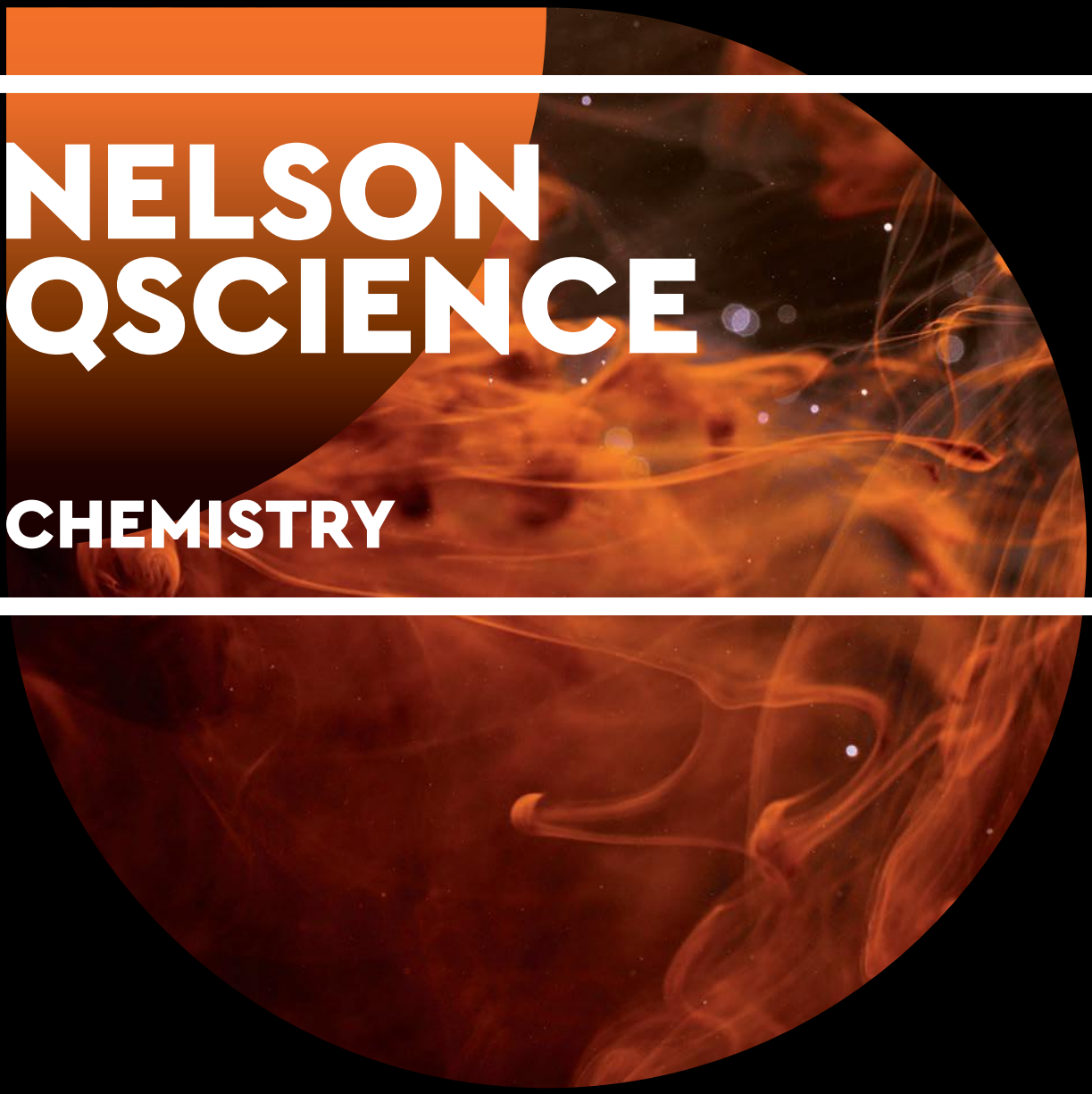

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UNITS 3 4

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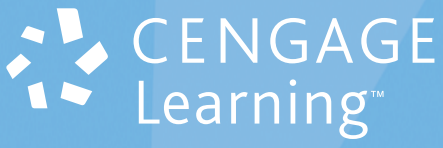

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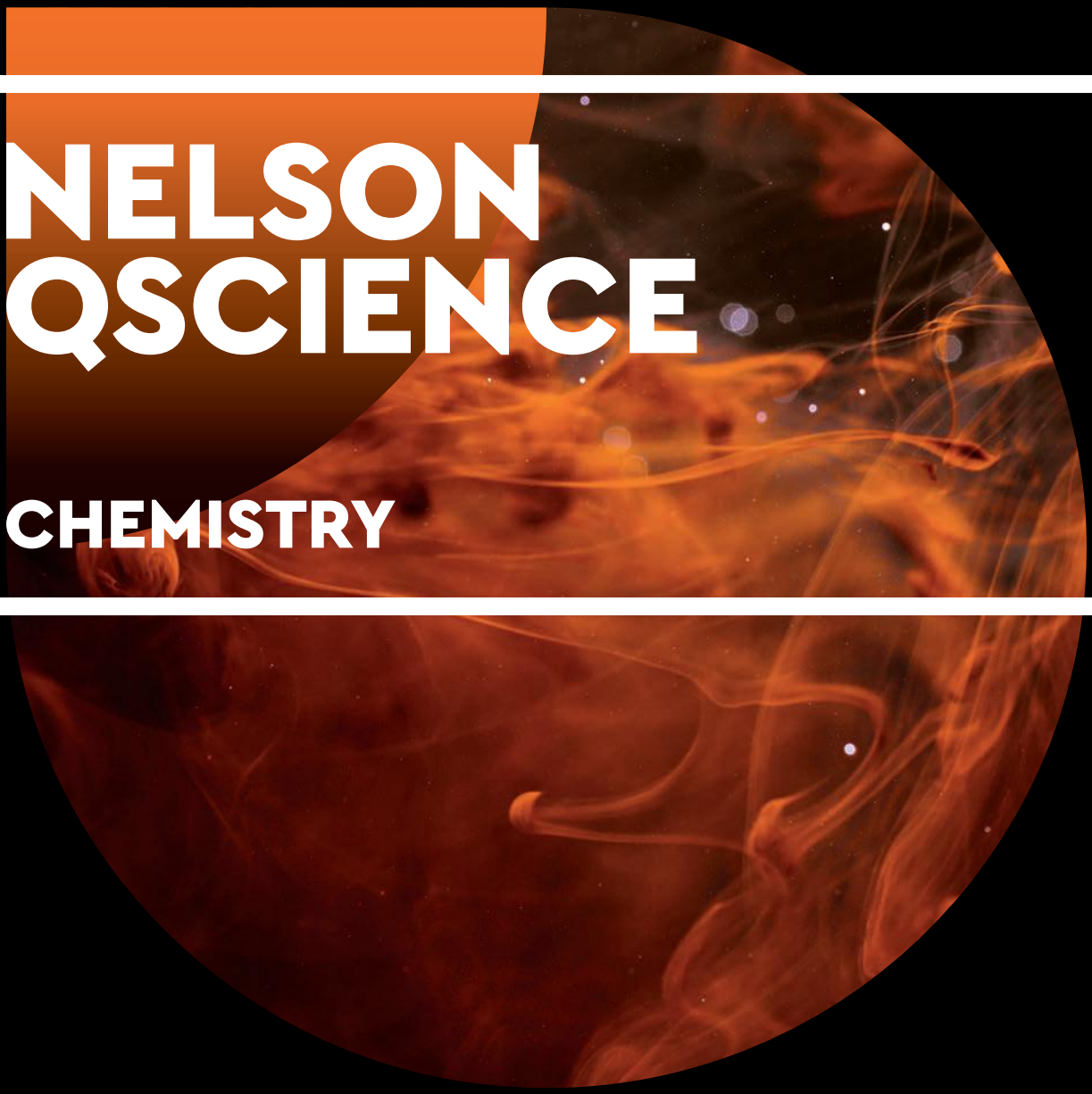

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CHEMISTRY

UNITS 3 4

Nicholas Stansbie
Brett Steeples
Dr Sarah Windsor

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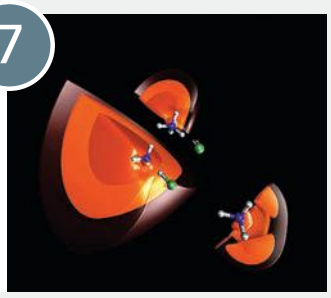

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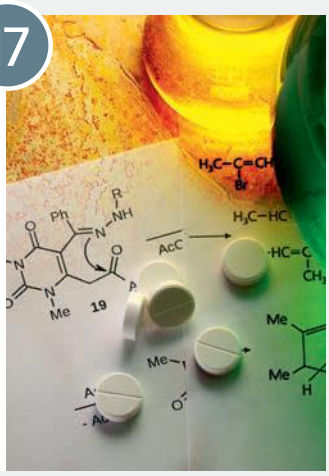

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PREFACE

Nelson QScience Chemistry Units 3 & 4 has been written to meet the requirements of the QCAA Senior Secondary Science Syllabus – Chemistry. Each page has been carefully considered to provide students with all of the information they need to meet the content and skills requirements of the new syllabus.

With the introduction of the QCE external examination, *Nelson QScience Chemistry* includes features such as practice exams at the end of each section, a Units 3 & 4 practice exam, chapter quizzes (available on NelsonNet) and ExamView (available on NelsonNet).

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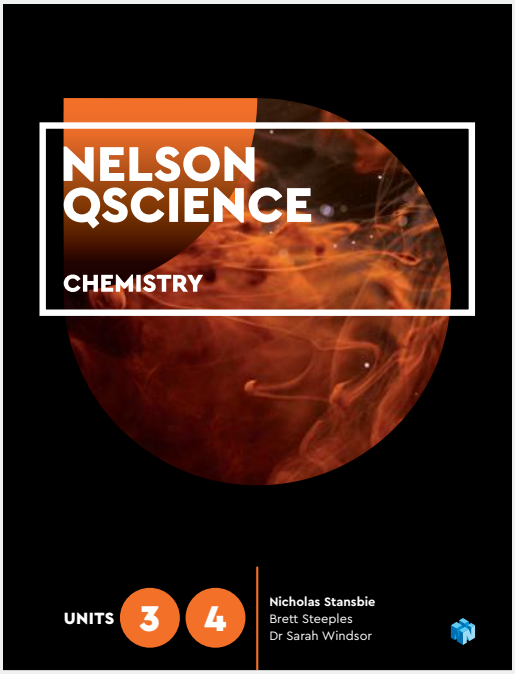

AUTHORS AND REVIEWER TEAM

Nelson QScience Chemistry is adapted from *Nelson Chemistry for the Australian Curriculum Units 1 & 2* and *Nelson Chemistry for the Australian Curriculum Units 3 & 4*, by Deb Smith, Anna Davis, Anne Disney, Veronica Hayes and Rachel Whan.

Nicholas Stansbie

Nicholas is an experienced science teacher and teacher of senior chemistry in the UK and in Australia. Nicholas' dedication to quality teaching and learning has enabled him to lead the *QScience Chemistry* team in the development of this text.

Brett Steeples

Brett was a research chemist and lecturer at Manchester University before becoming a chemistry teacher. Brett has worked on the moderation panel and is a member of the Chemistry state review panel.

Dr Sarah Windsor

Dr Sarah Windsor is an associate lecturer in science at the University of the Sunshine Coast. Sarah's research interests include analytical chemistry and education and she has brought her extensive knowledge in both of those areas to the development of *Nelson QScience Chemistry*.

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All NelsonNet material for *QScience* has been written by Stephen Bird and Louise Munro.

Review team

The following people have contributed to the review of the *QScience Chemistry* series: David Austin, Neil Gordon, Rebecca Delaney and Catherine Munro.

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Chemistry 2019 v1.3 General Senior Syllabus © Queensland Curriculum & Assessment Authority

ABOUT THIS BOOK

At the beginning of unit and topic

- Unit introductions are an overview of the key content in the unit.
- Topic introductions are an overview of the key content in the topic.

At the beginning of each chapter

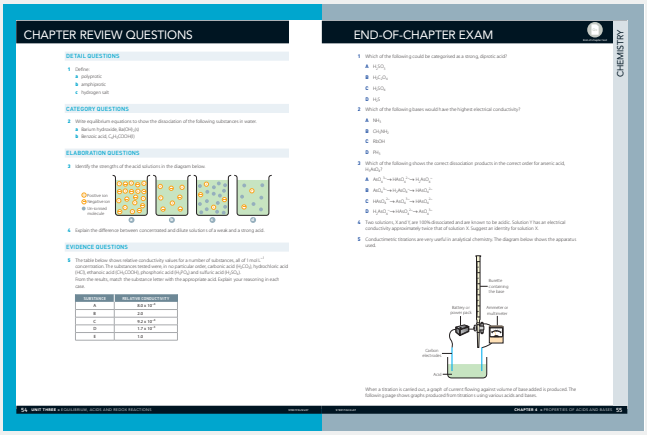
- A short chapter summary introduces students to the key content and skills covered.
- Stimulus questions can be used to focus on the topic and highlight existing knowledge.

In each chapter

- **Worked examples** are explained clearly step-by-step.
- **Key formulas** are highlighted in the margin.
- **Key glossary terms** are highlighted in the margin.
- **Science as a Human Endeavour** provides opportunities for students to connect to the importance of SHE and develop scientific research skills.
- **Inquiring further** provides opportunities for students to further investigate scientific concepts and develop scientific research skills.
- **Section reviews** are written in the style of Bloom's revised taxonomy.
- **Practical experiments** contain guided instructions on the materials, procedure, collection and analysis of the results and discussion.

At the end of each chapter

- **Chapter review questions** written in the style of Marzano and Simms (2014) questioning sequences.
- **Practice examinations** occur at the end of each chapter to help students develop skills in decoding and answering exam-style questions.



At the end of the book

- **Practice exam** questions provide an extended practice of the content and skills learnt across the text.
- **Glossary** provides explanations of all of the new terms introduced in the text.
- **Answers** provide complete answers for student reference.

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» UNIT THREE

EQUILIBRIUM, ACIDS AND REDOX REACTIONS

- Topic 1: Chemical equilibrium systems
- Topic 2: Oxidation and reduction

Reversible reactions occur in a variety of chemical systems including acid-base equilibrium systems. Applications include the principles of oxidation and reduction reactions and the production of electricity from electrochemical cells. Reversible processes respond to a range of factors and can achieve a state of dynamic equilibrium. Investigations explore the principles of dynamic chemical equilibrium and how these can be applied to electrochemical cells and pH scale. The concepts of equilibrium and redox are important in the real world in terms of environmental issues, such as acid rain, oceanic acidification and action for sustainability. In an industrial context, applications include food or wine production, corrosion and corrosion prevention, fuel cells and uses of electrochemistry.

