visible spectroscopy, two lights are used to produce radiation covering the visible and UV spectrum. The 'light' is passed through a prism to produce the desired wavelength; for UV analysis a silica sample holder is used. UV spectroscopy can be used to analyse many colourless compounds as well as coloured ones. It can give information about the structure of the substance. UV–visible spectroscopy can be used to determine the concentration of ions and molecules, including complex organic substances.

23 **a** **Calibration of AAS-lead**



b From the graph, the concentration of lead in the sample is 26 mg L^{-1}.

24

Technique	Feature
conductometric titration	Conductivity is measured while one solution is added to another.
atomic emission spectroscopy	A sample is injected into a flame.
colorimetry	A filter is used to select a range of wavelengths of visible light.
UV–visible spectrometry	A monochromator selects light of an exact wavelength that is strongly absorbed by the sample.
gravimetric analysis	The mass of a precipitate is used to determine the concentration of a salt.

25 **a** $Al_2(SO_4)_3(aq) + 3Ba(NO_3)_2(aq) \rightarrow 3BaSO_4(s) + 2Al(NO_3)_3(aq)$

$Na_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$

b $n(BaSO_4) = \frac{m}{M} = \frac{3.76}{233.39} = 0.0161$ mol

$n(SO_4^{2-}) = n(BaSO_4) = 0.0161$ mol

c The total number of moles of sulfate is 0.0161. Since $Al_2(SO_4)_3$ and Na_2SO_4 are present in equimolar amounts, the number of moles of sulfate from the $Al_2(SO_4)_3$ is three times that from the Na_2SO_4.

$n(SO_4^{2-}$ from $Na_2SO_4) = \frac{0.0161}{4} = 0.00403$ mol

$n(SO_4^{2-}$ from $Al_2(SO_4)_3) = 3 \times 0.00403 = 0.0121$ mol

26 **a** Fe_2O_3

b $n(Fe) = 2 \times n(Fe_2O_3) = 2 \times 2.4 = 4.8$ mol

c No. All compounds containing sodium ions are soluble in water.

27 **a** Use a green filter. (A complementary colour to red needs to be used in the colorimeter)

b The mole ratio will be 1.

c The absorbance obtained from a sample needs to be plotted on a calibration curve constructed from a series of standard solutions of the $FeSCN^{2+}$ complex.

d The lamp used must match the element being tested. A hollow-cathode lamp with an iron (Fe) filament should be used.

28 **a** The solution should show no reaction with HCl but should form a blue precipitate with ammonia.

b The solution should show no reaction with $AgNO_3$ but should form a white precipitate with $BaCl_2$.

c green

d a hollow-cathode lamp containing a copper filament

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

f $Cu^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}$ (aq), or
$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$

29 Student answers will vary. A possible answer is to compare the electrical conductivity of a salt solution and a sugar solution. Students could set up an electrical circuit using electrode plates in a solution of salt and then a solution of sugar. They could read results from an ammeter, or observe a light bulb to see if it glows when the electrodes are placed in the solution.

The salt solution will conduct electricity because the salt dissociates in water to release Na^+ and Cl^- ions. These ions are free to move within the solution and can therefore gain or lose an electron at the electrode they are attracted to, creating a circuit. When sugar dissolves in water it does not dissociate into ions, so it does not conduct electricity.

Chapter 16 Analysis of organic substances

16.1 Chemical tests for functional groups

16.1 Review

1 Test a solution of the compound by adding some solid $NaHCO_3$ to it. The presence of an acid is indicated by the formation of bubbles of CO_2. The presence of CO_2 is confirmed by bubbling the gas through limewater. An indicator will change colour in the presence of an acid. Carboxylic acids react with alcohols, forming esters that have fruity odours. This reaction occurs in the presence of a catalyst such as sulfuric acid.

2 Add some bromine water to the liquid. This will become colourless as it reacts with the carbon–carbon double bond if the liquid is an alkene.

3 **a** A small piece of metallic sodium will react with an alcohol, producing hydrogen gas.

  b Primary and secondary alcohols react with an acidified dichromate solution, which changes colour from orange to green. Tertiary alcohols do not react with an acidified dichromate solution. Similarly, when primary and secondary alcohols react with acidified permanganate solution, the colour changes from purple to colourless. Tertiary alcohols do not react with acidified permanganate solution.

  Primary alcohols do not react with a $ZnCl_2$/concentrated HCl mixture. Secondary alcohols react slowly with a $ZnCl_2$/concentrated HCl mixture, and tertiary alcohols react quickly.

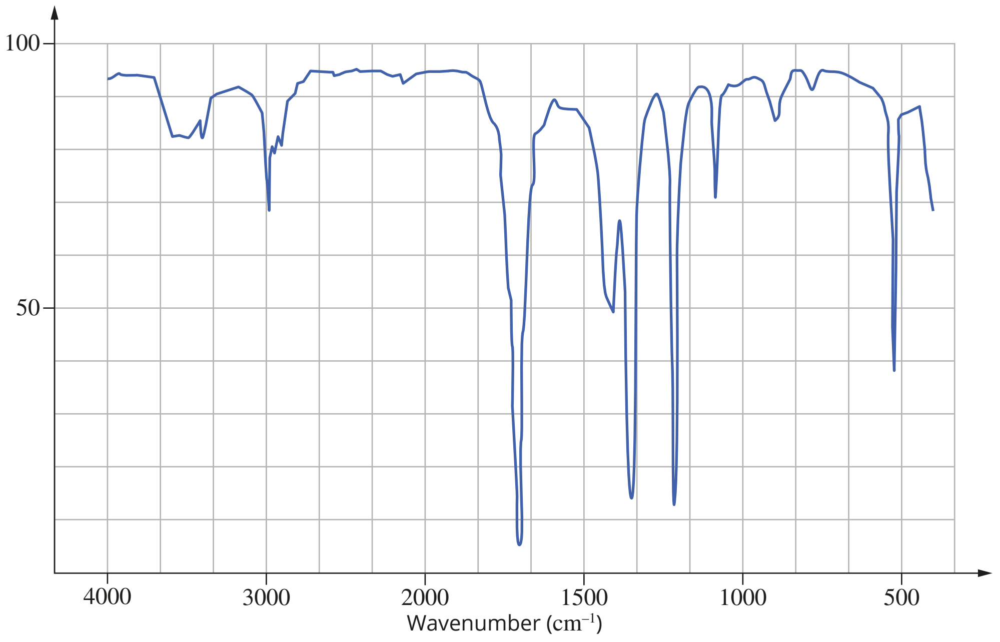
4 The bromine test indicated the presence of a carbon–carbon double bond while the reaction with sodium hydrogen carbonate indicated the presence of the carboxyl functional group (–COOH).

16.2 Infrared spectroscopy

Worked example: Try yourself 16.2.1

INTERPRETING THE INFRARED SPECTRUM OF AN UNIDENTIFIED COMPOUND

Use the following infrared spectrum of an unidentified compound to identify the functional groups present. The molecular formula of the compound is C_3H_6O. You will need to refer to the IR absorption data in Table 16.2.4 (page 473).



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Thinking	Working
Identify the absorption bands that correspond to the absorption bands of bonds in the IR absorption data table.	There is a strong, narrow band at approximately 1700 cm^{-1}, which corresponds to the absorption by a carbonyl group (C=O). There is a weak, narrow band at approximately 2900 cm^{-1}, which corresponds to the absorption by a C–H bond.
Identify the functional group or groups that are present.	The spectrum shows absorption bands corresponding to the presence of C=O carbonyl group and C–H bonds. This, in conjunction with the molecular formula, suggests that the compound is propanone (CH_3COCH_3).

16.2 Review

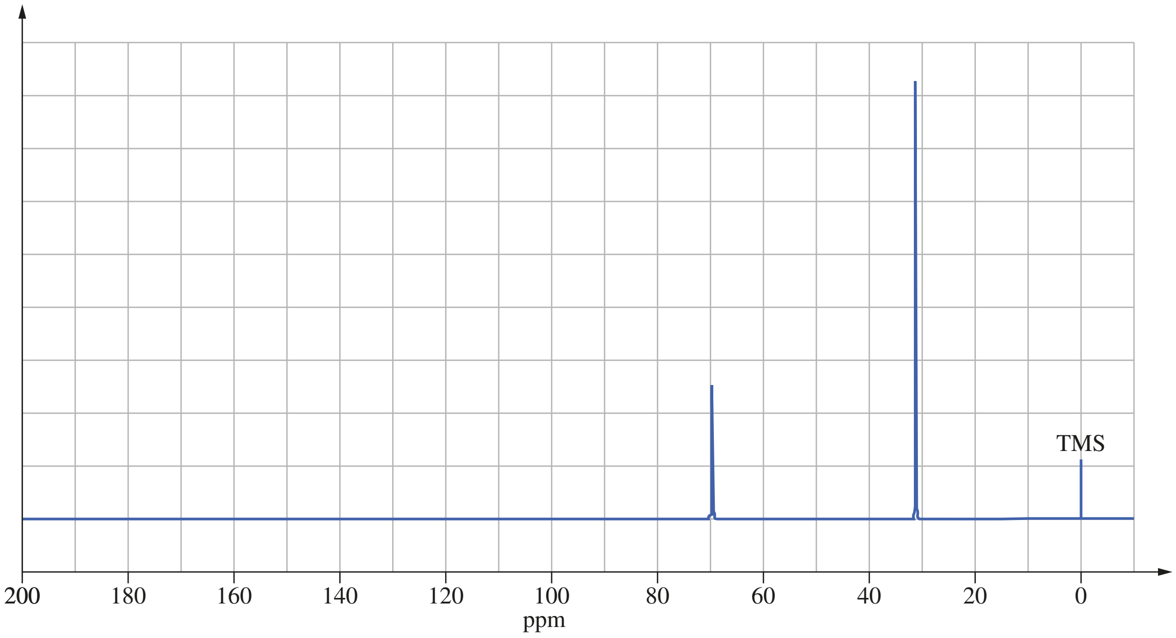
1 **a** vibrational
  b valence electron movement
  c valence electron movement
2 **a** microwave
  b infrared
  c radio
  d gamma rays
3 **a** O–H at 3230–3550 cm^{-1} and C–O at 1000–1300 cm^{-1}
  b N–H at 3300–3500 cm^{-1} and C=O at 1680–1750 cm^{-1}
  c N–H at 3300–3500 cm^{-1}
  d O–H at 2500–3000 cm^{-1}, C=O at 1680–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
  e C=O at 1680–1750 cm^{-1} and C–O at 1000–1300 cm^{-1}
  f C=O at 1680–1750 cm^{-1}
4 The absorption bands from C–O and C–C bonds are in the fingerprint region below 1400 cm^{-1}. Many molecules contain these bonds in various functional groups, so they give few clues to the structure of a compound. The exact wavenumber of C–O and C–C absorption bands are highly specific to an individual molecule. Along with the rest of the molecule's spectrum. they can be compared to a spectral data base for positive identification.
5 **a** O–H (acids) at approx. 3000 cm^{-1}, C=O at approx. 1700 cm^{-1}
  b C–H at approx. 2800 cm^{-1}, C=O at approx. 1700 cm^{-1}
  c O–H (alcohols) at approx. 3300 cm^{-1}, C–H at approx. 2800 cm^{-1}
  d N–H (amines) at approx. 3400 cm^{-1}, C–H at approx. 2900 cm^{-1}, C=O at approx. 1700 cm^{-1}

16.3 Nuclear magnetic resonance spectroscopy

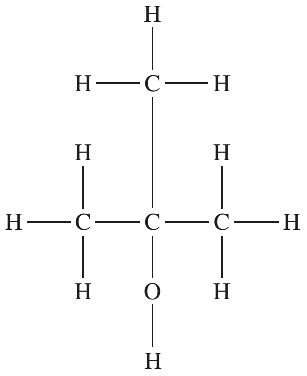
Worked examl: Try youself1.3.1

NTERPRETNG A CARBON-13 NUCLEAR MAGNEIC RESONANCE SPECTRUM

The carbon-13 NMR spectrum of an alcohol that has the molecular formula $C_4H_{10}O$ is shown below. Determine the structure and identity of the alcoho.



Thinking	Working
What information does the formula provide about the compound?	Four alcohol isomers are possible from the formula: butan-1-ol, butan-2-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol.
Identify the number of different carbon environments.	There are two signals so there must be two different carbon environments.
Identity the number of equivalent carbon atoms	The formula indicates that there are four carbon atoms in a molecule of the compound. The number of peaks indicates that there are two different carbon environments. So there must be three equivalent carbon atoms.
If possible, use the chemical shifts in Table 16.3.1 (page 483) to identify the types of carbon atoms. Remember that the ranges are broad.	The peak at 70 ppm indicates the presence of a carbon atom attached to a hydroxyl group (C–OH). The peak at 30 ppm is generated by the carbon atom in a $–CH_3$ group.

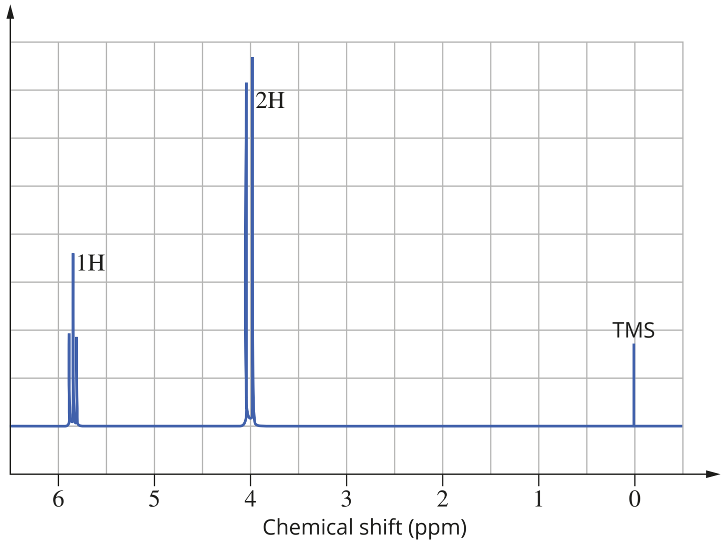
Determine a structure of the compound that is consistent with the information you have gathered. Remember that equivalent carbon atoms generate peaks with the same chemical shift.	The molecular formula of the alcohol is $C_4H_{10}O$. The compound is either butan-1-ol, butan-2-ol, 2-methylpropan-1-ol or 2-methylpropan-2-ol. The carbon-13 NMR spectrum has two peaks, indicating two unique carbon environments. However, the molecule has four carbon atoms so there must be three carbon atoms that are equivalent. This suggests that there are three identical $-CH_3$ groups in the structure. The structure of the compound consistent with this data is: 
Identify the compound.	The compound is 2-methlypropan-2-ol.

Worked example: Try yourself 16.3.2

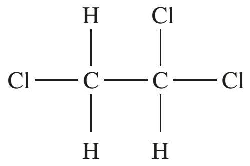
INTERPRETING A PROTON NUCLEAR MAGNETIC RESONANCE SPECTRUM

The proton NMR spectrum of a compound with a molecular formula of $C_2H_3Cl_3$ is shown below. Relative peak areas are shown on the spectrum.

Identify this compound using the information provided in the NMR spectrum.



<table>
<tr><th>Thinking</th><th>Working</th></tr>
<tr><td>What information does the formula provide about the compound?</td><td>Two molecules are possible from the formula: either 1,1,1-trichloroethane or 1,1,2-trichloroethane.</td></tr>
<tr><td>Summarise the information provided in the NMR spectrum in a table.</td><td><table>
<tr><th>Chemical shift</th><th>Peak splitting</th><th>Relative peak area</th></tr>
<tr><td>4.0</td><td>doublet (2-line pattern)</td><td>2</td></tr>
<tr><td>5.8</td><td>triplet (3-line pattern)</td><td>1</td></tr>
</table></td></tr>
<tr><td>Identify the number of different hydrogen environments.</td><td>There are two signals so there must be two different hydrogen environments.</td></tr>
</table>

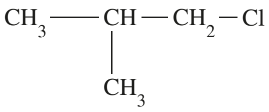
If possible, use the chemical shifts in Table 16.3.2 (page 489) to identify the types of protons. Remember the ranges are broad.	The table does not give information about compounds containing three chloro groups, so continue on to the next step.
Use the relative peak area to deduce the number of hydrogen atoms in each environment.	The relative area peak areas of the signals at 5.8 and 4.0 ppm are 1:2, so the relative number of hydrogen atoms must be 1:2. The sum of hydrogen atoms in the formula is 3, which means that the peak areas are directly equal to the number of hydrogens in each environment. This also supports the splitting information, confirming that the molecule contains one –CH– group and one $–CH_2–$ group.
Use the peak splitting of the signals to identify the types of hydrogen environments.	The signal at 4.0 ppm is a doublet (2-line pattern). The number of lines in the pattern is given by $n + 1$. This signal must be generated by an environment that has 1 neighbouring hydrogen atom, i.e. a –CH group. The signal at 5.8 ppm is a triplet (3-line pattern). The number of lines in the pattern is given by $n + 1$. This signal must be generated by an environment that has 2 neighbouring hydrogen atoms, i.e. a $–CH_2–$ group.
Use the information you gathered to identify the compound.	The molecular formula of the compound is $C_2H_3Cl_3$. The compound is either 1,1,1-trichloroethane or 1,1,2-trichloroethane. The splitting patterns and peak area indicates that the molecule contains a $–CH_2–$ group adjacent to a –CH– group. The molecule must be 1,1,2-trichloroethane because its structure fits the evidence from the spectrum. 