Adapted from the Chemistry 2019 v1.3, General Senior Syllabus QCAA syllabus Unit 3, page 37

UNIT OBJECTIVES

By the end of this unit, students should be able to:

1. describe and explain chemical equilibrium systems and oxidation and reduction
2. apply understanding of chemical equilibrium systems and oxidation and reduction
3. analyse evidence about chemical equilibrium systems and oxidation and reduction
4. interpret evidence about chemical equilibrium systems and oxidation
5. investigate phenomena associated with chemical equilibrium systems and oxidation and reaction
6. evaluate processes, claims and conclusions about chemical equilibrium systems and oxidation and reduction
7. communicate understandings, findings, arguments and conclusions about the properties and structure of atoms and materials, and chemical reactions in terms of reactants, products and energy change.

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» UNIT THREE

EQUILIBRIUM, ACIDS AND REDOX REACTIONS

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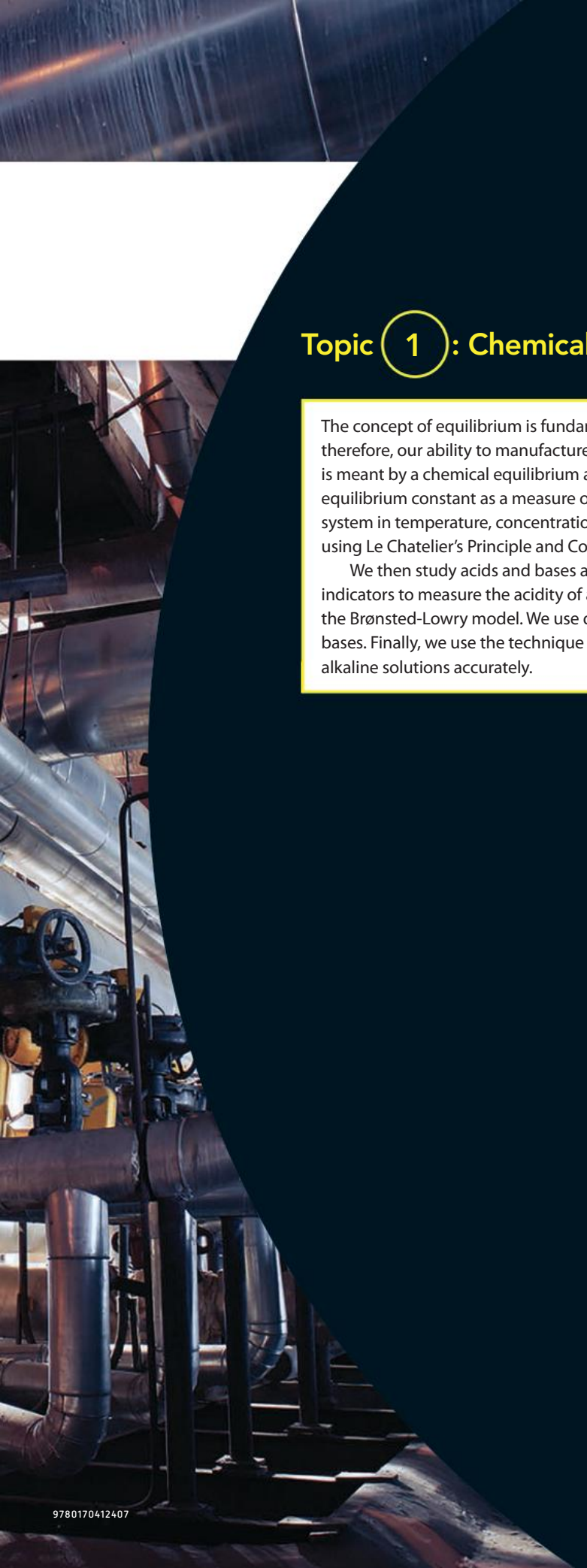

Topic 1: Chemical equilibrium systems

The concept of equilibrium is fundamental to our understanding of chemical processes and, therefore, our ability to manufacture and synthesise chemicals. In this topic, we examine what is meant by a chemical equilibrium and how to represent a system at equilibrium. We use the equilibrium constant as a measure of the equilibrium position and understand how changes to a system in temperature, concentration or pressure can affect the system. We explain these changes using Le Chatelier's Principle and Collision Theory.

We then study acids and bases as examples of systems at equilibrium. We use the pH scale and indicators to measure the acidity of a solution, and explain the behaviour of acids and bases using the Brønsted-Lowry model. We use dissociation constants to measure the strength of acids and bases. Finally, we use the technique of volumetric analysis to determine the concentration of acid or alkaline solutions accurately.

SCIENCE AS A HUMAN ENDEAVOUR

Students should have a chance to investigate:

- Chemical balance in wine
- Carbon dioxide in the atmosphere and hydrosphere
- Development of acid/base models

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1 CHEMICAL EQUILIBRIUM

Introduction

In our everyday lives, there are many examples of balance or equilibrium. A see-saw is in equilibrium when the forces on either side are balanced, and the see-saw remains horizontal. Water in a rainforest is in equilibrium when the amount of rainfall balances the amount of evaporation and use. A person's weight is in equilibrium when the amount of food they eat balances the amount of energy they use.

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FIGURE 1.1.1 A see-saw can represent equilibrium

In the latter case, when a person continues to take in energy in the form of food, by eating regularly, then the body uses that energy continuously to grow. This equilibrium is a dynamic equilibrium, where both processes occur continuously but at the same rate, so that there is no overall change to the person's weight. Similarly, in chemistry, reversible reactions can occur in both directions simultaneously at the same rate, and so achieve a balance where the amount of reactants and products remain constant, and the chemical system is in equilibrium.

Stimulus questions

What is the difference between an open and a closed system?

Are all physical and chemical changes reversible?

What is the role of activation energy in the reversibility of chemical reactions?

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1.1 Equilibrium – systems in balance

1.1.1 What is equilibrium?
1.1.2 Equilibria

The chemicals involved in a reaction form the **chemical system**, while anything around these chemicals but not involved in the actual reaction forms the **surroundings**. For example, in the reaction between hydrogen gas and oxygen gas to form water vapour, the molecules of hydrogen, oxygen and water make up the system, while the other molecules in the air (e.g. nitrogen, carbon dioxide) form the surroundings. In an aqueous environment, the water will form part of the system if it is involved in the reaction and it will form the surroundings if it is not involved.

If the chemicals in the reaction are all contained within a certain space, the system is a **closed system**. For example, if hydrochloric acid was added to calcium carbonate in a sealed container, then nothing can enter or leave the system and it is a closed system.

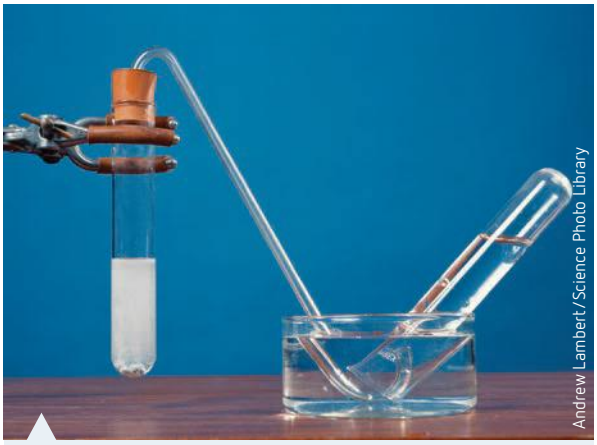

FIGURE 1.1.2 A closed system does not allow chemicals to enter or leave.

Conversely, if substances can either be added or lost, then the system is described as an **open system**. For example, if hydrochloric acid is added to calcium carbonate in an open beaker, then the carbon dioxide gas produced would escape into the air. Therefore, this is an open system.

It is important to note that energy, such as heat or light, can enter or leave a system, regardless of whether it is open or closed.

chemical system the chemicals involved in a reaction

surroundings everything except the chemicals involved in a reaction

closed system where the chemicals involved in a reaction are all contained within a fixed space

open system where one or more reactants or products in a reaction can be either added or lost

physical change a change where no new substance is created

chemical change a change involving the creation of a new substance

reversible a reaction where the products can be converted back to the reactants

Physical and chemical changes

The change that occurs in a chemical system can be described as a **physical change** or a **chemical change**. During a physical change, the products do not include any new substances. Instead the physical properties of the reactant change, which can include a change of state. For example, when water is boiled, it changes from a liquid to a gas. The molecules remain the same; they are simply further apart (Figure 1.1.3). We can represent this change with the equation:

$$H_2O(l) \rightarrow H_2O(g)$$

During a chemical change, the reactants produce new substances with different physical and chemical properties from those of the original substances. For this to happen, the atoms rearrange and form products that are different from the reactants. An example of a chemical change occurs when we pass an electric current through water (Figure 1.1.4). The atoms in the reactant, water, rearrange to form the new substances of oxygen gas and hydrogen gas:

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

When we think of a chemical reaction we often think of a situation where the reaction continues producing the products until one of the reactants is used up. In reality, this only happens for some reactions. In many reactions, as the products are formed, some of them will react to become reactants again. This means that when the reaction appears 'complete', there are both reactants and products present, as shown in Figure 1.1.4 on the next page.

Reactions where the reactants are able to form products and the products can form reactants are known as **reversible** reactions. All physical changes are reversible reactions. However, only some chemical changes are reversible. The reaction where the reactants form products is called the *forward reaction*, and the reaction where the products form reactants is called the *reverse reaction* (Figure 1.1.5).

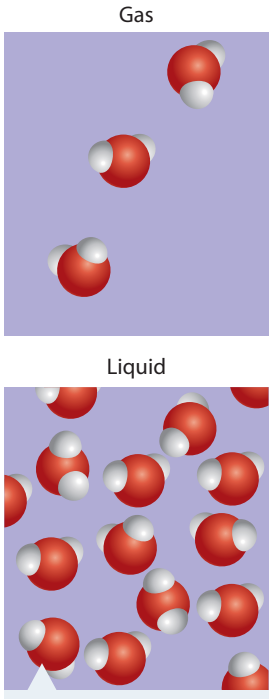

FIGURE 1.1.3 Water boiling is a physical change.

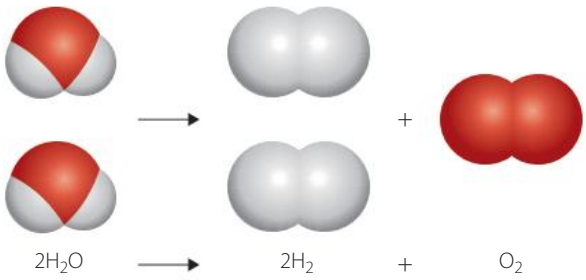

FIGURE 1.1.4 The electrolysis of water is a chemical change.

The reaction between hydrogen gas and nitrogen gas is also a reversible reaction and can be represented by the following equation.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

A double arrow $\rightleftharpoons$ is used to show that the reaction can occur in both directions. In this example, carbon monoxide reacting with nitrogen dioxide is the forward reaction; carbon dioxide reacting with nitrogen monoxide is the reverse reaction.

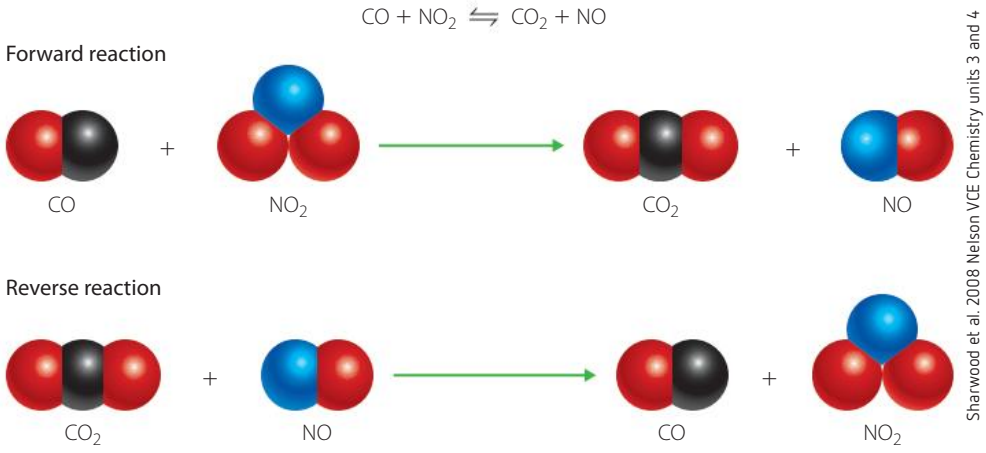

FIGURE 1.1.5 Forward and reverse reactions

1.1.3 Reversible reactions

PRACTICAL ACTIVITY 1.1.1

Blue bottle experiment – a reversible reaction

AIM

To observe a reversible reaction.

PROCEDURE

1. Watch the video on the weblink The blue bottle reaction.
2. Alternatively, your teacher may demonstrate the reaction. (The instructions can be found at the weblink.) »

1.1.3 The blue bottle reaction

» 3 In the blue/colourless bottle, how could you tell that this was a reversible reaction?

4 In the yellow/red/green bottle, how could you tell that this was a reversible reaction?

5 What other reversible reactions have you observed?

SECTION REVIEW 1.1

REMEMBERING

1 State the difference between a forward and a reverse reaction.

2 State the requirements for a closed system.

3 Are all reactions reversible? Explain.

UNDERSTANDING

4 Why are double arrows used in equations for reversible reactions?

5 In a particular chemical reaction, if the forward reaction is exothermic, then the reverse reaction must be endothermic. Explain why.

APPLYING

6 The reaction for the self-ionisation of water is an endothermic reaction.

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

a Write the equation for the forward reaction.

b Write the equation for the reverse reaction.

c Sketch an energy profile diagram for the forward reaction.

d Sketch an energy profile diagram for the reverse reaction.

1.2 Dynamic equilibrium

In a closed chemical system involving a reversible reaction, as the reactants form products the products will also form reactants. This means that the reaction will not go to completion. Rather, it will reach a state of *dynamic equilibrium*.

Dynamic equilibrium is a specific example of a system in a *steady state*. Systems in steady state have constant properties. All systems at dynamic equilibrium must be in a steady state as their properties will remain constant. However, not all systems in a steady state will be in dynamic equilibrium, as a steady state may be achieved without a reversible reaction or a closed system. For example, if reactants are added to a reaction mixture at the same rate that the products are removed, then a steady state will be achieved even though the system will not be at equilibrium.

1.2.1 Dynamic equilibrium

1.2.2 Dynamic equilibrium animation

dynamic equilibrium a system in balance but where forwards and backwards reactions occur at the same rate

equilibrium a system in balance

Equilibrium in chemical systems

When reactants are initially placed in a system, their concentrations are high compared to the concentration of products. This means that the rate of the forward reaction is relatively high. As there are initially no products, the reverse reaction is unable to occur.