16.3 Review

1 **a** The carbon atoms in the two $–CH_3$ groups attached to the second carbon atom from the left are equivalent since both are bonded to the same –CH– group. The $–CH_3$ group on the right is not equivalent to these as it is attached to the $–CH_2–$ group rather than a –CH– group.

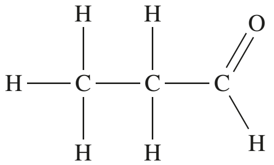
b The carbon-13 NMR spectrum has four peaks since the two equivalent carbon atoms identified in part **a** generate peaks having the same chemical shift.

2 C. From the structure of 1-chloro-2-methylpropane it can be seen that the carbon atoms in the two $–CH_3$ groups bonded to the –CH– carbon are equivalent. There are three different carbon environments in the molecule and therefore three peaks in the carbon-13 NMR spectrum.

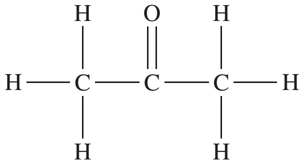


$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—Cl$$

3 The structres of propanal and propanone are shown below.



propanal



propanone

The carbon-13 NMR spectrum of propanal has three peaks since there are three different carbon environments in the molecule.

The carbon-13 NMR spectrum of propanone has two peaks since the carbon atoms in each $–CH_3$ group are equivalent and will generate peaks that have the same chemical shift. The carbon atom in the carbonyl group (C=O) generates the second peak.

4 **A** 20 ppm
B 170 ppm
C 60 ppm
D 14 ppm

5 **a** The number of signals indicates the number of non-equivalent hydrogen environments.
b The chemical shift of a signal indicates the type of hydrogen environment.
c The relative peak areas indicate the relative number of hydrogen atoms in each hydrogen environment.
d The splitting pattern of a signal indicates the number of hydrogen atoms neighbouring a specific hydrogen environment.

6 **a** **i** 2, **ii** 3, **iii** 4, **iv** 4
b **i** 2, **ii** 4, **iii** 4, **iv** 3
c triplet (3-line pattern), a quartet (4-line pattern) and a singlet (1-line pattern)
d 3:2

7 The signal is likely to be caused by $RCH{=}CHC\mathbf{H}_3$. This group has three hydrogen atoms, one hydrogen atom on a neighbouring atom and a typical chemical shift of 1.6–1.9 ppm.

8 **a** There are three peak sets, each representing a different hydrogen environment.
b From Table 16.3.2, the expected chemical shifts are:

$–COC\mathbf{H}_3$	2.1–2.7 ppm
$–C\mathbf{H}_3$	0.8–1.0 ppm
$–OC\mathbf{H}_2–$	3.3 ppm

c Relative number of protons for the peak sets is:
A:B:C = 2:3:3

d Using the *n* + 1 rule:

- The quartet at A indicates that there are three hydrogens attached to an adjacent atom.
- The single peak at B indicates that there are no hydrogens attached to the adjacent atom.
- The triplet at C indicates that there are two hydrogens attached to the adjacent atom.

e A = $–CH_2–$ group
B = methyl group of $CH_3COO–$
C = methyl group of $–CH_2CH_3$

f There will be four peaks in the carbon-13 NMR spectrum because there are four different carbon environments in the ethyl ethanoate molecule.

16.4 Mass spectrometry

Worked example: Try yourself 16.4.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak at $m/z = 58$. Determine the molecular formula of the alkane and give its name.

Thinking	Working
The *m/z* value of the molecular ion is equal to the relative molecular mass of the molecule.	The relative molecular mass of the alkane is 58.
Identify the general formula for the molecule.	The general formula for an alkane is C_nH_{2n+2}.
Use the general formula to set up an equation linking the relative molecular mass M_r to the relative atomic masses A_r of the constituent atoms.	$A_r\,(C) = 12$ $A_r\,(H) = 1$ $M_r\,(C_nH_{2n+2}) = (12 \times n) + 1 \times (2n + 2) = 58$
Solve the equation for *n*.	$12n + 2n + 2 = 58$ $14n + 2 = 58$ $14n = 56$ $n = 4$
Use the value of *n* to find the molecular formula and the name.	C_4H_{10}, which is butane.

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16.4 Review

1 **a** 114 $g\,mol^{-1}$. The molecular ion peak has a m/z value of 114. The relative molecular mass can be determined from the m/z value of the molecular ion peak. The molar mass of the compound is equal to its relative molecular mass.

b 43. The highest peak is called the base peak and is produced by the most abundant ion. The base peak is assigned a relative intensity of 100%.

c The general formula of an alkane is C_nH_{2n+2}. The relative molecular mass is given by:

$$\begin{aligned}(12 \times n) + 1 \times (2n + 2) &= 114\\ 14n + 2 &= 114\\ 14n &= 112\\ n &= 8\end{aligned}$$

The formula of the alkane is C_8H_{18}. The alkane is octane.

d $C_6H_{13}{}^+$. The fragment peak at m/z 85 has lost a fragment of relative mass 114 – 85 = 29. This corresponds to the loss of a C_2H_5 fragment. The formula of the fragment ion is $C_8H_{18}{}^+ - C_2H_5 = C_6H_{13}{}^+$.

2 $C_2H_4{}^{79}Br_2{}^+$, $C_2H_4{}^{79}Br^{81}Br^+$, $C_2H_4{}^{81}Br_2{}^+$

3 **a** The general formula of a bromoalkane is $C_nH_{2n+1}Br$

$$\begin{aligned}(12 \times n) + 1 \times (2n+1) + 81 &= 124\\ 14n + 82 &= 124\\ 14n &= 42\\ n &= 3\end{aligned}$$

The general formula is C_3H_7Br. A possible formula is $CH_3CH_2CH_2Br$.

b The peak at $m/z = 122$ is due to the molecular ion containing the ^{79}Br isotope and the peak at $m/z = 124$ is due to the molecular ion containing the ^{81}Br isotope.

c The two isotopes of bromine, ^{79}Br and ^{81}Br, are found in almost equal abundances so the peaks are almost equivalent in height.

d $CH_3CH_2CH_2{}^+$. The fragment peak at m/z 124 has lost a fragment of relative mass 125 – 43 = 81. This corresponds to the loss of a Br fragment.

4 **a** The general formula of a ketone is is $C_nH_{2n}O$. The relative molecular mass is given by:

$$\begin{aligned}(12 \times n) + (1 \times (2n)) + (16 \times 1) &= 72\\ 14n + 2n + 16 &= 72\\ 14n &= 56\\ n &= 4\end{aligned}$$

The formula of the compound is C_4H_8O.

b The general formula of a primary amide is $C_nH_{2n+1}ON$

The relative molecular mass is given by $(12 \times n) + 1 \times (2n + 1) + 16 + 14 = 59$

$$\begin{aligned}14n + 2n + 31 &= 59\\ 14n &= 28\\ n &= 2\end{aligned}$$

The formula of the compound is C_2H_5ON.

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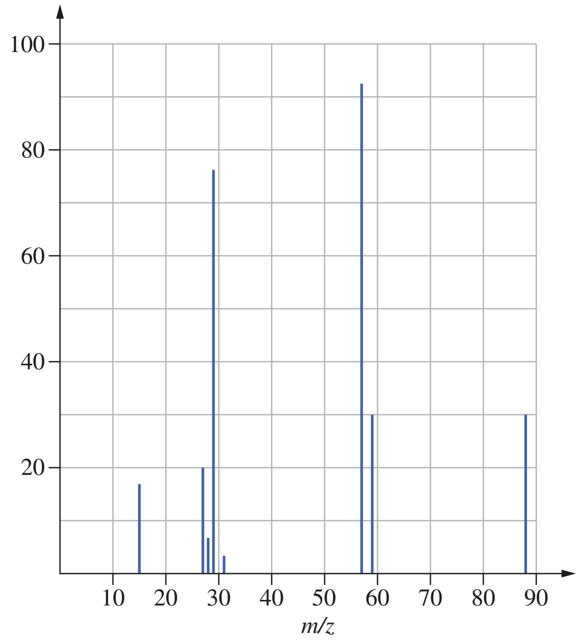
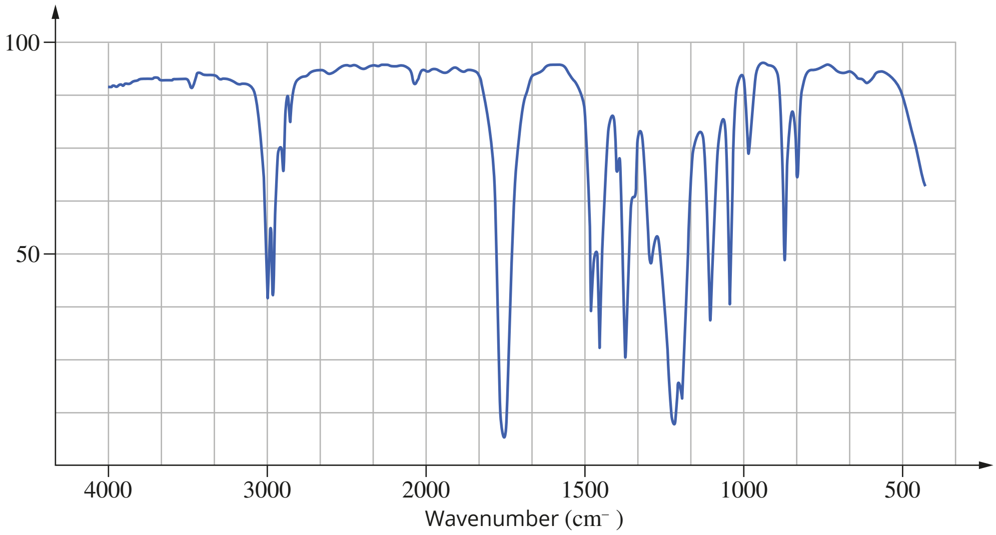
16.5 Determination of molecular structure by spectroscopy

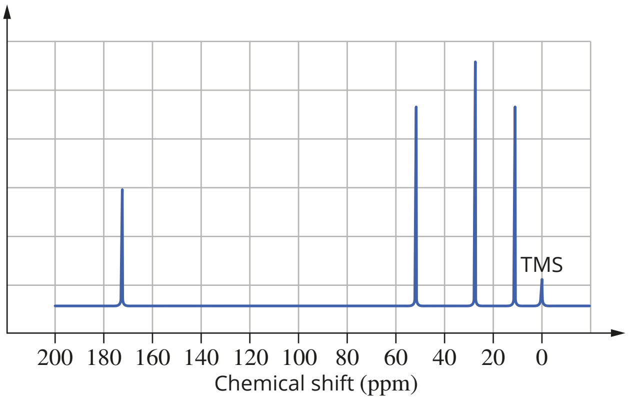
Worked example: Try yourself 16.5.1

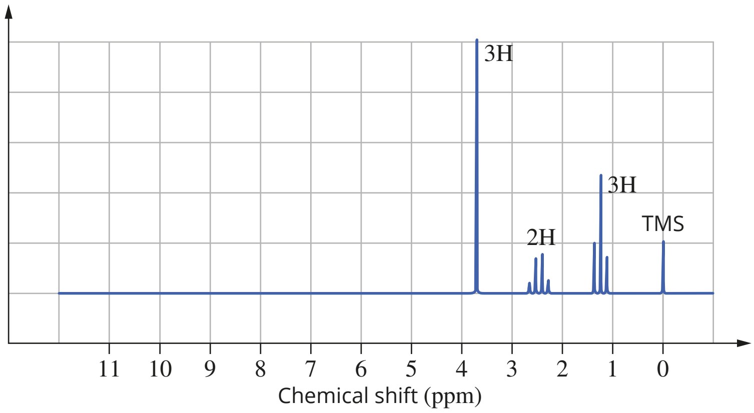
DEDUCING MOLECULAR STRUCTURE FROM SPECTROSCOPIC DATA

A fruity smelling liquid has an empirical formula of C_2H_4O. Chemical tests show that the compound is not an aldehyde or ketone. The chemical does not react with a solution of sodium hydrogen carbonate. Use this information and the mass, IR and NMR spectra provided to deduce the structure and name of the compound.









Thinking	**Working**
Use the mass spectrum to identify the molecular ion, and hence the relative molecular mass. Use this information to determine the molecular formula of the compound.	The peak with the largest mass-to-charge ratio is at $m/z = 88$ so the relative molecular mass is 88. This molecular mass is twice as heavy as the empirical formula mass, so the molecular formula must be $C_4H_8O_2$.
Use the molecular formula and any physical and chemical data provided to identify the categories of organic compounds to which the substance might belong.	The formula is consistent with that of a carboxylic acid or an ester. The fruity odour and lack of reactivity with a sodium hydrogen carbonate solution suggests that the compound is an ester.
Use the IR spectrum to identify functional groups present in the compound. (Refer to Table 16.2.4 on page 473).	The IR spectrum shows a strong absorption band at 1700 cm^{-1}, suggesting the presence of a C=O bond, and hence a carbonyl group. The IR spectrum does not contain a strong, broad absorption band in the range of 2500–3500 cm^{-1} that shows there is no O–H bond in the molecule and that the –COOH functional group found in carboxylic acids is not present. This confirms that the compound is an ester.
Use the carbon-13 NMR spectrum to identify the different carbon environments. (Refer to Table 16.3.1 on page 483.)	There are four signals in the carbon NMR spectrum and so the molecule contains four different carbon environments. The number of carbon environments corresponds to the number of carbons in the molecular formula, so each environment represents one carbon atom. The signal at 175 ppm is consistent with a carbon in a carbonyl group. The signal at 51 ppm is consistent with a carbon attached to an oxygen atom by a single bond. The signal at 27 ppm is consistent with a $-CH_2-$ group. The signal at 9 ppm is consistent with a methyl group ($-CH_3$).
Use the proton NMR spectrum to identify the different hydrogen environments. (Refer to Table 16.3.2 page 489.)	The proton NMR data is summarised in the following table. **Chemical shift (ppm)** / **Splitting pattern** / **Relative peak area** 1.1 / triplet (3-line pattern) / 3 2.3 / quartet (4-line pattern) / 2 3.7 / singlet (1-line pattern) / 3 The spectrum contains three signals and so there are three different hydrogen environments. The sum of the relative peak areas is 8, which is consistent with the molecular formula; each unit of peak area corresponds to one hydrogen atom.

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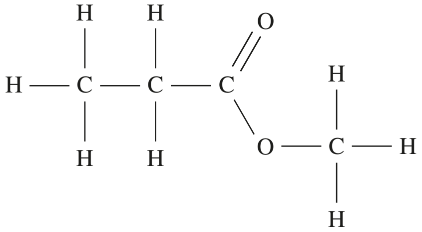
	The signal at 1.1 ppm is consistent with the signal produced by a –CH_3 group with two hydrogen atoms in a neighbouring environment. The signal at 2.3 ppm is consistent with the signal produced by a –CH_2– group bonded to the carbon of an ester group, with three hydrogen atoms in a neighbouring environment. The signal at 3.7 ppm is a singlet, indicating that there are no hydrogen atoms attached to adjacent atoms. The chemical shift is consistent with a methyl group singly bonded to an oxygen atom.
Use the data from the spectra to deduce the structure of the compound.	From the data provided by the spectra it can be summarised that: • the molecular formula of the compound is $C_4H_8O_2$ • the compound has a carbonyl group, but no hydroxyl group • it is not a carboxylic acid • it is an ester • the compound has a –CH_2CH_3 group attached to the carbon of a carbonyl group • the compound has a methyl group attached by a single bond to an oxygen atom. A structure consistent with this data is: 
Name the compound.	The compound is methyl propanoate.

16.5 Review

1 a IR spectroscopy

b mass spectrometry

c carbon-13 NMR spectroscopy

d proton NMR spectroscopy

2 a The absorption band at 3000 cm^{-1} is generated by the O–H bond in an acid. The absorption band at 1750 cm^{-1} is generated by the C=O bond in a carbonyl group. Together the two absorption bands indicate the presence of a –COOH functional group. The compound is a carboxylic acid.

b A carboxylic acid has the formula $C_nH_{2n}O_2$. The m/z of the molecular ion peak is the same as the relative molecular mass. Assigning relative atomic masses to C, H and O gives the following equation.

$$(12 \times n) + (1 \times 2n) + (2 \times 16) = 60$$
$$14n + 32 = 60$$
$$14n = 28$$
$$n = 2$$

The molecular formula is $C_2H_4O_2$ which is consistent with the formula of ethanoic acid (CH_3COOH).

c There are two carbon environments in CH_3COOH so the carbon-13 NMR will have two peaks: one peak with a chemical shift of about 20 ppm, corresponding to the carbon in the –CH_3 group; the other peak with a chemical shift of about 180 ppm, corresponding to the carbon in the –COOH group. There are also two hydrogen environments in CH_3COOH so the proton NMR will also have two peaks: one peak with a chemical shift of about 2 ppm, corresponding to the hydrogens in the –CH_3 group; the other peak with a chemical shift of about 11.5 ppm, corresponding to the hydrogen in the –COOH group.

3 a 60. The relative molecular mass of the compound shown is $(12 \times 3) + (1 \times 8) + (1 \times 16) = 60$. The molecular ion will therefore generate a peak at $m/z = 60$.

b The molecular formula shows that the compound is an alcohol with a hydroxyl (–OH) functional group, which generates a broad absorption band between 3230 and 3550 cm^{-1}.

c The two terminal $-CH_3$ are equivalent as both are attached to the same $-CH_2-$ group. The two $-CH_3$ will therefore generate signals that have the same chemical shift and are represented as a single peak in the carbon-13 NMR spectrum. The carbon atom in $-CH_2-$ is in a different chemical environment and will generate a signal having a different chemical shift. The carbon-13 NMR spectrum will show two peaks.

d The six hydrogen atoms on the two terminal $-CH_3$ groups are equivalent and will generate a single peak in the proton NMR spectrum. The hydrogen attached to the central carbon atom and the hydrogen attached to the oxygen atom will generate separate peaks since they are in different environments. The proton NMR spectrum will show three peaks.