As the products form from the forward reaction, their concentration increases. This means that the reverse reaction will start to occur, and its rate will increase as the concentration of the products increases. This will occur only in a closed system where the products remain in the chemical system and so are available for the reverse reaction.

Figure 1.2.1 shows how the concentrations of the reactants changes as an equilibrium is reached. The equation for the reaction described is:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

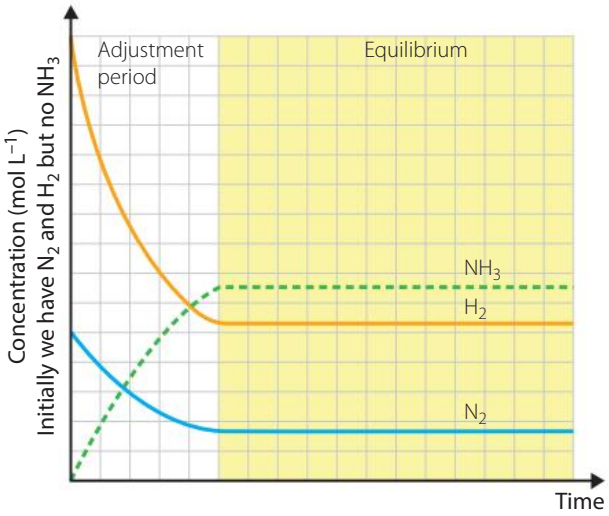

FIGURE 1.2.1 Concentration of reactants and products vs time during the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

Therefore the:

- rate of the forward reaction will decrease as the concentration of the reactants decreases
- rate of the reverse reaction will increase as the concentration of the products increases.

This trend will continue until the rate of the forward reaction is the same as the rate of the reverse reaction. At this point, products are formed at the same rate that they are used up. Therefore, the concentrations of the reactants and products will remain constant. When this happens, the system is said to be in dynamic equilibrium.

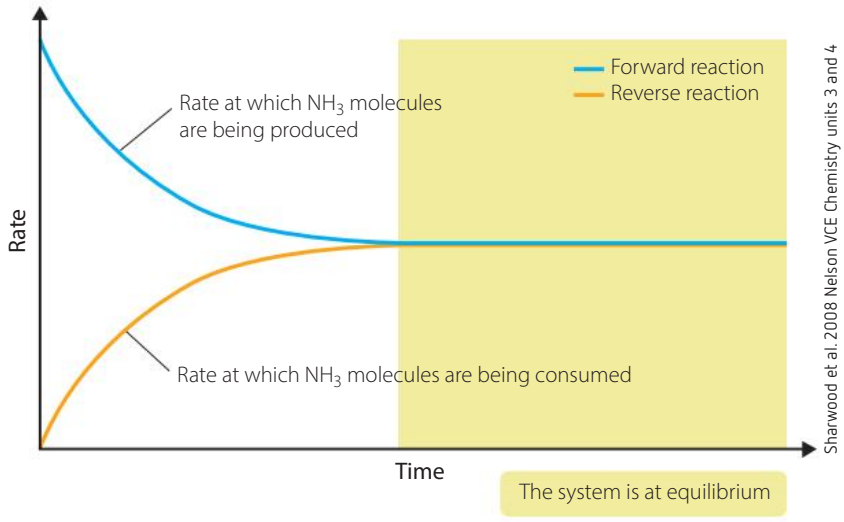

FIGURE 1.2.2 Rates of reactions vs time during the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, when N_2 and H_2 are mixed.

When a system is at dynamic equilibrium, the concentrations of the reactants and products remain constant. This means that the macroscopic properties will also remain constant. For example, the colour will remain constant or the mass of a solid will stay the same. Note that although the concentrations must be constant for the system to be at equilibrium, they do not need to be equal. In fact, it is unlikely that they will be equal.

Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

FIGURE 1.2.3
A system at dynamic equilibrium will maintain constant macroscopic properties.

SECTION REVIEW 1.2

REMEMBERING

1 Define:
- **a** equilibrium
- **b** dynamic equilibrium
- **c** open system
- **d** closed system
- **e** steady state.

2 True or false: a chemical system will reach equilibrium if it:
- **a** is an open system.
- **b** involves a reversible reaction.

3 True or false: at equilibrium, the:
- **a** rate of the forward reaction is the same as the rate of the reverse reaction
- **b** concentrations of the reactant and products do not remain constant
- **c** macroscopic (large-scale) properties are not constant.

UNDERSTANDING

4 In your own words, describe the process shown in figures 1.2.1 and 1.2.2.

1.3 Predicting reversibility

In *QScience Chemistry Units 1&2* you considered collision theory to predict the rate of reactions. Collision theory states that for a reaction to occur, the particles must collide with sufficient energy to break the bonds and the appropriate orientation to allow the new bonds to form. This theory can also be used to understand why some reactions are reversible and others are not.

You will recall that the amount of energy required to break the bonds of the reactants is known as the **activation energy, E_a**. This is the difference in **enthalpy** between the reactants and the **activated complex**, as shown in Figure 1.3.1.

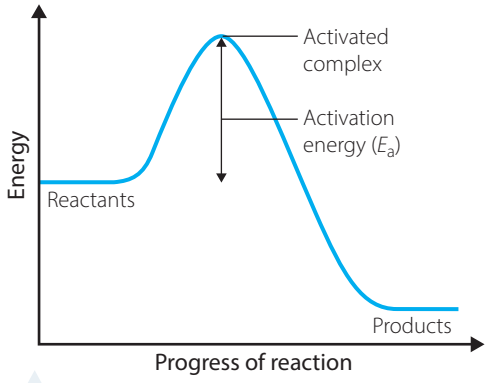

FIGURE 1.3.1 Activation energy of a reaction

If the reactant particles in a collision do not have enough energy to break the bonds, then they are unable to form the products. If the activation energy is lower, then more particles will have enough energy to break the reactant bonds and form the products. Therefore, the size of the activation energy will influence the likelihood of a reaction proceeding.

activation energy, E_a
the minimum amount of energy required in order for a reaction to occur

enthalpy
heat energy which is either absorbed or released in the breaking and making of chemical bonds during a reaction

activated complex
a transition or intermediate state formed during a reaction as a precursor to the product, but which has a high energy and so is relatively unstable

1.3.1 What triggers a chemical reaction?

In a reaction, we can consider the activation energy of both the forward and reverse reactions. If the activation energy of either of these is very high, then that reaction is unlikely to proceed because very few particles will have enough energy for a successful collision. Therefore, for a reaction to be reversible, the activation energies of both the forward and reverse reactions must be low enough that sufficient particles will have enough energy for a successful collision.

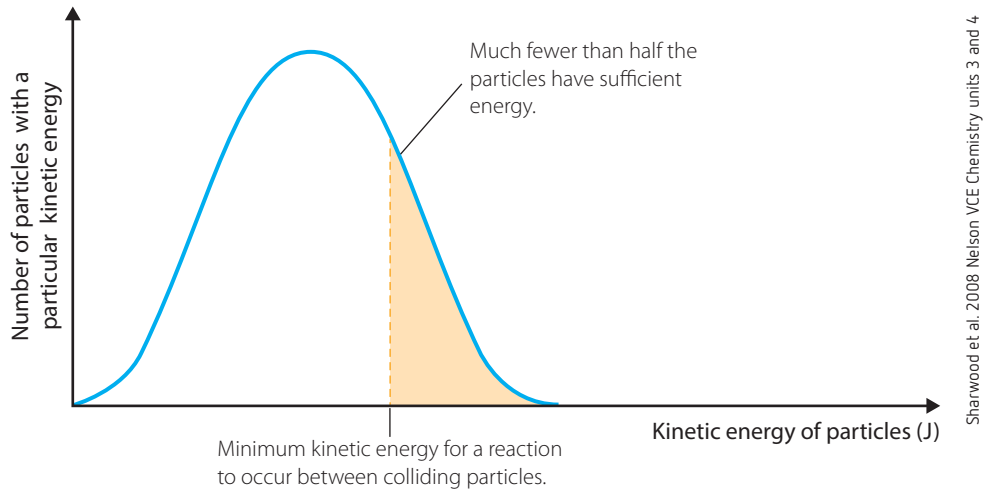

FIGURE 1.3.2 The number of particles with enough energy for a successful collision.

SECTION REVIEW 1.3

REMEMBERING

1 Define activation energy.
2 Define activated complex.

UNDERSTANDING

3 Complete the following sentence: 'The reversibility of chemical reactions is dependent on …'

1.4 Analysing data to identify the position of equilibrium

Graphing is used in many situations to visually represent data. When you are studying chemical systems involving equilibrium, you can use graphs to consider either the rates of the reactions or the concentrations of the substances over time.

Reaction rate against time

In a graph of reaction rate against time, when we start with reactants only, you will observe that the rate of the:

1 forward reaction is initially high
2 reverse reaction is initially zero
3 forward reaction will decrease – quickly initially but then more slowly

4 reverse reaction will increase – quickly initially but then more slowly

5 two reactions will become equal – this is when equilibrium is reached.

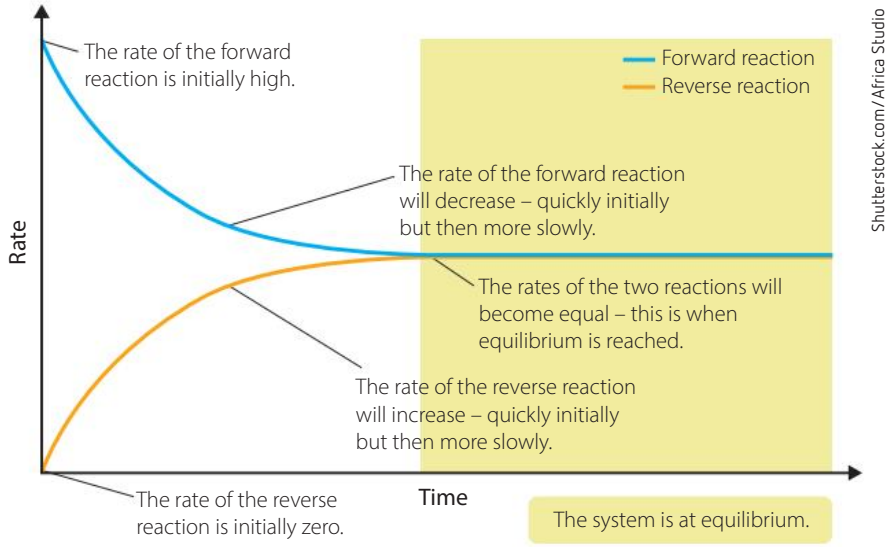

FIGURE 1.4.1 Reaction rate vs time for the reaction: $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$.

Concentration against time

Similarly, you can use a graph to represent the changes in concentration during a reaction as it reaches equilibrium. Typically, the reaction will start with only reactants; therefore, the concentration(s) of:

1 reactants is initially large

2 products is initially zero

3 reactants decreases, initially quickly (steep graph) and then more slowly

4 products increase, initially quickly (steep graph) and then more slowly

5 all will plateau when the system reaches equilibrium.

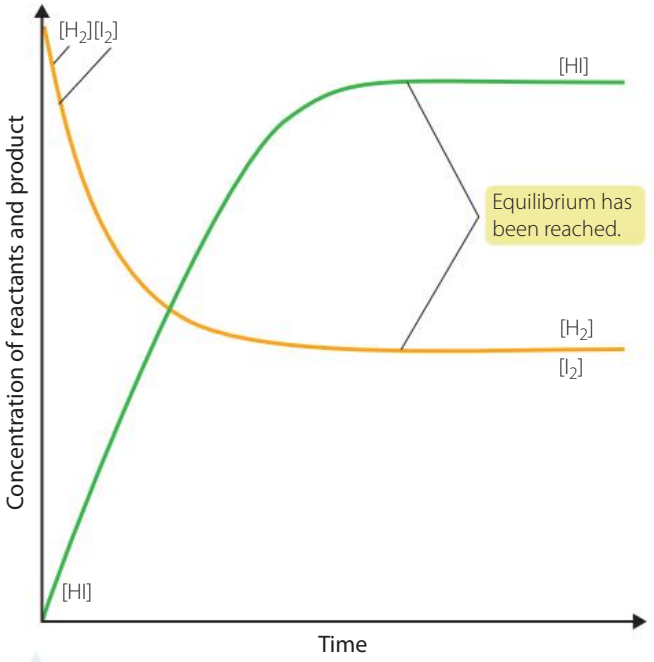

FIGURE 1.4.2 Reaction rate vs time for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

TABLE 1.4.1 Graphing concentration and reaction rate vs time

GRAPH	NUMBER OF LINES	POSITION OF LINE AT EQUILIBRIUM
Concentration vs time	Any number depending on the number of reactants and products. Each may be represented on the graph by a separate line.	All lines plateau as concentrations are constant. They do not need to be of equal value.
Reaction rates vs time	Two lines – forward and reverse reaction.	The two lines meet and plateau as the two rates are equal.

SECTION REVIEW 1.4

UNDERSTANDING

1. Explain what is meant by a dynamic equilibrium.
2. Explain why the rate of a reaction is highest as a reaction starts and then decreases.

APPLYING

3. Describe how the concentrations of reactants and products can indicate whether or not equilibrium has been reached.
4. Describe how monitoring the rate of the forward and backward reactions can determine whether or not equilibrium has been reached.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** equilibrium
- **b** dynamic equilibrium
- **c** reversible
- **d** chemical system
- **e** surroundings
- **f** closed system
- **g** open system
- **h** physical change
- **i** chemical change
- **j** activation energy
- **k** enthalpy
- **l** activated complex.

CATEGORY QUESTIONS

2 Describe what happens to the rates of the forward and backward reactions as an equilibrium is reached.

3 Describe how a concentration vs time graph would look as an equilibrium is reached.

4 Contrast the answer to Question 3 with a rate of reaction vs time graph for a system as equilibrium is reached.

ELABORATION QUESTIONS

5 Explain why an open system can never reach equilibrium.

6 Explain why some reactions are much more likely to be reversible than others.

END-OF-CHAPTER EXAM

End-of-chapter test

1 Which one of the following statements regarding a dynamic equilibrium is false?

A At equilibrium, there is no net change in the system.

B At equilibrium the concentrations of reactants and products stay the same.

C At equilibrium, the forward and backward reactions cease to occur.

D At equilibrium, the rates of the forward and backward reactions are equal.

2 A system in which no reactants or products leave the reaction mixture is known as:

A an open system.

B a closed system.

C a semi-open system.

D a partially closed system.

3 Chemical equilibrium is known as dynamic because, at equilibrium, the:

A equilibrium constant changes.

B reactants and products continue reacting.

C rates of the forward and backward reactions change.