4 **a** The absorption band at 3400 cm^{-1} is generated by the N–H bond in a primary amine.

b The molar mass of the amine is 59. The general formulae of an amine can be written as $C_nH_{2n+3}N$.

The molar mass of $C_nH_{2n+3}N = 59$

$$(12 \times n) + 1 \times (2n + 3) + 14 = 59$$

$$14n + 17 = 59$$

$$14n = 42$$

$$n = 3$$

The molecular formula is C_3H_9N.

c There are three peaks in the carbon-13 NMR, representing three different carbon environments. There are no equivalent carbon atoms since there are also three carbon atoms in the formula.

The proton NMR spectrum indicates that there are four hydrogen environments.

d $CH_3CH_2CH_2NH_2$, propan-1-amine.

5 The general formula of an alkane is C_nH_{2n+2}

$$(12 \times 2n) + 1 \times (2n + 2) = 72$$

$$14n + 2 = 72$$

$$14n = 70$$

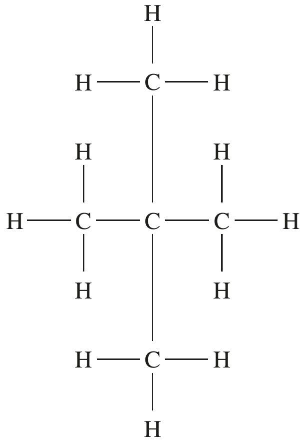
$$n = 5$$

The molecular formula is C_5H_{12}.

The carbon-13 NMR spectrum indicates that there are two different carbon environments. The molecular formula indicates that there are five carbon atoms in a molecule of the compound so there must be one carbon environment with four equivalent carbon atoms and another carbon environment with one carbon atom.

The proton NMR spectrum indicates that there is only one hydrogen environment, i.e. all the hydrogen atoms are equivalent.

The following structural formula is consistent with the data provided. The compound is 2,2-dimethylpropane.



6 The molecular formula suggests that the compound is either a ketone or an aldehyde.

A strong absorption band around 1750 cm^{-1} in the IR spectrum is consistent with the presence of C=O. A strong absorption band at 3000 cm^{-1} corresponds to the presence of a C–H bond.

The carbon-13 NMR spectrum indicates four peaks and therefore four different carbon environments. There are no equivalent carbon atoms because there are four carbon atoms in the molecular formula. The peak at 210 ppm indicates a carbonyl group (C=O). The peak at about 10 ppm is consistent with a $-CH_3$ carbon. The peak at 40 ppm suggests a $-CH_2-$ carbon.

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The proton NMR data is summarised in the following table:

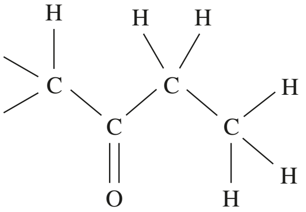
Chemical shift	Peak splitting	Relative peak area
1.0	triplet	3
2.1	singlet	3
2.4	quartet	2

There are three signals so there must be three hydrogen environments.

The sum of the peak heights is the same as the number of hydrogen atoms in the molecular formula so the relative peak heights indicates the actual number of hydrogen atoms in each environment. It can be deduced that there two different $-CH_3$ environments and one $-CH_2-$ environment.

Since there are four carbon environments and three hydrogen environments, one carbon atom has no hydrogen atoms attached to it and that is the C=O carbon.

In summary, the molecule has two different $-CH_3$ groups, a $-CH_2-$ group and a C=O group, suggesting that it has the following structure.



The compound is butanone ($CH_3CH_2COCH_3$).

7 100 g of the unidentified organic compound contains 48.6 g carbon, 8.2 g hydrogen and 43.2 g oxgyen. The molar masses are 12.01 g, 1.008 g and 16.01 g respectively.

$n(\mathrm{C}) = \frac{m}{M} = \frac{48.6}{12.01} = 4.05$

$n(\mathrm{H}) = \frac{m}{M} = \frac{8.2}{1.008} = 8.1$

$n(\mathrm{O}) = \frac{m}{M} = \frac{43.2}{16.00} = 2.7$

C:H:O = 1.5:3:1 = 3:6:2

The empirical formula is $C_3H_6O_2$.

In the mass spectrum, the peak due to the molecular ion has an *m/z* value of 74. This is equal to the relative molecular mass of the compound so the molecular formula is $C_3H_6O_2$.

The IR spectrum has a narrow band at about 1700 cm^{-1}, which indicates a C=O bond. There is a very broad band centred around 3000 cm^{-1}, which indicates an –OH group of a carboxylic acid. This slightly masks a peak just below 3000 cm^{-1} produced by C–H bonds.

The carbon-13 NMR spectrum shows that there are three different carbon environments. The peak at 9 ppm is generated by a $-CH_3$ carbon; the peak at 28 ppm is generated by a $-CH_2$ carbon. The carbonyl carbon generates the peak at 180 ppm.

The proton NMR spectrum shows that there are three different hydrogen environments. The sum of the peak heights is the same as the number of hydrogen atoms in the molecular formula so the relative peak heights indicates the actual number of hydrogen atoms in each environment.

The peak at 1.2 ppm is a triplet, indicating that there are two equivalent hydrogen atoms in the adjacent environment. The peak area indicates that there are three hydrogen atoms associated with this peak.

The peak at 2.5 ppm is a quartet, indicating that there are three equivalent hydrogen atoms in the adjacent environment. The peak area indicates that there are two hydrogen atoms associated with this peak.

The relative peak area and splitting pattern of the two peaks at 1.2 ppm and 2.5 ppm indicate the presence of an ethyl group ($-CH_2CH_3$).

The peak at 12 ppm is a singlet, indicating no hydrogen atoms in an adjacent environment, and therefore indicates a hydrogen of a carboxyl group.

The data suggests that the compound is a carboxylic acid with three carbons atoms, i.e. propanoic acid.

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CHAPTER 16 REVIEW

1 **a** Bromine water will become colourless when mixed with an alkene, indicating the presence of a C=C bond.

b Carboxylic acids react with $NaHCO_3$ solution to form CO_2 gas, which can be detected with limewater. Carboxylic acids contain the –COOH functional group.

c The –OH functional group in alcohols can be detected using a small piece of metallic sodium, which reacts slowly with alcohols to form bubbles of hydrogen gas.

2 An acidified dichromate solution turns green when added to a primary or secondary alcohol. No colour change occurs when acidified dichromate solution is added to a tertiary alcohol. This means that an acidified dichromate solution can be used to test for primary and secondary alcohols but not for tertiary alcohols. This test does not distinguish between primary and secondary alcohols.

3 Lowest to highest: C–Br, C–O, C–H. One factor affecting the frequency or wavenumber of IR radiation absorbed by a bond is the mass of the atoms in a bond. The higher the mass, the lower the frequency of radiation absorbed.

4 **a** Both spectra contain broad, strong absorption bands at 3300 cm^{-1}, which corresponds to the expected absorbance by alcohol O–H bonds. The spectra do not contain peaks at 1700 cm^{-1} and so they cannot be carboxylic acids.

b The two spectra have different absorption bands in the fingerprint region (below 1400 cm^{-1}) and so cannot be from the same molecule.

5 **a** broad absorption band at 3230–3550 cm^{-1}

b absorption bands at 3300–3500 cm^{-1} and 1680–1750 cm^{-1}

c absorption band at 1680–1750 cm^{-1}

d absorption band at 700–800 cm^{-1}

6 TMS is used as a reference in NMR spectroscopy. The location of a signal is compared to the TMS signal and called the chemical shift. The chemical shift is in units of ppm.

7 **A** Methyl ethanoate. The proton NMR spectrum of methyl ethanoate (CH_3COOCH_3) has two hydrogen environments and consequently has two peaks in the proton NMR spectrum. The number of hydrogen atoms in each environment is the same, as shown by the relative peak areas in the spectrum. This is consistent with the number of hydrogen atoms attached to the two carbon atoms as indicated in the molecular formula.

B Ethyl methanoate. The proton NMR spectrum of ethyl methanoate ($HCOOCH_2CH_3$) has three peaks because it has three hydrogen environments. The number of hydrogen atoms in each environment (as shown by the relative peak areas) match the number of hydrogen atoms attached to the carbon atoms as indicated in the molecular formula. The triplet and quartet splitting pattern of the peaks at 1 ppm and 4ppm respectively is characteristic of the ethyl group ($-CH_2CH_3$).

C Propanoic acid. Propanoic acid (CH_3CH_2COOH) has three hydrogen environments and the proton NMR spectrum has 3 peaks. The peak at 12 ppm is typical of a the peak generated by the hydrogen atom in a –COOH group. The triplet and quartet splitting pattern of the peaks at 1 ppm and 2.5 ppm respectively is characteristic of a $-CH_2CH_3$ group.