D concentrations of the reactants and products continue to change.

4 Reactions in which products cannot turn back into reactants are termed as:

A irreversible reactions.

B reversible reactions.

C equilibrium reactions.

D redox reactions.

5 The following statement is a common misconception about equilibria: 'At equilibrium, the concentrations of reactants and products will be equal.'

Write a paragraph to correct this misconception and explain why it persists.

6 Sketch a graph showing the relative concentrations of all species over time if equal amounts of NO and O_2 are introduced to a closed container and are allowed to reach equilibrium in the following reaction:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Explain the shape of your graph.

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2 FACTORS THAT AFFECT EQUILIBRIUM

Introduction

When equilibrium is established in a chemical system, this means that the rates of the forward and reverse reactions are the same and, therefore, that the relative amounts of products and reactants present in the system are constant. If the rates of these reactions alter because of changes in conditions, such as temperature, concentration of chemicals or increasing pressure, the subsequent change in rate of reaction means that the system is no longer at equilibrium. The relative amount of products and reactants has changed and will cause the equilibrium to be re-established in a different position.

Either the forward or reverse reaction is favoured as equilibrium is re-established. If the forward reaction is favoured, then we say that equilibrium has shifted to the right. This is because more products will be produced, and products lie on the right-hand side of the equation. If the reverse reaction is favoured, then equilibrium shifts to the left, as more reactants are produced.

By understanding what happens during a reaction, we can explain the changes in equilibrium when conditions are altered. This also allows us to choose conditions that best suit the purpose of the reaction.

Stimulus questions

How does temperature affect the change in chemical systems at equilibrium?

Does concentration affect chemical systems at equilibrium?

What is the relationship between collision theory and forward and reverse reactions?

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2.1 Changing temperature

endothermic reaction
the products have more enthalpy than the reactants, meaning that energy will be absorbed from the surroundings

exothermic reaction
the reactants have more enthalpy than the products and therefore energy will be released to the surroundings

Chapter 9 of *QScience Chemistry Units 1&2* explores how endothermic and exothermic reactions relate to the law of conservation of energy, and the relationship between temperature and enthalpy changes. In an **endothermic reaction**, the products have more enthalpy than the reactants, meaning that energy will be absorbed from the surroundings. Alternatively, in an **exothermic reaction**, the reactants have more enthalpy than the products and therefore energy will be released to the surroundings. In a reversible reaction, the reaction in one direction will be endothermic while the reaction in the opposite direction will be exothermic.

In both reactions, the activation energy is the difference between the enthalpy of the activated complex and the reactants. The lower enthalpy of the reactants in the endothermic reaction means that the endothermic reaction will have a greater activation energy than the exothermic reaction for the same reversible reaction.

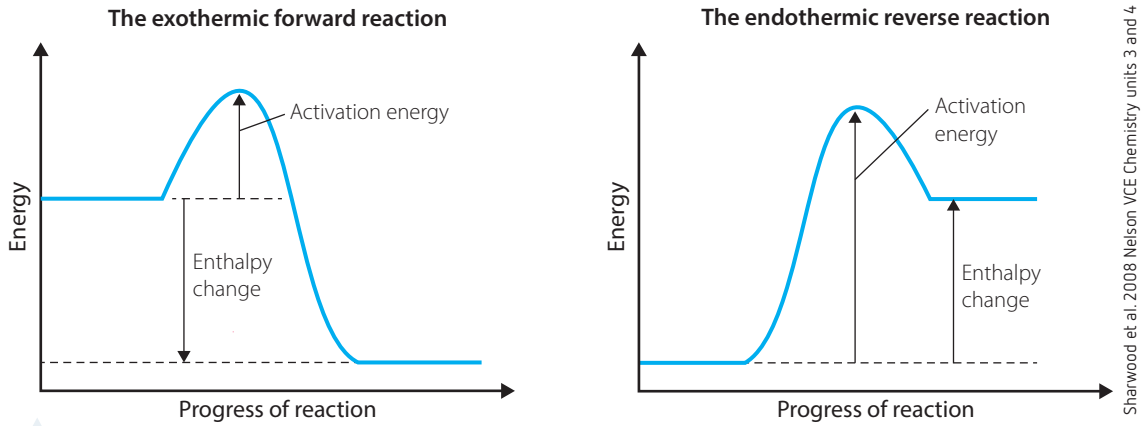

FIGURE 2.1.1 Comparing the activation energy for the forward and reverse reactions

Increasing the temperature

When the temperature of a system increases, the rate of both the forward and reverse reactions will increase. The rate of the endothermic reaction will increase more than that of the exothermic reaction. This is due to the higher activation energy – the increase in temperature will affect the percentage of particles able to react in the endothermic reaction more than in the exothermic reaction.

As more of the products of the endothermic reaction are produced, the rate of the opposite, exothermic reaction will increase. At the same time, the rate of the endothermic reaction will decrease as these reactants are used up. This trend will continue until the two rates are once again equal and the system is at equilibrium.

The effect of temperature changes on a chemical system can be explained by considering the enthalpy changes for the forward and the reverse reactions. For example, the reaction between sulfur dioxide and oxygen to produce sulfur trioxide is an exothermic reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$$

This means that the forward reaction is exothermic while the reverse reaction is endothermic. If the temperature of the system increases, then the endothermic reaction will be favoured. This will result in an increase in the concentrations of $SO_2(g)$ and $O_2(g)$ and a decrease in the concentration of $SO_3(g)$. Therefore, the equilibrium constant, K_C at the higher temperature will be lower than at the original temperature for this reaction. Equilibrium constants are further discussed in Chapter 3.

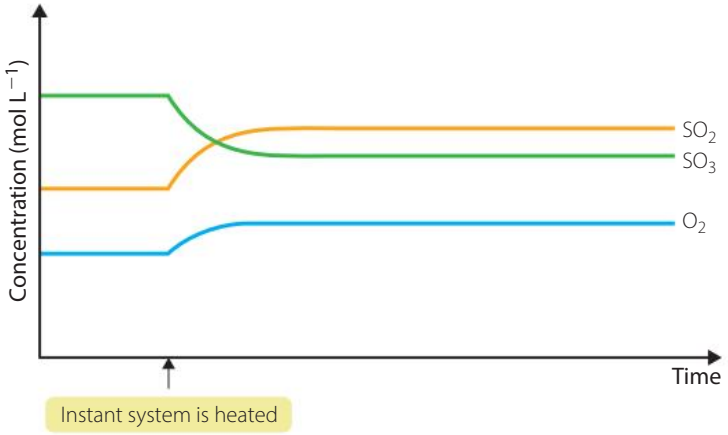

FIGURE 2.1.2 Concentrations with a change in temperature for the reaction

Decreasing the temperature

When the temperature of a system decreases:

- the rate of both the forward and reverse reactions will decrease
- the rate of the endothermic reaction will decrease more, meaning that the rate of the exothermic reaction will increase
- over time, the rate of the endothermic reaction will increase while the rate of the exothermic reaction will decrease until the two are equal again and equilibrium is re-established.

Consider the reaction between hydrogen gas and nitrogen gas to form ammonia. This reaction is exothermic:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4 \text{ kJ}$$

If the temperature of the system decreases, then the forward reaction will be favoured to counteract the change and produce more energy. This means that the concentration of ammonia will increase while the concentrations of hydrogen gas and nitrogen gas will decrease. Therefore, the magnitude of the equilibrium constant K_C at the reduced temperature would be higher than at the original temperature. This is shown in Figure 2.1.3.

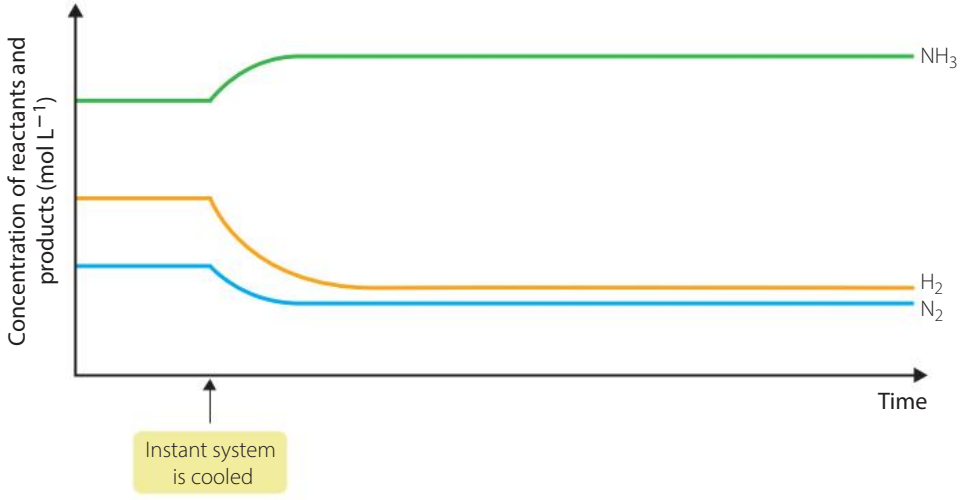

FIGURE 2.1.3 Concentrations with a change in temperature for the reaction

When the temperature of a system at equilibrium alters, there are no sudden initial changes in concentration. This is reflected in the shape of the graph in figure 2.1.3. However, one reaction will be favoured as equilibrium is being re-established. Therefore, the concentrations will gradually change as the system counteracts the change.

A change in temperature will result in a shift in equilibrium that will affect the equilibrium constant, as shown in Table 2.1.1. If the change in temperature favours the forward reaction, then there will be an increase in the concentration of products and a decrease in the concentration of the reactants. Therefore, the magnitude of the equilibrium constant will increase. Alternatively, if the reverse reaction is favoured, then there will be an increase in the concentration of the reactants and a decrease in the concentration of products. This will decrease the magnitude of the equilibrium constant.

TABLE 2.1.1 The effect of a change in temperature on the equilibrium constant

CHANGE IN TEMPERATURE	FORWARD REACTION	REVERSE REACTION	FAVOURED REACTION	EQUILIBRIUM CONSTANT
Increase	Exothermic	Endothermic	Endothermic/ reverse	Decrease
	Endothermic	Exothermic	Endothermic/ forward	Increase
Decrease	Exothermic	Endothermic	Exothermic/forward	Increase
	Endothermic	Exothermic	Exothermic/reverse	Decrease

PRACTICAL ACTIVITY 2.1.1

Effect of temperature on a system at equilibrium (teacher demonstration only)

An equilibrium will exist between $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ when they are in a solution. The equation representing this is:

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

The $[Co(H_2O)_6]^{2+}$ ion is a pink colour while the $[CoCl_4]^{2-}$ ion is a deep blue colour. Therefore, the relative concentrations of the ions and the position of equilibrium will be indicated by the colour of the solution. A blue solution indicates a high concentration of $[CoCl_4]^{2-}$ compared to $[Co(H_2O)_6]^{2+}$. Alternatively, a pink solution indicates a high concentration of $[Co(H_2O)_6]^{2+}$ compared to $[CoCl_4]^{2-}$.

AIM

To observe the effect of changing the temperature of a system at equilibrium.

EQUIPMENT

- 3 g cobalt(II) chloride-6-water $[CoCl_2.6H_2O]$
- Distilled water
- 5 mL of concentrated hydrochloric acid
- Three large test tubes
- Bunsen burner
- Test-tube tongs

- Heat mat
- Forceps
- Test-tube racks

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Concentrated HCl is very corrosive to skin and clothes.	Wear gloves and an apron. If any acid comes in contact with skin, wash it immediately with plenty of water.
Cobalt(II) chloride-6-water may be an irritant to eyes, skin and respiratory systems. It may cause cancer.	Use in a well ventilated area. Wear gloves, safety glasses and an apron. If any of the chemical comes in contact with skin, wash it immediately with plenty of water.
Heating chemicals in a test tube can be hazardous.	Always point test tube away from people

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Use the forceps to pick up a pea-sized amount of $CoCl_2.6H_2O$. Dissolve it in 1–2 mL of distilled water in a test tube. Observe and record the colour of the resultant solution. This colour is due to the $[Co(H_2O)_6]^{2+}$ ion. Place this test tube in a test-tube rack and keep as a reference.
2. Dissolve a pea-sized amount of $CoCl_2.6H_2O$ in 1–2 mL of concentrated hydrochloric acid in a clean test tube. Observe and record the colour of the resultant solution. This colour is due to the $[CoCl_4]^{2-}$ ion. Place in test-tube rack and keep this test tube as a reference.
3. Dissolve a pea-sized amount of $CoCl_2.6H_2O$ in 1–2 mL of distilled water in the third test tube. Gently heat the solution over the Bunsen burner until the solution is almost boiling. Place in a test-tube rack and then observe and record the colour change.
4. Allow the third test tube to cool down, observing and recording the colour change.

RESULTS

Record your results in a carefully formatted table.

ANALYSIS

1. What colour change was observed when the test tube was heated? What does this colour indicate regarding the relative proportion of the two ions?
2. What colour change was observed when the test tube cooled down? What does this colour indicate regarding the relative proportion of the two ions?

DISCUSSION

1. Which reaction was favoured when the test tube was heated?
2. Is the forward reaction exothermic or endothermic? Explain your answer.
3. How would the equilibrium constant for this reaction change with an increase in temperature? Explain your answer.
4. What other factors may have contributed to the observations?

CONCLUSION

What conclusion can you make regarding the effect of temperature on the equilibrium between $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$?

SECTION REVIEW 2.1

REMEMBERING

1 Complete the following sentences, using the words 'exothermic' or 'endothermic'.

- **a** Raising the temperature of a system at equilibrium will favour the _____ reaction.
- **b** Lowering the temperature of a system at equilibrium will favour the _____ reaction.
- **c** The activation energy of an _____ reaction is greater than that of an _____ reaction.

UNDERSTANDING

2 Explain why raising the temperature affects the rate of exothermic and endothermic reactions differently.

2.2.1 Collision theory

2.2 Changing concentration

collision theory the theory that a reaction will occur when two particles collide with sufficient energy. The faster the collisions occur, the higher the rate of reaction.

concentration the amount of substance per unit volume

From our understanding of **collision theory** and reaction rates, we know that an increase in the **concentration** of a reactant will increase the rate of the reaction because of the increased number of collisions. In reversible reactions, if the concentration of a reactant is increased, then the rate of the forward reaction will increase. Alternatively, if the concentration of a product is increased, then the rate of the reverse reaction will increase.