8 Proton NMR spectra can give an indication of the number of different hydrogen environments. The peak splitting indicates the environments of neighbouring hydrogens. For example, $-CH_2-$ splits signals from hydrogens on adjacent atoms into 3 peaks. The peak areas provide information about the number of equivalent hydrogen atoms. Carbon-13 NMR spectra give an indication of the number of different carbon environments. For example, two peaks indicate two different carbon environments. Chemical shift data can be used to indicate the type of carbon and hydrogen environments (e.g. C=O).

Because C_3H_6O is a ketone, it must be propanone. All of the hydrogens would be found in a $-CH_3$ bonded to a C=O, so there would be only one peak in the proton NMR spectrum. The chemical shift data from the carbon-13 NMR spectrum would show two peaks for the two carbon environments. One peak would correlate to a chemical shift indicating a $-CH_3$ carbon environment and another would correlate to the C=O carbon environment.

9

Compound	No. of peaks in carbon-13 NMR spectrum	No. of peaks in proton NMR spectrum
propane	2	2
CH_3CH_2Br	2	2
$CH_3COOCH_2CH_3$	4	3

10 **a** The molecular ion has an *m/z* of 44 due to $C_3H_8^+$.

b The base peak has an *m/z* of 29, which 15 less than that of the molecular ion and is caused by the loss of a CH_3 fragment. The peak at *m/z* = 29 is generated by the ion fragment $C_2H_5^+$.

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11 The *m/z* of the molecular ion is 54. Hence the relative molecular mass is 54. The general formula of an alkyne is C_nH_{2n-2}. Substituting the relative atomic masses of carbon and hydrogen into the general formula of an alkyne gives the following equation:

$$\begin{aligned}(12 \times n) + 1 \times (2n - 2) &= 54\\ 14n - 2 &= 54\\ 14n &= 56\\ n &= 4\end{aligned}$$

The molecular formula is C_4H_6.

12 **a** C_4H_{10}. The general formula of an alkane is C_nH_{2n+2}.

$$\begin{aligned}(12 \times n) + 1 \times (2n + 2) &= 58\\ 14n + 2 &= 58\\ 14n &= 56\\ n &= 4\end{aligned}$$

The molecular formula is C_4H_{10}.

b C_3H_6O. Carbon and hydrogen contribute $58 - 16 = 42$ mass units to the relative molecular mass of the compound. Three carbon atoms contribute $3 \times 12 = 36$ mass units to this amount leaving 6 mass units contributed by six hydrogen atoms. The formula of the compound is C_3H_6O.

c $C_2H_6N_2$. The two amine groups contribute $2 \times (1 \times 14 + 3 \times 1) = 34$ mass units to the relative molecular mass of the compound. This leaves 24 mass units that are contributed by carbon and hydrogen atoms. Two carbon atoms contribute 24 mass units to this amount. The molecule therefore does not contain any hydrogen in addition to those in the two amine groups. The formula of the compound is $C_2(NH_3)_2$ or $C_2H_6N_2$.

13 **a** **i** 98 corresponds to the molecular ion with two ^{35}Cl isotopes.

ii 100 corresponds to the molecular ion with one ^{35}Cl and one ^{37}Cl isotope.

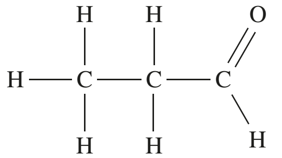
iii 102 corresponds to the molecular ion with two ^{37}Cl isotopes

b The most abundant Cl isotope is ^{35}Cl, so it has a higher peak.

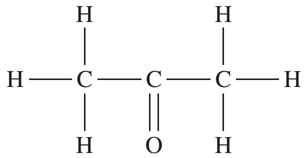
c If the haloalkane is 1,1-dichloroethane, it would be reasonable to expect peaks with $m/z = 15$ and $m/z = 83$ due to the fragment ions CH_3^+ and $CH^{35}Cl_2^+$ respectively that are produced when the molecular ion $CH_3CH^{35}Cl_2^+$ fragments. Since these peaks are not present, the haloalkane must be 1,2-dichloroethane.

d $^{35}ClCH_2CH^+$

14 Propanal. The molecular formula is that of either an aldehyde or a ketone i.e. either propanal or propanone. Their structural formulae are provided below.



propanal



propanone

Both compounds have a carbonyl group (C=O) which generates the IR absorption band at 1750 cm^{-1}.

The carbon-13 NMR spectrum indicates that there are three carbon environments in the molecule. This suggests that the compound is propanal. Propanone has only two only carbon environments since the carbon atoms in the two $-CH_3$ groups are equivalent. Consequently the carbon-13 NMR spectrum of propanone will only have two peaks.

The proton NMR data supports the conclusion that the compound is propanal. Propanal has three hydrogen environments each generating a peak. The triplet–quartet peak splitting pattern indicates the presence of a $-CH_2CH_3$ group. The proton NMR spectrum of propanone will only show a single peak since the six hydrogens in the two $-CH_3$ groups are equivalent.

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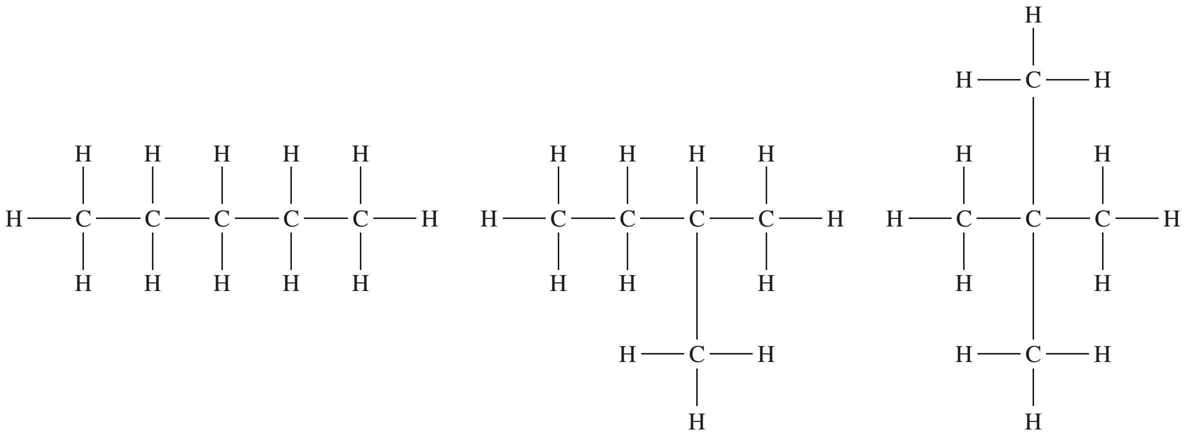
15 The compound is 2,2-dimethylpropane. The sum of the relative atomic masses shown in the empirical formula is 72. The *m/z* of the molecular ion peak indicates that the relative molecular mass of the compound is 72. Hence the molecular formula of the compound is C_5H_{12}, which is pentane. The three structural isomers of pentane are shown below.



The carbon-13 NMR indicates that there are two different carbon environments in the molecule which means that a number of carbon atoms must be equivalent. The single proton NMR spectrum peak indicates that all 12 hydrogen atoms are in the same environment i.e. there are four $–CH_3$ groups in the molecule. The structure of 2,2-dimethyl propane is consistent with the NMR data.

16 The mass spectrum shows a molecular ion with an *m/z* of 88, so the molecular formula is twice the empirical formula: $C_4H_8O_2$. This formula, together with the reaction with sodium hydrogen carbonate solution suggests that the compound is a carboxylic acid.

The IR spectrum shows strong absorption bands at 1700 and 3000 cm^{-1}, indicating the presence of carboxylic acid carbonyl and hydroxyl groups respectively, confirming that the compound is a carboxylic acid.

The proton NMR spectrum shows three signals, so there are three hydrogen environments. The sum of the relative peak areas is the same as the number of hydrogen atoms in the molecular formula. The signal at 1.1 ppm is a doublet with relative peak area of 6, and represents two equivalent $–CH_3$ groups with one hydrogen in a neighbouring environment. The signal at 2.6 ppm is a 7-line pattern with relative peak area of 1, and represents a –CH– neighbouring two $–CH_3$ groups. The singlet at 11.8 ppm represents a hydrogen in a –COOH group.

The carbon-13 spectrum shows only three signals, giving three carbon environments. Since there are four carbon atoms in the molecular formula so two carbon atoms must be equivalent. The carbon at 184 ppm is most likely a carbon in a –COOH group. The carbon signal at 19 ppm represents carbons in $–CH_3$ groups. The carbon signal at 35 ppm represents a carbon with two or more alkyl groups attached.

All the information gives a condensed structural formula of $(CH_3)_2CHCOOH$, with the name 2-methylpropanoic acid.