If the concentration of one chemical in a system at equilibrium is increased, then the rate of the reaction that uses that chemical will increase. This will use up some of the additional chemical, reducing the concentration, therefore, this rate will gradually decrease. At the same time, the rate of the opposite reaction will increase, as more of its reactants are produced. Eventually the rates of the two reactions will once again become equal, so equilibrium is re-established. As an example, consider the reaction between hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

- If more iodine is added to the system, then the concentration of iodine is increased.
- As the iodine is a reactant for the forward reaction, the rate of the forward reaction will increase, as shown in Figure 2.2.1.
- This means that the concentration of hydrogen gas and iodine will decrease while the concentration of the hydrogen iodide will increase.
- As more hydrogen iodide is produced, the rate of the reverse reaction will begin to increase.
- This pattern will continue until the rates of the forward and reverse reactions are once again equal. At this time, the concentrations of each chemical will remain constant.
- The new concentration of iodine will be lower than the concentration following the addition of the extra iodine. However, it will not return to the original concentration.

2.2.2 Equilibria: concentration

The same logic can be applied to a decrease in concentration:

- A decrease in concentration will lead to a decrease in the rate of the reaction that uses that substance.
- Over time, the concentration of the reactants for that reaction will increase as less of each is used up, while the concentration of the products for that reaction will decrease.
- However, the concentration of the substance that was removed will not return to its original concentration.

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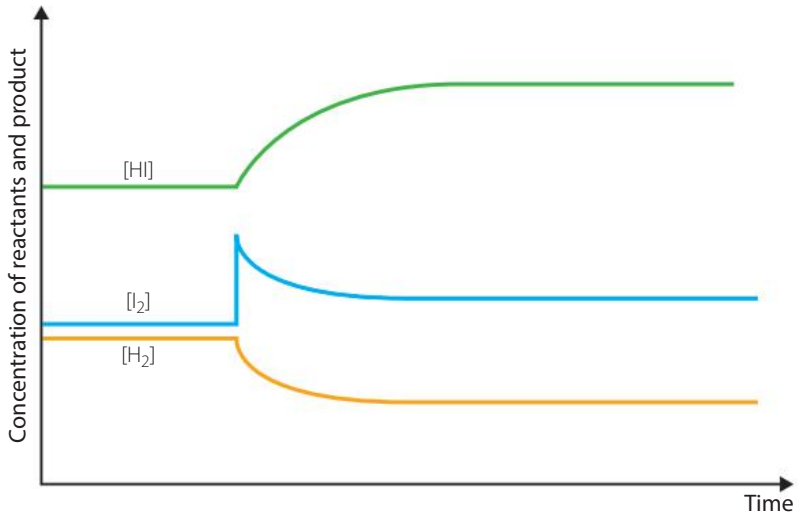

FIGURE 2.2.1 Concentrations of [HI] and [H_2] following a change in [I_2]

TABLE 2.2.1 The effect of a change in concentration on equilibrium

IMPOSED CHANGE		REACTION FAVOURED (FORWARD OR REVERSE)	SHIFT IN EQUILIBRIUM (LEFT OR RIGHT)	RESULTANT CHANGE IN CONCENTRATION OF REACTANTS	RESULTANT CHANGE IN CONCENTRATION OF PRODUCTS
PRODUCT OR REACTANT ALTERED	INCREASE OR DECREASE IN CONCENTRATION				
Reactant	Increase	Forward	Right	Decrease	Increase
Reactant	Decrease	Reverse	Left	Increase	Decrease
Product	Increase	Reverse	Left	Increase	Decrease
Product	Decrease	Forward	Right	Decrease	Increase

PRACTICAL ACTIVITY 2.2.1

Effect of changes in concentration on equilibrium

In an aqueous solution of chromate or dichromate salts, an equilibrium will exist between the two ions:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

The chromate ion is yellow and the dichromate ion is orange. Therefore, the colour of the solution will indicate the relative proportions of the two ions, and hence the position of equilibrium. If the solution is yellow, then there are more chromate ions than dichromate ions and the equilibrium lies more to the left. Alternatively, if the solution is orange, there are more dichromate ions than chromate ions and equilibrium lies to the right.

AIM

To observe the effect of a change in concentration on a system at equilibrium

EQUIPMENT

- 5 mL of 0.1 mol L^{-1} potassium chromate (K_2CrO_4)
- 5 mL of 0.1 mol L^{-1} potassium dichromate ($K_2Cr_2O_7$)
- 5 mL of 0.2 mol L^{-1} sodium hydroxide (NaOH)
- 5 mL of 0.2 mol L^{-1} hydrochloric acid (HCl)
- Distilled water
- Four test tubes
- 10 mL measuring cylinder

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
0.2 mol L^{-1} HCl is corrosive to skin and clothing.	Wear gloves, safety glasses and an apron.
0.2 mol L^{-1} NaOH may cause irritation to eyes and skin.	Wear gloves, safety glasses and an apron.
Potassium dichromate and potassium chromate are oxidising agents and may cause cancer and respiratory allergic reactions.	Handle with care. Wear gloves, safety glasses and an apron. Keep away from combustible materials. Do not dispose of these chemicals down the sink.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Place approximately 1 mL of 0.1 mol L^{-1} potassium chromate into a test tube. Observe the colour and keep this test tube as a reference for the colour of the chromate ion.
2. Place approximately 1 mL of 0.1 mol L^{-1} potassium dichromate into a test tube. Observe the colour and keep this test tube as a reference for the colour of the dichromate ion.
3. Place approximately 1 mL of 0.1 mol L^{-1} potassium chromate into a clean test tube. Add 0.2 mol L^{-1} hydrochloric acid to the solution drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
4. To the same test tube used in step 3, add 0.2 mol L^{-1} sodium hydroxide drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
5. Place approximately 1 mL of 0.1 mol L^{-1} potassium dichromate into a clean test tube. Add 0.2 mol L^{-1} sodium hydroxide to the solution drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
6. To the same test tube used in step 5, add 0.2 mol L^{-1} hydrochloric acid drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
7. Follow your teacher's instructions to dispose of the chemicals.

RESULTS

Present your observations in a simple table.

ANALYSIS

1. **a** What happened to the colour of the chromate solution when the hydrochloric acid was added?
   b Why did this happen?
2. **a** What happened to the concentration of hydrogen ions when the sodium hydroxide was added to the chromate solution?
   b Write an equation to demonstrate this reaction.
   c What colour change was observed in step 4?
   d Explain why this colour change happened.
3. Account for the colour changes observed in steps 5 and 6.

DISCUSSION

1. Compare the colours observed in steps 3–6 to the reference test tubes. Suggest a reason for any changes that occurred.
2. The volumes used in this experiment were approximate volumes. Did this affect the results? Explain your answer.

CONCLUSION

1. What conclusion can you make regarding the shift in equilibrium following:
   a. an increase in concentration of a reactant or product?
   b. a decrease in concentration of a reactant or product?

SECTION REVIEW 2.2

REMEMBERING

1. Explain what is meant by 'concentration'.
2. Explain collision theory.

UNDERSTANDING

3. Explain why altering the concentration of one reactant will affect the position of equilibrium of a system.

2.3 Volume, pressure and catalysts

2.3.1 Equilibria: pressure

When the volume or pressure of a gaseous system changes, the concentrations of all gaseous substances are altered. This means that the concentration of both reactants and products may change. The one that changes the most will have the greatest influence on the change of equilibrium.

If you consider the reaction between nitrogen gas and hydrogen gas producing ammonia, then you can see that there is a 4:2 ratio of gas molecules between the reactants and products. 3 molecules of H_2 and 1 molecule of N_2 are used for every 2 molecules of NH_3 produced:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

- If the volume of the system was halved, then the pressure and, therefore, the concentration of all the gases would double.
- The rate of both the forward and reverse reactions would therefore increase.
- There would be a greater proportion of gas molecules in the reactants and so the rate of the forward reaction would increase more than the reverse reaction.
- As the reactions proceeded, the concentrations of hydrogen and nitrogen would decrease and the concentration of ammonia would increase.
- Similarly, the rate of the forward reaction would decrease and the rate of the reverse reaction would increase until equilibrium was re-established.
- The opposite would happen if the volume of a gaseous system was increased.

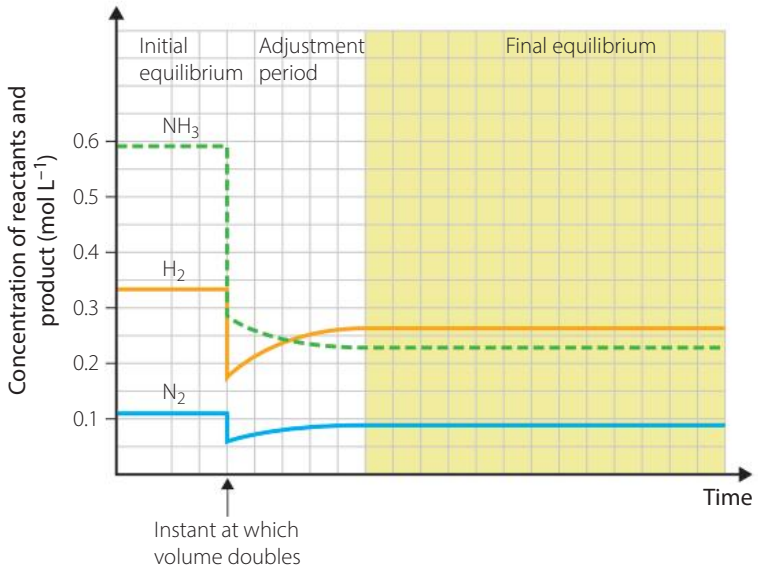

FIGURE 2.3.1 Changing the volume of a gaseous system

Another situation to consider is where there are equal numbers of molecules of gases in the reactants and products of the equation. This means that if the volume changes, then the concentration of reactants and products change equally, and therefore the rates of both the forward and reverse reactions also change equally and remain equal. Therefore, equilibrium has not been altered.

For example, in the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

there is an equal number of moles of gas on both sides. A change in the volume of the container would not alter the position equilibrium.

PRACTICAL ACTIVITY 2.3.1

Changing the volume of a gaseous system at equilibrium

An equilibrium exists between the gases nitrogen dioxide and dinitrogen tetraoxide:

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

Nitrogen dioxide is a brown gas, while nitrogen tetraoxide is colourless. This means the colour can indicate the proportion of gases in the mixture. A darker brown indicates a greater concentration of nitrogen dioxide and therefore an equilibrium that lies further to the left. Conversely, a lighter brown colour indicates a lower concentration of nitrogen dioxide and therefore an equilibrium that lies further to the right.

2.3.2 Changing the volume of a gaseous system at equilibrium

AIM

To observe the effect of changing the volume of a gaseous system at equilibrium.

EQUIPMENT

- Large, transparent syringe containing NO_2/N_2O_4
- Digital camera

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WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
NO_2/N_2O_4 is hazardous if inhaled or if it comes into contact with skin, eyes or mucous membranes.	Ensure the syringe is sealed. Conduct experiment in a fume hood.

RISK ASSESSMENT

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Your teacher will demonstrate this experiment.
2. Observe the colour of the gas mixture in the syringe.
3. Quickly push in the plunger of the syringe to reduce the volume. Observe the immediate change in the colour of the gas mixture and then the changes that occur over the next few seconds as equilibrium is re-established.

RESULTS

Record your observations in a table or video the results using the digital camera.

ANALYSIS

1. What happened to the intensity of the colour when the volume was initially reduced? Why did this occur?
2. What happened to the intensity of the colour as equilibrium was re-established? Why did this occur?

DISCUSSION

1. Use your knowledge of collision theory to account for the changes that were observed.
2. Predict the changes that would be observed if the volume of the system was increased. Your teacher may demonstrate this for you so that you can see whether your prediction is correct.
3. What factors would affect the change observed in a gaseous system when the volume is altered?

CONCLUSION

What conclusion can you make about the changes observed when the volume is changed in a gaseous system?

Diluting an aqueous system

If the volume of a solution is changed by adding or removing water, then the same principle will apply, as the concentration of all aqueous substances will change.

- If water is added to the solution, then the concentration of all aqueous components will decrease.
- The rate of the reaction that uses the greater proportion of aqueous molecules will initially decrease the most.
- The rate of this reaction will then gradually increase while the rate of the opposite reaction will decrease until the two are once again equal and equilibrium is re-established.

Consider the equilibrium between chromate and dichromate:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Figure 2.3.2 shows the changes in concentration when a mixture of chromate and dichromate at equilibrium is diluted.

- When water is added to the solution, then the concentration of all the aqueous substances will decrease.
- In aqueous solution the concentration of water is assumed to be constant. Therefore, on the graph there will be sudden drops in the concentration of chromate, hydrogen ions and dichromate.

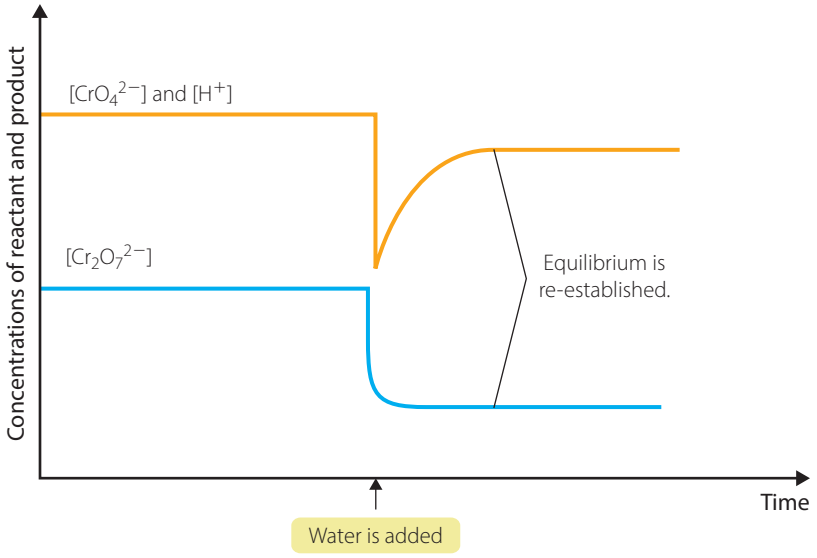

FIGURE 2.3.2 Concentrations of reactant and product following a change in volume

catalyst
a substance that increases the rate of a reaction without being consumed in the reaction

- As four aqueous molecules are used to produce only one, the reverse reaction will be favoured. This will use up dichromate and produce chromate and hydrogen ions.
- Therefore, the concentration of chromate and hydrogen ions will increase while the concentration of dichromate will decrease until the concentrations once again plateau and remain constant.

Adding a catalyst does not affect equilibrium. However, it does affect how quickly equilibrium is attained. A catalyst will decrease the activation energy of both the forward and reverse reactions equally. The rates of both the reactions will increase; however, they change by the same proportion. Hence, the equilibrium is not disturbed.

2.3.2 Activation energy: catalyst

SECTION REVIEW 2.3

REMEMBERING

1 Which of these reactions will not be affected in terms of equilibrium position by a change in total volume? Why is this?
   - **a** $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$
   - **b** $H_2(g) + I_2(g) \rightarrow 2HI(g)$
   - **c** $3H_2(g) + 2N_2(g) \rightarrow 2NH_3(g)$

UNDERSTANDING

2 Explain why altering the volume of a gaseous system affects the position of equilibrium.

3 Why is the effect of diluting an aqueous system the same as the effect of increasing the volume of a gaseous system?

Le Chatelier's principle
the principle that if a change is imposed on a system at equilibrium, then the system will act in order to partially oppose the change

2.4 Le Chatelier's principle

Henri Louis Le Chatelier summarised the trends involved in a change in the conditions of a system at equilibrium in Le Chatelier's principle. This principle can be used to predict the changes that will occur following a change in concentration of chemicals, pressure, volume or temperature of a system.

KEY CONCEPT

- Le Chatelier's principle states that: '*If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way so as to partially counteract the change.*'

2.4.1 Le Chatelier's principle

To use Le Chatelier's principle to predict the outcome of a change in conditions, we need to consider:

1. What is the change imposed?
2. What is the opposite of the change? This is what the system will do.
3. Which reaction is favoured – the forward or reverse?
4. Does equilibrium shift to the left or right?
5. What happens to the concentrations of each aqueous substance or gas?

Using Le Chatelier's principle to predict the effect of changes in temperature

If the temperature of the system is increased, then according to Le Chatelier's principle the system will react to decrease the temperature. To do this, the endothermic reaction will be favoured, as it uses up energy. Alternatively, if the temperature is decreased, then the exothermic reaction will be favoured, in order to produce heat energy to increase the temperature.

Consider again the production of ammonia:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

- this reaction as written is an exothermic reaction
- therefore, if the temperature of the system is increased, the endothermic reaction will be favoured to use up the added heat energy
- this will favour the reverse reaction, resulting in an increase in the concentrations of hydrogen and nitrogen gas and a decrease in the concentration of ammonia
- conversely, if the temperature is decreased, then the exothermic reaction will be favoured
- this will result in the forward reaction being favoured, increasing the concentration of ammonia and decreasing the concentrations of hydrogen and nitrogen gas.

Using Le Chatelier's principle to predict the effect of changes in concentration

According to Le Chatelier's principle, when the concentration of a substance involved in a reaction is altered, the system will react to counteract the change and return the concentration towards its original level.

This means that:

- if the concentration of a reactant is increased, then the system will respond to decrease it by favouring the forward reaction, which uses up the reactant
- this shifts equilibrium to the right, increasing the concentration of the products and decreasing the concentration of the reactants
- however, the concentration of the substance added will not return to its original concentration, as the system can only partially counteract the change.

Alternatively, if the concentration of a product is decreased, then the system will favour the reaction that produces products to increase the concentration again. Therefore, the forward reaction will be favoured and equilibrium will shift to the right.

Consider the equilibrium established during the production of ammonia:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

- if more hydrogen gas is added to the container without a change in volume, then the concentration of hydrogen gas will increase
- according to Le Chatelier's principle, the system will react to reduce this increased concentration, thus favouring the forward reaction, which uses up hydrogen gas
- therefore, the reaction will shift to the right, the concentrations of hydrogen gas and nitrogen gas will decrease, while the concentration of ammonia will increase.

Using Le Chatelier's principle to predict the effect of changes in volume

If the volume of a gaseous system is changed, then the concentration of all the gaseous substances will be altered.

According to Le Chatelier's principle, the system will react to reverse the change in the total concentration (or pressure). To determine whether the forward or reverse reaction will achieve this change, you must consider the number of gaseous molecules in the reactant and products. The reaction that will produce more molecules of gaseous substances will increase the total concentration or pressure, while the reaction that uses more molecules will decrease the total concentration or pressure.

For example, in the reaction between nitrogen gas and hydrogen gas to produce ammonia, 4 gaseous molecules are used to make 2 gaseous molecules:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

- if the volume of the system is decreased, then the total pressure will increase
- according to Le Chatelier's principle, the system will react to decrease the total pressure
- in this reaction, the forward reaction uses more molecules than it produces, thus decreasing the total number of particles and therefore pressure.

SECTION REVIEW 2.4

REMEMBERING

1 State Le Chatelier's principle.

UNDERSTANDING

2 Explain why adding a catalyst to a system at equilibrium does not affect the position of equilibrium.

APPLYING

3 Silver ions can be removed from solution by adding carbonate ions:

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

Describe two processes that would increase the amount of silver removed.

4 People use soluble sodium hypochlorite pellets in swimming pools to help kill bacteria and algae:

$$ClO^-(aq) + H^+(aq) \rightleftharpoons HClO(aq) + \text{heat}$$

Use Le Chatelier's principle to predict the changes that would occur for each of the following (assume the pool is covered and is therefore a closed system).

a Adding more sodium hypochlorite pellets

b Adding sodium hydroxide

c The pool warming up on a hot day

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** endothermic reaction
- **b** collision theory
- **c** Le Chatelier's principle
- **d** catalyst.

CATEGORY QUESTIONS

2 Use the concept of activation energy to explain why some reactions are not reversible.

3 Explain why changing the pressure of a gaseous reaction can affect the position of the equilibrium.

ELABORATION

4 The graph in Figure 2.5.1 shows the concentration of the reactant and product for the reaction:

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

Use Le Chatelier's principle to explain the changes seen in the graph.

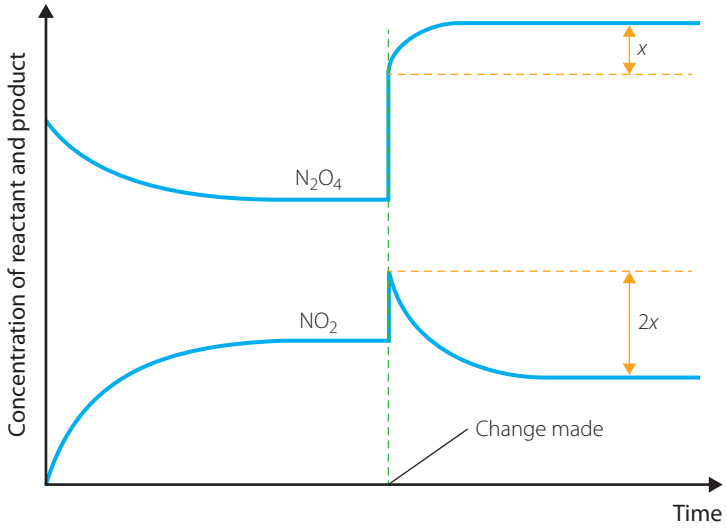

FIGURE 2.5.1 The concentration of the reactant and product for the reaction

5 Use collision theory to explain the effect of removing hydronium ions from the following reaction mixture at equilibrium.

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

6 For the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = +57.2 \text{ kJ}$$

what would be the effect of each of the following changes on an equilibrium mixture of N_2O_4 and NO_2?

a Adding N_2O_4

b Adding NO_2

c Adding heat

d Removing N_2O_4

e Increasing the pressure

EVIDENCE QUESTIONS

7 Research the role equilibrium plays in transporting oxygen in our blood.

END-OF-CHAPTER EXAM

End-of-chapter test

1 The equation below describes a system at equilibrium:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$

The graph below reflects what happens when a change is made to the equilibrium system in the reaction above at time t_1.

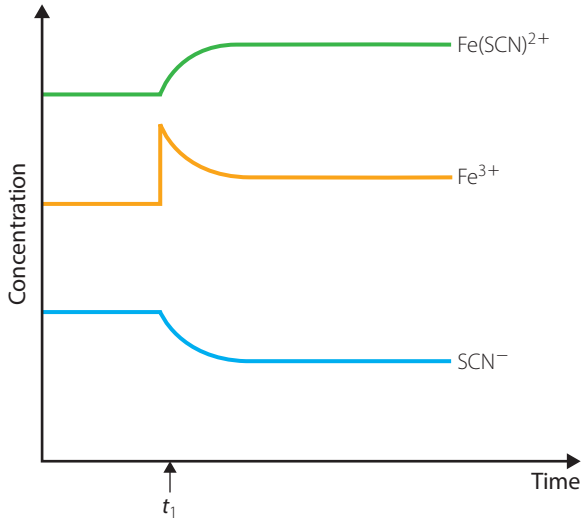

FIGURE 2.5.2 What happens when a change is made to the equilibrium system in the reaction above at time t_1

Which one of the following would be a valid reason for the changes at time t_1?

A An increase in temperature

B A decrease in temperature

C Addition of Fe^{3+}

D Removal of $Fe(SCN)^{2+}$

2 If the system above was diluted, then which of the following would be the situation after equilibrium was re-established?

A The position of equilibrium would have shifted to the right

B The concentration of all reactants would have decreased

C The number of $Fe(SCN)^{2+}$ ions present would have increased

D The total number of ions present would have decreased

3 The following reaction can be used to generate hydrogen iodide:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -56\,kJ\,mol^{-1}$$

If this reaction is carried out, the equilibrium yield of hydrogen iodide will be increased by:

A an increase in pressure at constant temperature.

B a decrease in temperature.

C the use of a suitable catalyst.

D removal of iodine from the mixture.

4 The following reaction is studied in a laboratory:

$$3H_2(g) + 2N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\,kJ\,mol^{-1}$$

A mixture of hydrogen, nitrogen and ammonia is held in a sealed container at equilibrium. 1 mole of ammonia (NH_3) is added to the container and equilibrium is re-established.
Explain why the rate of the reaction:

$$3H_2(g) + 2N_2(g) \rightarrow 2NH_3(g)$$

will never be greater than the rate of the reaction:

$$2NH_3(g) \rightarrow 3H_2(g) + 2N_2(g)$$

a while the system is reaching equilibrium.

b once equilibrium is re-established.

3 EQUILIBRIUM CONSTANTS

Introduction

A chemical system involving a reversible reaction is said to have reached a state of equilibrium when the rates of the forward and back reactions are equal, and the concentrations of the reactants and products are therefore constant.

Importantly, these concentrations do not need to be equal. There is a mathematical relationship between the concentrations of the reactants and products. This relationship is known as the equilibrium constant or K_C.

Stimulus questions

How can we represent the position of equilibrium for a reversible reaction?

What information does the equilibrium constant provide about a chemical reaction?

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3.1 The equilibrium law

equilibrium constant the value ratio between the concentrations of the reactants and products, represented as K_C

equilibrium expression the ratio of the concentration of products to reactants used to calculate the equilibrium constant

When a system is at *equilibrium*, at a fixed temperature, the product of concentration of the products divided by the product of the concentrations of the reactants, each being raised to the coefficient of the substance in the equation, must be equal to a constant.

This constant is known as the **equilibrium constant**, and represented as K_C, and can therefore be calculated from the concentrations of the reactants and products at equilibrium in the **equilibrium expression**.

KEY FORMULA

For the reaction:

$aA + bB \rightleftharpoons cC + dD$

the equilibrium expression is:

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

As the equilibrium expression is determined from the way the equation is written, the magnitude of K will also depend on the equation.

Calculating the equilibrium constant

Consider the reaction where dinitrogen tetroxide forms nitrogen dioxide:

$$N_2O_4 \rightleftharpoons 2NO_2$$

Table 3.1.1 shows the concentrations of N_2O_4 and NO_2 that were recorded in a series of trial experiments. The experiments were all carried out at the same temperature and the concentrations were recorded after a period of time had elapsed.

TABLE 3.1.1 The concentrations of N_2O_4 and NO_2 recorded in a series of trial experiments

Trial	$[N_2O_4]$ (mol L^{-1})	$[NO_2]$ (mol L^{-1})	$[N_2O_4]^2$	$[NO_2]^2$	$\frac{[NO_2]}{[N_2O_4]}$	$K_C \frac{[NO_2]^2}{[N_2O_4]}$
1	3.476	1.048	12.083	1.098	0.301	0.316
2	2.560	0.899	6.554	0.808	0.351	0.316
3	0.830	0.512	0.689	0.262	0.617	0.316
4	0.012	0.062	0.000	0.004	5.065	0.316
5	2.680	1.235	7.182	1.525	0.461	0.569

Looking at the results, we can make a few observations:

- Trials 1–4 involve a system at equilibrium, where the K_C value is the same in each trial.
- The table demonstrates the equilibrium law – namely that simply calculating the ratio of products to reactants does not give a constant value. In order to calculate the equilibrium constant, the concentrations must be raised to the power of their reaction coefficient.
- In trial 5, for some reason the system is not at equilibrium, as the calculated value of K_C is not the same as in trials 1–4, despite the temperature being the same.

Now consider the same reaction, but written in reverse:

$$2NO_2 \rightleftharpoons N_2O_4$$

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TABLE 3.1.2 The concentrations of N_2O_4 and NO_2 recorded in a series of trial experiments

Trial	$[N_2O_4]$ (mol L^{-1})	$[NO_2]$ (mol L^{-1})	$[N_2O_4]^2$	$[NO_2]^2$	$\frac{[N_2O_4]}{[NO_2]}$	K_C $\frac{[N_2O_4]}{[NO_2]^2}$
1	3.476	1.048	12.083	1.098	3.316	3.165
2	2.560	0.899	6.554	0.808	2.847	3.165
3	0.830	0.512	0.689	0.262	1.621	3.165
4	0.012	0.062	0.000	0.004	0.197	3.165
5	2.680	1.235	7.182	1.525	2.170	1.757

Table 3.1.2 shows the same reaction, with the same raw data as for Table 3.1.1; however, the reaction is written in reverse, and therefore the K_C value is the inverse of that in Table 3.1.1. Trials 1–4 are still representative of systems at equilibrium. Importantly, however, this demonstrates that the value of K_C is dependent on the way in which the reaction is written in the equation.

Equilibrium constants for homogeneous and heterogeneous equilibria

Solutions and gases vary in concentration and therefore are included in the equilibrium expression. With gases, the partial pressure (the pressure of the individual gas) is proportional to the concentration of the gas and therefore can also be used in the equilibrium expression for a gaseous system.

However, solids and liquids do not vary in their concentration. Therefore, in a **heterogeneous system** where the substances are in more than one phase, solids and liquids are not included in the equilibrium expression. We only include the concentrations of solutions or gases. In a **homogeneous system**, where all substances are in the same phase, we include solids and liquids because the relative proportions are important.

heterogeneous system
a system where there is a mixture of phases of reactants and products

homogeneous system
a system where all the reactants and products are in the same phase

WORKED EXAMPLE 3.1.1

A Write the equilibrium expression for $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

ANSWER

1. Put the products on top of the expression; the reactants underneath.
2. Add square brackets around each substance to indicate concentration.
3. The coefficient for each species from the equation becomes the power in the expression.
4. Multiply concentrations if there is more than one reactant or product.
5. $K = \dfrac{[NH_3]^2 \times [H^+]}{[H_2]^3[N_2]}$

B Write the equilibrium expression for $CaCl_2(s) \rightleftharpoons Ca^{2+}(aq) + 2Cl^-(aq)$

ANSWER

1. Put the products on top, reactants on bottom.
2. Add square brackets around each substance to indicate concentration.
3. The coefficient for each species from the equation becomes the power in the expression.