17 NMR spectroscopy is used to identify types of atoms within the molecule and can give information about their chemical environment and connectivity. IR spectroscopy is usually used to identify general functional groups in a molecule but can also be used for positive identification by analysing the fingerprint region compared to a reference. Mass spectrometry gives information about the molecular mass and possible fragments within a molecule, which can lead to confirmation of a possible structure.

18 **a** Proton NMR spectroscopy gives a large amount of information about organic molecules. It can be used to identify the number and types of hydrogen chemical environments, the relative amounts of hydrogen atoms in each environment and the connectivity of adjacent environments. It is fairly difficult to confirm which functional groups are present in a molecule by proton NMR spectroscopy alone.

b IR spectroscopy is extremely useful for identifying functional groups. Many molecules have isolated or symmetrical hydrogen environments, which leads to simpler and less informative spectra. Carbon NMR spectroscopy can be used to identify sections of a molecule that contain no hydrogen environments. Mass spectrometry is useful for ensuring that a proposed structure is correct. In many cases mass spectrometry is more powerful for the identification of molecules when the proton NMR spectroscopy is too complex to easily analyse.

19 The computer could look for specific ion peaks that would correspond to the molecular ions of illegal substances. It could then confirm the presence of these compounds by identifying the fragment ions of that compound.

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20 **a** carboxylic acids, esters, alcohols, aldehydes and ketones

b The chemical test suggests that the unknown substance is either an aldehyde or a primary or secondary alcohol, because these classes of organic compounds react with an acidified dichromate solution. The reaction of X with methanoic acid suggests that X might be an alcohol. Carboxylic acids react with alcohols to produce esters, which generally have a fruity smell. Since X did not react with bromine water it can be assumed that there no carbon–carbon double bonds in X. The lack of reaction with $NaHCO_3$ solution indicated that X was not a carboxylic acid.

c The broad absorption band centred at 3300 cm^{-1} in the IR spectrum indicates that X is an alcohol. The absence of an absorption band between 1680 cm^{-1} and 1750 cm^{-1} generated by substances that have a carbonyl carbon (C=O) indicates that X is not a carboxylic acid, ester, aldehyde or ketone.

d The evidence from the IR spectrum and chemical analysis indicates that X is an alcohol that contains no carbon–carbon double bonds. The general formula for a saturated alcohol is $C_nH_{2n+2}O$. The molecular ion peak of X occurs at $m/z = 74$, indicating that the relative molecular mass of X is 74.

$$\begin{aligned} M_r(X) = M_r(C_nH_{2n+2}O) &= 74 \\ (12 \times n) + 1 \times (2n + 2) + 16 &= 74 \\ 14n + 18 &= 74 \\ 14n &= 56 \\ n &= 4 \end{aligned}$$

The molecular formula of X is $C_4H_{10}O$.

e $CH_3CH_2CH_2CH_2OH$ $(CH_3)_2CHCH_2OH$

$CH_3CH_2CHOHCH_3$ $(CH_3)_3COH$

f The carbon-13 NMR spectrum has three peaks indicating that there are three different carbon environments. The formula for X indicates that a molecule of X has four carbon atoms, one more than the number of distinct carbon environments. Therefore two carbon atoms must have the same environment and be equivalent. Equivalent carbon atoms generate signals that have the same chemical shift.

g The compound is 2-methylpropan-1-ol.

21 The ball bearings with different sizes represent atoms with different masses.

In the ball bearing model of the mass spectrometer, steel ball bearings are accelerated as they move down the ramp. The interaction with the magnetic field causes them to move in a curved path. The radius of the path depends on the mass of the ball bearing.

In a mass spectrometer, atoms are ionised into positively charged ions by a beam of high-energy electrons. The positive ions are accelerated in an electric field, then move into a magnetic field where they travel in a curved path. The radius of the path depends on both the mass and charge of the ion. A computerised detector represents this information as a mass spectrograph showing the intensity of the ions and their mass-to-charge ratio, *m*/*z*.

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Chapter 17 Chemical synthesis and design

17.1 Chemical synthesis and design

Worked example: Try yourself 17.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

80.0 g of propan-1-ol was oxidised to propanoic acid using an acidified solution of $K_2Cr_2O_7$. The propanoic acid obtained at the end of the reaction had a mass of 55.0 g. Calculate the percentage yield of this oxidation reaction.

Thinking	**Working**
Write an equation for the reaction.	$C_3H_7OH \xrightarrow{H^+/Cr_2O_7^{2-}} C_2H_5COOH$ In this case it is not necessary to write a full equation. Because a molecule of the organic product has the same number of carbon atoms as the organic reactant, the number of moles of the product is equal to the number of moles of the reactant.
Use the formula $n = \frac{m}{M}$ to determine the amount of reactant.	$n(C_3H_7OH) = \frac{m}{M}$ $= \frac{80.0}{60.09}$ $= 1.33$ mol
Use the mole ratio for the reaction to determine the amount, in mol, of the product that would be made if all of the reactant reacted.	$\text{mole ratio} = \frac{\text{coefficient of } C_2H_5COOH}{\text{coefficient of } C_3H_7OH} = \frac{1}{1}$ $n(C_2H_5COOH) = n(C_3H_7OH)$ $= 1.33$ mol
Use the formula $m = n \times M$ to determine the mass of the product if all of the reactant reacts. This is the theoretical yield of the product.	$m(C_2H_5COOH) = n \times M$ $= 1.33 \times 74.08$ $= 98.5$ g
Calculate the percentage yield for this reaction from the formula: $\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$	$\text{percentage yield} = \frac{55.0}{98.5} \times \frac{100}{1}$ $= 55.8\%$

Worked example: Try yourself 17.1.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of D from A if it proceeds by a three-step synthesis:

A → B followed by B → C followed by C → D

The yield of A → B is 90%, the yield of B → C is 80% and the yield of C → D is 60%.

Thinking	**Working**
Calculate the overall yield of D by multiplying the percentage yields together and expressing as a percentage (multiplying by 100).	The overall yield of D is: $\frac{90}{100} \times \frac{80}{100} \times \frac{60}{100} \times \frac{100}{1}$ $= 43\%$

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Worked example: Try yourself 17.1.3

CALCULATING ATOM ECONOMY

Calculate the percentage atom economy in the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol. The equation for the reaction is: $CH_3CH_2CH_2OH(aq) + NaI(aq) + H_2SO_4(aq) \rightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$

Thinking	**Working**
Calculate the total molar mass of the reactants.	$M(CH_3CH_2CH_2OH) + M(NaI) + M(H_2SO_4)$ $= [(3 \times 12.01) + (8 \times 1.008) + 16.00] + (22.99 + 126.9)$ $+ [(2 \times 1.008) + 32.07 + (4 \times 16.00)]$ $= 308.1\,g\,mol^{-1}$
Calculate the molar mass of the required product.	$M(\text{iodopropane}) = (3 \times 12.01) + (7 \times 1.008) + 126.9$ $= 170.0\,g\,mol^{-1}$
Calculate the atom economy for the reaction using the formula: $\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$	$\text{atom economy} = \frac{170.0}{308.1} \times 100$ $= 55.18\%$ In this process 55.18% of the starting materials are converted to the desired product. The remainder of the chemicals used is waste.

17.1 Review

1 A significant reason is globalisation. Many Australian chemical companies have closed because labour and energy can be sourced more cheaply in other countries. The surviving industries in Australia are often ones where the raw materials are readily available.

2 **a** Port Kembla offers port facilities for transport. Port Kembla already has a steel industry, so it has technical expertise and a skilled workforce. The short travel time for transporting sulfuric acid to the steelworks reduces costs and risks associated with transport.

b Sulfuric acid is extremely corrosive. It has to be stored and transported carefully. Leaks into local waterways would not be tolerated. SO_2 is a toxic gas. Emissions near a city would need to be controlled and limited.

3 **a** Manildra is close to a wheat-growing area, so the raw materials are readily available. It is also an area where many vehicles that might use bioethanol blends are operating. It would be costly to transport the wheat to Broken Hill and then the bioethanol from Broken Hill.

b Fertile land is required to grow wheat. Australia is a very dry continent with a high percentage of arid land. Farming also requires resources such as fuel and fertiliser. Too high a level of crop growth would lead to more energy being put into the farming than would be provided by the bioethanol. There are also incentives given to grow wheat for food, rather than for biofuel production.

4 **a** mass of reactants $= M(C_2H_6) + M(Cl_2)$

$$= [(2 \times 12.01) + (6 \times 1.008)] + (2 \times 35.45)$$
$$= 100.97\,g\,mol^{-1}$$

mass of product $= M(C_2H_5Cl)$

$$= (2 \times 12.01) + (5 \times 1.008) + 35.45$$
$$= 64.51\,g\,mol^{-1}$$

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$
$$= \frac{64.51}{100.97} \times 100$$
$$= 63.89\%$$

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b $M(\text{ethane}) = 30.08\,\text{g mol}^{-1}$

$n(\text{ethane}) = \frac{m}{M} = \frac{4.00}{30.08} = 0.133\,\text{mol}$

$n(\text{chloroethane possible}) = n(\text{ethane}) = 0.133\,\text{mol}$

$m(\text{chloroethane possible}) = n \times M = 0.133 \times 64.53 = 8.58\,\text{g}$

$$\begin{aligned}\text{percentage yield} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}\\ &= \frac{5.40}{8.58} \times 100\\ &= 62.9\%\end{aligned}$$

5 High temperature: For endothermic reactions, the yield increases with temperature.

Low pressure: This reaction has two reactant particles and four product particles. The use of low pressure favours the forward reaction, increasing the yield.