4 Multiply concentrations if there is more than one reactant or product.

5 Exclude solids and liquids in heterogeneous equilibria.

6 $K = [Ca^{2+}][Cl^-]^2$

WORKED EXAMPLE 3.1.2

Calculate the magnitude of the equilibrium constant for the reaction:

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+(aq)$$

given that, at equilibrium, $[CH_3COOH] = 0.92$ mol L^{-1}, $[CH_3COO^-] = 1.62 \times 10^{-2}$ mol L^{-1} and $[H^+] = 1.02 \times 10^{-3}$ mol L^{-1}.

ANSWER

1 Write the equilibrium expression.

$$K = \frac{[CH_3\,COO^-] \times [H^+]}{[CH_3\,COOH]}$$

2 Substitute the given concentrations into the expression.

$$K = \frac{(1.62 \times 10^{-2}) \times (1.02 \times 10^{-3})}{0.92}$$

3 Calculate the answer.

$$K = 1.8 \times 10^{-5}$$

SECTION REVIEW 3.1

UNDERSTANDING

1 Define:

- **a** equilibrium expression
- **b** equilibrium constant
- **c** homogenous system
- **d** heterogeneous expression.

APPLYING

2 Write the equilibrium expression for each of the following reactions.

- **a** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- **b** $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$
- **c** $CaCO_3(s) \rightleftharpoons CaO(s) + O_2(g)$
- **d** $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$
- **e** $2CrO_4^-(aq) + 2H^+ \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

3 Calculate the magnitude of the equilibrium constant for each of the following examples.

- **a** $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, given that $[CO_2] = 2.00$ mol L^{-1}, $[H_2] = 3.00$ mol L^{-1}, $[CO] = [H_2O] = 0.17$ mol L^{-1}.
- **b** $2H_2S(g) \rightleftharpoons 2H_2(g) \rightleftharpoons S_2(g)$, given that $[H_2S] = 0.2$ mol L^{-1}, $[H_2] = 7.0 \times 10^{-3}$ mol L^{-1} and $[S_2] = 3.5 \times 10^{-3}$ mol L^{-1}.

3.2 Using the equilibrium constant to describe the position of equilibrium

The magnitude of K_C can tell us whether there are more products or reactants at equilibrium. As the products are on top of the fraction, a large value of K_C indicates the concentration of products is much greater than the concentration of reactants. Therefore:

- a large value of K indicates that the reaction goes towards completion, meaning that nearly all of the reactants become products. We say that equilibrium lies to the right, as more products than reactants are present at equilibrium.
- a small value of K indicates that the reaction only occurs to a small extent. We say that equilibrium lies to the left, as more reactants than products are present at equilibrium.
- a value of K close to 1 indicates that there are significant concentrations of both reactants and products present at equilibrium.

For example, the equilibrium constant for the 'pop test', which is the reaction between hydrogen and oxygen gas to form water vapour, is 2.4×10^{47} at 500 K.

The equation for this reaction is:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

Therefore, the equilibrium expression is:

$$K_C = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

The very high value of the equilibrium constant shows that, at equilibrium, there is a large amount of product (H_2O) and only a very small amount of reactants (H_2 and O_2). This indicates that most of the reactants react to become products, so the reaction occurs to a large extent. In this case, we say that the position of equilibrium is to the right.

In contrast, the reaction for hydrogen molecules splitting into hydrogen atoms has an equilibrium constant of 1.2×10^{-42} at 500 K.

$$H_2(g) \rightleftharpoons 2H(g)$$

$$K_C = \frac{[H]^2}{[H_2]}$$

The very low value for the equilibrium constant indicates that, at equilibrium, there is a large proportion of the reactant, H_2 molecules, compared to the product, H atoms. This shows the reaction only occurs to a very small extent. In this case, we say that the position of equilibrium is to the left.

Reaction quotient

The ratio of products to reactants $\frac{[C]^c[D]^d}{[A]^a[B]^b}$ will only equal the equilibrium constant (K_C) when the system is at equilibrium. The **reaction quotient** (Q) is also calculated from the same ratio and gives a mathematical value that can be compared with the equilibrium constant and can indicate the following.

reaction quotient the value of the equilibrium expression when calculated, Q

- If $Q = K_C$, then the system is at equilibrium.
- If $Q < K_C$, then there are less products and more reactants than at equilibrium. This indicates that the forward reaction will be favoured for the system to reach equilibrium.
- If $Q > K_C$, then there are more products and less reactants than at equilibrium. This indicates that the reverse reaction will be favoured for the system to reach equilibrium.

WORKED EXAMPLE 3.2.1

The equilibrium constant for the reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

is 14.5 at a temperature of 483 K. If the concentrations of CO and H_2 are both 0.5 mol L^{-1} and the concentration of CH_3OH is 5 mol L^{-1}, is the system at equilibrium?

ANSWER

From the equation, the expression for the reaction quotient is:

$$Q = \frac{[CH_3\,OH]}{[CO][H_2]^2}$$

Using the values stated, the value of Q at 483 K is:

$$Q = \frac{5}{0.5 \times 0.5^2} = 40$$

Therefore, as Q is not equal to K_C, the system is not at equilibrium. $Q > K_C$ (40 >14.5), so there are more products and fewer reactants than at equilibrium. Therefore, the reverse reaction would be favoured, as the system moves towards equilibrium.

SCIENCE AS A HUMAN ENDEAVOUR

WINE

The taste and stability of a wine depends upon the acidity of the wine. Wine should have a pH of 3.1–3.5. This range is optimum for fermentation and ensures the desired balance of sugar and acid. Higher pH values (above pH 4.2) may allow bacteria to multiply.

If the pH of wine is too high, then the total acidity of the wine can be increased by adding tartaric acid. Tartaric acid is the most common acid in wine, and is stable and less likely to be attacked by bacteria.

If the pH of wine is too low, then the wine may be inoculated with a culture of lactic acid bacteria. This second fermentation (malolactic fermentation) converts diprotic acid (malic acid) to the monoprotic acid (lactic acid).

If the wine has a pH ≥ 3.9, then cold stabilisation causes an increase in pH. But if the wine has a pH < 3.9, then cold stabilisation causes a decrease in pH. This can be explained by Le Chatelier's principle. At pH < 3.9, the first reaction (1) dominates – cold stabilisation removes HT^- from solution, thus lowering its concentration (T represents the tartaric acid group). The system tries to partially oppose this change by shifting the equilibrium to the right, producing more HT^- and H_3O^+. The production of H_3O^+ therefore decreases the pH of the wine.

When wine pH ≥ 3.9, the equilibrium reaction between the tartaric anion (T^{2-}) and the hydrogen tartrate form (HT^-) is the main reaction (2) (When the concentration of HT^- is reduced, then the system tries to partially oppose the change by shifting the equilibrium to the left. This consumes the free H^+ ions and HT^{2-} and produces more HT^- and the pH of the wine increases.

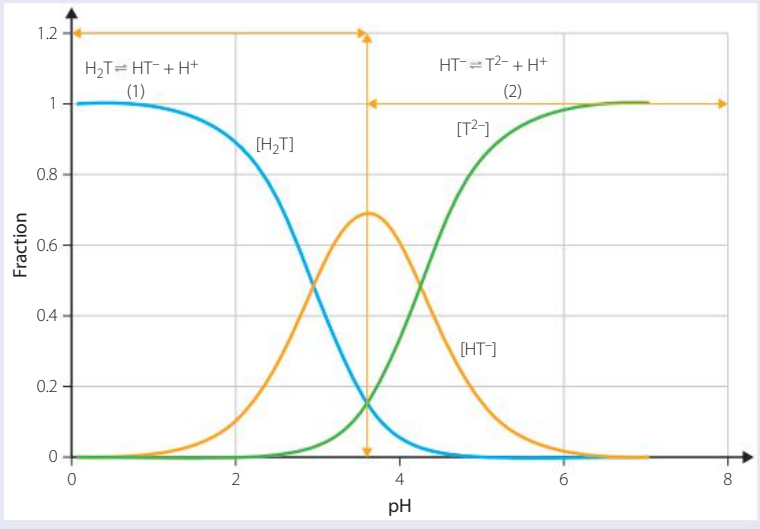

FIGURE 3.2.1 The main species of tartaric acid present in wine at various pH levels

SECTION REVIEW 3.2

UNDERSTANDING

1 Complete the following statements.

If $Q = K_C$, then the system _____.

If $Q < K_C$, then there are less products and more reactants than at equilibrium. This indicates _____.

If $Q > K_C$, then there are more products and less reactants than at equilibrium. This indicates _____.

3.3 Calculating equilibrium concentrations

We can determine value of the equilibrium constant if we know the equilibrium concentrations of the reactants and products. By considering the ratios in which the reactants react with each other and products are subsequently formed, we can also determine the equilibrium constant. We can determine K_C, if the starting concentrations of the reactants and products are given as well as the equilibrium concentration of at least one reactant or product.

WORKED EXAMPLE 3.3.1

Hydrogen and fluorine react together to form hydrogen fluoride in a reversible reaction:

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

1 mole of H_2 and 2 moles of F_2 are introduced to a 1 L container and the system is left to reach equilibrium. When equilibrium is reached, there are 0.032 moles of H_2 remaining in the container.

A Calculate the equilibrium concentrations of F_2 and HF.

B Calculate the equilibrium constant.

ANSWER

	H_2	F_2	HF
Initial number of moles	1	2	0
Number of moles at equilibrium	0.032		

As the system has reached equilibrium, the change in number of moles of H_2 is $1 - 0.032 = 0.968$.

When the reaction takes place, the reaction equation indicates that the number of moles of H_2 and F_2 reacting will be the same, and that the number of moles of HF formed will be twice that of reactants lost. Therefore:

	H_2	F_2	HF
Initial number of moles	1	2	0
Number of moles lost/gained	−0.968	−0.968	+1.936
Number of moles at equilibrium	0.032	1.032	1.936
Equilibrium concentration (number of moles/volume)	0.032	1.032	1.936

Therefore, the equilibrium constant will be:

$$K_C = \frac{[HF]^2}{[H_2][F_2]} = \frac{1.936^2}{0.032 \times 1.032} = 113.5$$

SECTION REVIEW 3.3

UNDERSTANDING

1 Explain how the value of the equilibrium constant describes the position of equilibrium.

APPLYING

2 The equilibrium constant for:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

is 14.5 at 483 K.

If the concentration of CO and H_2 are both 0.5 mol L^{-1} and the concentration of CH_3OH is 5 mol L^{-1}, is the system at equilibrium?

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define the equilibrium constant.

2 What is the only characteristic that will change the magnitude of the equilibrium constant for a reaction?

CATEGORY QUESTIONS

3 Explain the difference between the reaction quotient and the equilibrium constant.

4 Explain why solids and liquids are not included in the equilibrium expression for a heterogeneous system.

5 Describe the relative concentrations of reactants and products for a reaction with an equilibrium constant of 5.0×10^{-17}.

ELABORATION QUESTIONS

6 Write the equilibrium expression for:

a $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

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

7 When 0.40 moles of PCl_5 is heated in a 10.0 L container, an equilibrium is established in which 0.25 moles of Cl_2 is present.

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

a What is the number of moles of PCl_5 and PCl_3 at equilibrium?

b What are the equilibrium concentrations of all three components?

END-OF-CHAPTER EXAM

End-of-chapter test

1 Hydrogen chloride, HCl, can decompose to form an equilibrium mixture of HCl, Cl_2 and H_2, according to the following equation:

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

At 30°C, $K_C = 6.2 \times 10^{20}$ and at 60°C, $K_C = 7.4 \times 10^{18}$. What valid conclusion can we draw from this finding?

A HCl is less stable at the higher temperature.

B The equilibrium concentrations of $[H_2]$ and $[Cl_2]$ are equal.

C The equilibrium concentration of HCl is lower at 30°C than at 60°C.

D The forward reaction is exothermic.

2 An important stage in the production of sulfuric acid is the reaction of sulfur dioxide and oxygen to form sulfur trioxide.

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

In an investigation of this reaction, 2 moles of SO_3 are placed in an empty 1 L flask, and allowed to reach equilibrium.

The temperature is kept constant. If $[O_2] = 0.3$ mol L^{-1} or just M at equilibrium, what is the equilibrium concentration of SO_3?

A 0.80 M

B 1.00 M

C 1.10 M

D 1.40 M

3 Hydrogen iodide can be formed in the following reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_C = 200 \text{ at } 50°C$$

In an experiment, gases were added to a sealed container in the following concentrations:

$$[H_2] = 0.04 \text{ M}, [I_2] = 0.02 \text{ M and } [HI] = 0.8 \text{ M}$$

When the reaction reaches equilibrium at 50°C, the concentration of HF will be:

A 0.80 M.

B less than 0.80 M.

C 1.00 M.

D between 0.80 M and 1.00 M.

4 Dinitrogen tetroxide can dissociate to form nitrogen dioxide according to the following equation:

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

0.67 moles of N_2O_4 gas were placed in an empty 2 L vessel at 50°C. When the system reached equilibrium, there were 0.20 moles of NO_2 present in the vessel.

a Calculate the value of the equilibrium constant at 50°C.

b At 60°C, the value of the equilibrium constant for the reaction is 0.07. Is this reaction exothermic or endothermic? Explain your answer.

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4 PROPERTIES OF ACIDS AND BASES

Introduction

Early chemists could identify an acid or a base from its properties. But to develop a conceptual definition of an acid requires an understanding of the structure of the molecules or ions of acids and bases and the mechanism of acid–base reactions. Arrhenius defined acids in terms of their ability to produce H^+ ions in solution. Understanding the strength of an acid is complicated by the realisation that an acid can be monoprotic or polyprotic and that acids and bases dissociate or break apart to differing degrees.

Another complicating factor is the concentration of the acid or base, which must not be confused with the strength of the acid or base.

Stimulus questions

What is the difference between a strong acid and a weak acid?

How can scientists identify strong and weak bases?

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4.1 What is an acid?

Le Chatelier's principle can be applied to acid–base systems. The Ancient Greeks first identified sour-tasting substances as *oxein*. This was translated to Latin as *acetum* and later anglicised to its current name, 'acid'. Acidic substances were found to change the colour of litmus paper and corrode metals.

Bases were known to counteract the effects of acids. Bases were originally known as *alkaline*, from the Arabic word for roasting. This was because producing soap (a base) involved roasting ashes and reacting them with water and slaked lime.