Catalyst: The surface of the nickel acts as a catalyst for this reaction, weakening the bonds in the reactant particles. More product can be produced in a given time if the rate of reaction is increased.

6 Some factors would include:

- the difference between the atom economies of each process
- the degree of hazard of the starting material
- the cost of disposing of or recycling waste materials from the first method
- the cost of managing the hazardous material from the second method
- whether the hazardous material in the second method can be degraded into a benign compound.

CHAPTER 17 REVIEW

1 A. A multivitamin manufacturer will require ingredients from a wide range of sources. It is easier to choose a location close to a transport hub.

2 **a** Student answers will vary. Possible answers include $CuSO_4$, NaCl, CH_4, CO_2, HCl and $CaCO_3$.

b Student answers will vary. Possible answers include NaCl, $NaHCO_3$ or vinegar.

c Student answers will vary. Possible answers include acids and bases at high concentrations.

d Student answers will vary. Possible answers include experiments using lead containing solutions or strong acids.

3 **a** Heat exchange systems save money by lowering energy costs. The energy produced in one part of the plant is transferred to another part instead of using external energy.

b Exothermic. Exothermic reactions release energy. It is desirable to try and use this energy elsewhere.

4 Student answers will vary. Possible answers include cheaper labour overseas, dwindling domestic supplies of oil, dangers of storing petrochemicals in large cities.

5 Student answers will vary. Possible answers include ammonium phosphate, which is used as a fertiliser in agriculture, and steel, which is used by the construction industry.

6 **a** The graph shows that significant rises in wholesale electricity prices occurred during 2015–2016.

b Coal-fired power stations are approaching the end of their lifespan, costing money to replace; electricity infrastructure is deteriorating.

c Global chemical markets are already very competitive. Increasing electricity prices place further financial pressure on industries. Increased costs reduce profit margins, which makes the Australian chemical industry less competitive.

d The impact will vary with the industry. The amount of energy required for some processes is much greater than others.

7 **a** Green-coal technology seeks to improve the efficiency of the production of electricity from coal and to lower the emissions produced.

b To improve the efficiency, coal is dried and ground before combustion. Sulfur is stripped off before combustion, or the SO_2 gas produced is stripped from the emissions before their release. The CO_2 produced is stored underground rather than released to the atmosphere.

8 **a** The yield will decrease as the temperature increases.

b An increase in pressure will increase the yield.

c Oxygen in the air is very cheap—an excess of oxygen helps push the reaction forwards.

d The use of a catalyst will not change the yield but equilibrium will be reached faster.

9 It can be difficult for the smelter to dispose of the SO_2 as it is a toxic emission. If it is used in the production of sulfuric acid, this solves the emissions problem and provides an inexpensive raw material for the sulfuric acid. Transport of the SO_2 is also simple.

10 **a** Pathway A offers the higher atom economy (100%). All atoms in the reactant end up in the product.

b Pathway A: addition reaction. Pathway B: substitution reaction

11 $n(\text{ethanol}) = \frac{m}{M} = \frac{20}{46.07} = 0.434\ \text{mol}$

Theoretical yield: $n(\text{ethanoic acid}) = n(\text{ethanol}) = 0.434\,\text{mol}$

$m(\text{ethanoic acid}) = n \times M = 0.434 \times 60.05 = 26.1\,\text{g}$

$\%\,\text{yield} = \frac{21.5}{26.1} \times \frac{100}{1} = 82.4\%$

12 **a** $\text{yield} = 0.70 \times 0.50 \times 0.90 = 0.32 = 32\%$

b $\text{yield} = 0.70 \times 0.10 \times 0.90 = 0.063 = 6.3\%$

13 Reaction 1:

$$\begin{aligned}\text{mass of reactants} &= 2 \times M(CH_2CH_2) + 2 \times M(Cl_2) + M(Ca(OH)_2)\\ &= 2 \times [(2 \times 12.01) + (4 \times 1.008)] + 2 \times (2 \times 35.45) + [40.08 + 2 \times (16.00 + 1.008)]\\ &= 272.00\,\text{g}\,\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{mass of product} &= 2 \times M(H_2COCH_2)\\ &= 2 \times [(2 \times 1.008) + (2 \times 12.01) + 16.00 + (2 \times 1.008)]\\ &= 88.10\,\text{g}\,\text{mol}^{-1}\end{aligned}$$

$\text{atom economy} = \frac{88.10}{272.00} \times 100 = 32.39\%$

Reaction 2:

$$\begin{aligned}\text{mass of reactants} &= M(CH_2CH_2) + 0.5 \times M(O_2)\\ &= [(2 \times 12.01) + (4 \times 1.008)] + 0.5 \times (2 \times 16.00)\\ &= 44.05\,\text{g}\,\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{mass of product} &= M(H_2COCH_2)\\ &= [(2 \times 1.008) + (2 \times 12.01) + 16.00 + (2 \times 1.008)]\\ &= 44.05\,\text{g}\,\text{mol}^{-1}\end{aligned}$$

$\text{atom economy} = \frac{44.05}{44.05} \times 100 = 100.0\%$

14

$$\begin{aligned}\text{total molar mass of reactants} &= M(C_6H_6) + M(H_2SO_4) + M(NaOH)\\ &= [(6 \times 12.01) + (6 \times 1.008)] + [(2 \times 1.008) + 32.07 + (4 \times 16.00)]\\ &\quad + 2 \times (22.99 + 16.00 + 1.008)\\ &= 256.19\,\text{g}\,\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{total molar mass of products} &= M(C_6H_5OH)\\ &= [(6 \times 12.01) + (5 \times 1.008) + 16.00 + 1.008]\\ &= 94.11\,\text{g}\,\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{atom economy} &= \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100\\ &= \frac{94.11}{256.19} \times 100\\ &= 36.73\%\end{aligned}$$

15

$$\begin{aligned}\text{atom economy} &= \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100\\ \frac{\text{atom economy}}{100} &= \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}}\\ \frac{76.7}{100} &= \frac{2.00}{x}\\ x &= \frac{2.00}{0.767}\\ &= 2.61\ \text{kg}\end{aligned}$$

16 **a** molar ratio of salicylic acid to aspirin is 1:1

$n(\text{salicylic acid}) = \frac{m}{M} = \frac{2.50}{138.12} = 0.0181\,\text{mol}$

$n(\text{aspirin}) = n(\text{salicylic acid}) = 0.0181\,\text{mol}$

$M(\text{aspirin}) = n \times M = 0.0181 \times 180.15 = 3.26\,\text{g}$

b $\%\ \text{yield} = \frac{2.35}{3.26} \times 100 = 72.1\%$

17 **a** Transport: This industry should be located on the coast near a port so that aluminium oxide can be brought in and aluminium exported.

b Energy: This industry will have high electricity use. Proximity to a cheaper or renewable source of electricity would be important.

c Emissions. Emissions will not be high as the ore does not contain sulfur. It will produce CO_2. This is a greenhouse gas but not a danger to surrounding residents.

d Tailings. The plant uses concentrated Al_2O_3 so the volume of tailings will not be high.

e Work force. A large refinery requires access to a large workforce of skilled operators. It would be helpful to be located near a city or large town.

f Economics. The global price of aluminium fluctuates significantly. It is difficult to predict the viability of the plant.

g Safety. This is an industry where care would need to be taken. Large volumes of very hot material are used, as well as large and heavy machinery.

18 **a** If the sulfur is not removed, toxic SO_2 will be produced during the production of ammonia.

b The reaction is exothermic so a relatively low temperature should be used. High pressure can be used as the number of product particles is less than the number of reactant particles. The removal of ammonia from the reaction will also push the reaction in the forward direction.

c Ammonium nitrate is used mainly as a fertiliser; it can also be used for explosives.

d Nitrogen can be obtained from the air, so any site will work. Hydrogen is obtained from methane. Methane would need to be piped or shipped from another state of Australia.

e It is close to a port, has a large population from which to draw a labour force, and is relatively close to conventional power supplies.

f The atom economy will be 100%, because NH_3 is the only product.

19 **a** safer, or no solvents

b increasing energy efficiency

c atom economy, use of solvents

d use of renewable raw materials

20
- There are reactants and products.
- Energy is required.
- Not all reactant atoms end up in the products.
- The reactants are changed in the reaction.
- There are optimum conditions for the process.
- Waste is created.

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