During the 18th century, Antoine Lavoisier studied the composition and structure of these substances and began to develop our modern understanding of acids and bases. Early chemists could identify an acid or a base from its properties, but to develop a conceptual definition of an acid requires an understanding of the structure of the molecules or ions of acids and bases, and the mechanism of acid–base reactions.

4.1.1 Acids, bases, pH
4.1.2 Acids, bases and pH

FIGURE 4.1.1 Acids and bases are everyday items. Examples of substances that contain acids are vinegar (ethanoic acid), lemon juice (citric acid) and aspirin (acetylsalicylic acid). Examples of substances that contain bases are oven cleaners (sodium hydroxide), some detergents and bicarbonate of soda.

PRACTICAL ACTIVITY 4.1.1

Testing the properties of acids and bases

In Year 11 you learnt that:

- acids have a sour taste, sting or burn the skin, conduct electricity in solution and turn blue litmus red
- bases have a bitter taste, a slippery feel in aqueous solution, conduct electricity in solution (not all bases are soluble) and turn red litmus blue.

AIM

To test for most of the properties listed above, using common acids and bases and some common chemicals you will find at home

EQUIPMENT

- 50 mL of 0.1 mol L^{-1} hydrochloric acid solution
- 50 mL citric acid
- 50 mL of 0.1 mol L^{-1} sodium hydroxide solution
- 50 mL of 0.1 mol L^{-1} sodium bicarbonate (sodium hydrogen carbonate) solution
- 50 mL beakers (one for each solution)
- Range of common chemicals such as detergent, coffee, lemon juice, milk
- Litmus paper (red and blue)
- Powerpack
- Leads
- Alligator clips
- Graphite rods
- Light bulb

Complete the risk assessment below in your workbooks to show any risks associated with completing this experiment and ways to manage them.

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Glassware may break and cut you.	Handle glass with care. Inspect and discard any chipped or cracked beakers, no matter how small the damage. Sweep up broken glass with a dustpan and brush; do not use fingers.
Litmus paper is flammable.	Store in a dry location, keep away from fire.
The powerpack may give an electrical shock.	Do not use if the cord is damaged or loose. Only use the powerpack if it is tagged as safe.
0.1 mol L^{-1} sodium hydroxide is slightly toxic.	Never ingest any laboratory chemicals.
Household chemical 1 (your choice)	
Household chemical 2 (your choice)	

PROCEDURE

1. Predict whether each of your common chemicals will be acidic, basic or neither.
2. Test each sample with a small strip of red litmus. Record the results.

»

3 Test each sample with a small strip of blue litmus. Record the results.

4 Test each sample for electrical conductivity by constructing an electrical circuit with the powerpack, leads, alligator clips, graphite rods and light bulb.

RESULTS

Record your results in a carefully formatted table.

ANALYSIS

1 Use the evidence you obtained to classify each substance as acidic or basic.

2 What difficulties did you experience when testing the common chemicals?

3 Were your predictions correct?

DISCUSSION

1 What trends did you observe?

2 Why shouldn't you test for some of the properties of acids, such as sour taste, stinging or burning the skin? Or for the bitter taste or slippery feel of bases in aqueous solution?

CONCLUSION

1 How useful are the common properties for distinguishing acids from bases?

2 Do these descriptions allow you to distinguish other solutions as neither acid nor base?

3 What would be the advantage of having alternative ways of distinguishing acids and bases?

INQUIRING FURTHER

Acids and bases are added to many processed foods. For example, acids are added to sour lollies. This is one way to safely taste acids. Add an acidic solution such as vinegar to a solution of sodium bicarbonate to see effervescence. Predict how self-raising flour works.

Design and carry out an experiment in which you make pancakes or a simple chocolate cake from plain flour and sodium bicarbonate, rather than self-raising flour, to safely test the taste of a base. Undertake this test outside a class laboratory. Why is this a safer method than a simple taste test?

In *QScience Chemistry Units 1 & 2* an acid was defined as a substance that produces hydrogen ions (H^+) in an aqueous solution. The reaction of the acid with water is called an **ionisation reaction**, as ions are formed.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Hydrogen ions do not exist in solution as H^+. The hydrogen atom consists of one proton and one electron. When the atom loses this electron, the resulting H^+ ion consists of just one **proton**, which is a very small, highly concentrated positive charge. This proton has a very strong attraction for electrons and so, in aqueous solution, readily attaches itself to a water molecule to form the **hydronium ion**, $H_3O^+(aq)$:

$$HCl(aq) + H_2O(l) \rightarrow \mathbf{H_3O^+}(aq) + Cl^-(aq)$$

hydronium ion

ionisation reaction
a chemical reaction when an uncharged molecule becomes an ion

proton
a particle found in the nucleus of an atom possessing a positive charge equal and opposite to that of an electron

hydronium ion
the ion that forms when a proton is donated to a water molecule (H_3O^+)

monoprotic
a substance that can donate one proton to a base

Polyprotic acids

Acids such as HCl and HNO_3 will give up one proton (H^+ ion) per molecule. These are called **monoprotic** acids.

Other acids, such as sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3), can give up two protons per molecule of acid. These are called **diprotic** acids. The ionisation of sulfuric acid is shown below:

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

The complete ionisation of sulfuric acid occurs in two steps:

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$
hydrogen sulfate ion

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

Phosphoric acid, H_3PO_4, is a triprotic acid and ionises in three steps:

$$H_3PO_4(s) + H_2O(l) \rightarrow \mathbf{H_2PO_4^-}(aq) + H_3O^+(aq)$$
dihydrogen phosphate ion

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

$$\mathbf{HPO_4^{2-}}(aq) + H_2O(l) \rightarrow \mathbf{PO_4^{3-}}(aq) + H_3O^+(aq)$$
phosphate ion

It can be seen that when polyprotic acids ionise, they form a number of different ions. When sulfuric acid ionises, it can form the sulfate ion (SO_4^{2-}) or the hydrogen sulfate ion (HSO_4^-). The hydrogen sulfate ion can combine with a cation to produce a hydrogen sulfate salt such as potassium hydrogen sulfate ($KHSO_4$). This is an example of what are called hydrogen salts or acid salts.

Below is a table showing some common polyprotic acids and the anions they form.

diprotic
a substance that can donate two protons to a base

triprotic
a substance that can donate three protons to a base

4.1.3 Polyproptic acids and bases

TABLE 4.1.1 Some common diprotic and triprotic acids and the anions they can form

ACID	FORMULA	ANIONS FORMED	FORMULA
Sulfuric	H_2SO_4	Hydrogen sulfate	HSO_4^-
		Sulfate	SO_4^{2-}
Carbonic	H_2CO_3	Hydrogen carbonate	HCO_3^-
		Carbonate	CO_3^{2-}
Sulfurous	H_2SO_3	Hydrogen sulfite	HSO_3^-
		Sulfite	SO_3^{2-}
Phosphoric	H_3PO_4	Dihydrogen phosphate	$H_2PO_4^-$
		Hydrogen phosphate	HPO_4^{2-}
		Phosphate	PO_4^{3-}
Citric	$C_6H_8O_7$	Dihydrogen citrate	$C_6H_7O_6^-$
		Hydrogen citrate	$C_6H_6O_6^{2-}$
		Citrate	$C_6H_5O_6^{3-}$

SECTION REVIEW 4.1

REMEMBERING

1 Define:
- **a** acid
- **b** base
- **c** hydronium ion
- **d** monoprotic acid
- **e** diprotic acid
- **f** triprotic acid.

UNDERSTANDING

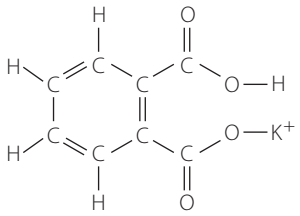
2 Write equations to show the complete dissociation of the following acids.

- **a** Oxalic acid ($H_2C_2O_4$)
- **b** Nitrous acid (HNO_2)
- **c** Ethanoic acid (CH_3COOH)
- **d** Arsenic acid (H_3AsO_4)

APPLYING

3 Potassium hydrogen phthalate ($C_8H_5KO_4$) has the structure given below. Is this a monoprotic, a diprotic or a triprotic acid? Justify your answer with appropriate dissociation equations.

FIGURE 4.1.2
Potassium hydrogen phthalate



4.2 Acid and base strength

strong acids
an acid that readily donates a proton to water; K_a is large

weak acids
an acid in which only a small proportion of the molecules will donate their proton; K_a is small

Acids in which almost all of the acid molecules ionise are defined as **strong acids**. Examples of strong acids are hydrochloric acid (HCl), nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Acids in which only some of the molecules ionise are defined as **weak acids**. Examples of weak acids are vinegar (a solution containing ethanoic acid), citric acid, hydrofluoric acid (HF), lactic acid and carbonic acid (H_2CO_3).

4.2.1 Strong and weak acids

FIGURE 4.2.1
Strong acid ionisation: $HCl \rightarrow Cl^- + H^+$

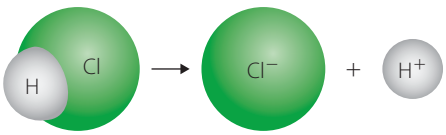


FIGURE 4.2.2
Comparison of how strong acid (HCl) and weak acid (HF) molecules ionise in water. **a** All of the HCl molecules are ionised. **b** Only some HF molecules are ionised.

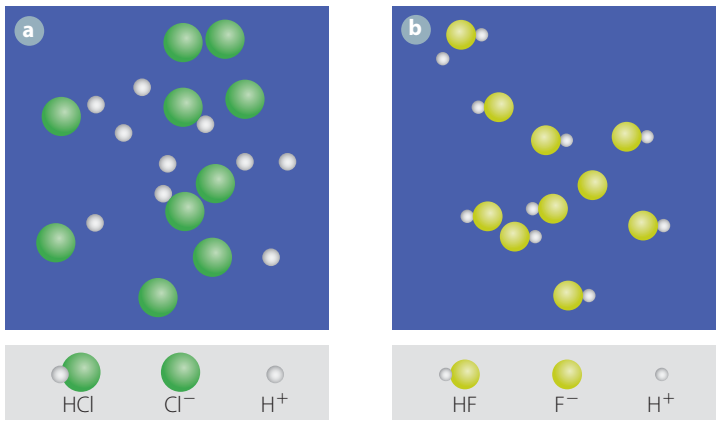


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TABLE 4.2.1 Examples of acids and bases

STRONG ACIDS	STRONG BASES
Hydrochloric acid, HCl(aq) Nitric acid, HNO_3 Sulfuric acid, H_2SO_4	Sodium hydroxide, NaOH Potassium hydroxide, KOH Barium hydroxide, $Ba(OH)_2$ Sodium oxide, Na_2O
WEAK ACIDS	**WEAK BASES**
Ethanoic acid, CH_3COOH Carbonic acid, $H_2CO_3(aq)$ Hydrofluoric acid, HF Citric acid, $C_6H_8O_7$	Ammonia, NH_3 Methylamine, CH_3NH_2

A base can be considered as a substance that produces a hydroxide ion in solution; for example, soluble salts containing the oxide (O^{2-}) ion or hydroxide (OH^-) ion. A soluble base is called an alkali. Strong bases always dissociate in water to form separate ions. This reaction is called a **dissociation** reaction. Examples of strong bases are sodium hydroxide (NaOH) and potassium hydroxide (KOH). Weak bases, such as ammonia (NH_3), have only a few ions dissociated in water.

dissociation reaction
a reaction in which an ionic substance separates in a solution

$$NaOH(s) \xrightarrow[\text{complete}]{\text{dissociation}} Na^+(aq) + OH^-(aq)$$

$$NH_3(aq) + H_2O(aq) \xrightarrow{\text{partial}} NH_4^+(aq) + OH^-(aq)$$

Concentration versus strength

The strength of an acid or base refers to its ability to ionise in solution. Stronger acids ionise completely in solution. If the concentrations of a strong acid and a weak acid are the same, the concentration of hydronium ions [H_3O^+] is higher in the strong acid solution than in the weak acid solution. Only a few particles of weak acid dissociate, so there is a lower concentration of weak acid ions in aqueous solution and therefore a solution of a weak acid has a lower concentration of hydronium ions.

As discussed in Year 11, the definitions of concentrated and dilute relate to the amount of solute per unit of solution. The most convenient measure of concentration used in chemistry is molarity.

- A concentrated solution is one in which the total concentration is high; for example, 4 M or 4 mol L^{-1}.
- A dilute solution is one in which the total concentration is low; for example, less than 2 M or 2 mol L^{-1}.

It is possible to have a dilute solution of a strong acid and a concentrated solution of a weak acid. This is also true of strong and weak bases. 'Concentrated', 'dilute', 'strong' and 'weak' have independent meanings in chemistry as shown, in Figure 4.2.3.

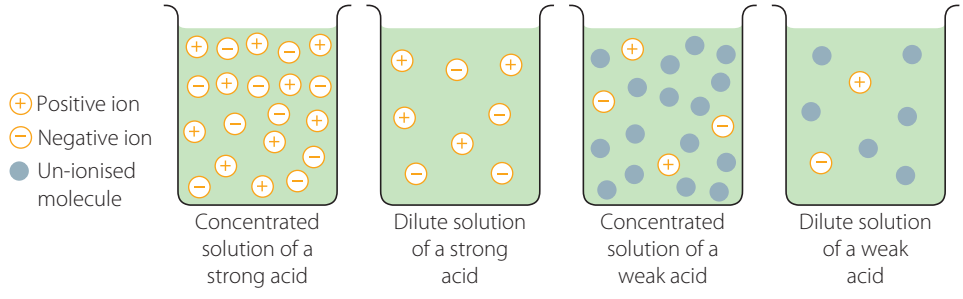


FIGURE 4.2.3 Concentrated and dilute solutions of a strong acid and a weak acid

When distinguishing between strong and weak acids, it is useful to think of the reaction between an acid and water as an equilibrium reaction, as shown in the formula:

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

HCl is a strong acid and so every HCl molecule dissociates to give a proton that attaches to a water molecule to give a hydronium ion. At equilibrium, there are no HCl molecules and so the equilibrium is shifted to the right. This can be represented with a modified equilibrium symbol:

$$\underset{0\%}{HCl(aq)} + H_2O(l) \rightleftharpoons \underset{100\%}{H_3O^+(aq)} + Cl^-(aq)$$

Ethanoic acid (CH_3COOH) is a weak acid and so only about 1% of the ethanoic acid molecules dissociate:

$$\underset{\approx 99\%}{CH_3COOH(aq)} + H_2O(l) \rightleftharpoons \underset{\approx 1\%}{H_3O^+(aq)} + CH_3COO^-(aq)$$

Similarly, strong and weak bases can be represented using equilibrium equations. Sodium hydroxide (NaOH) is a strong base and so dissociates fully:

$$\underset{0\%}{NaOH(s)} + H_2O(l) \rightleftharpoons \underset{100\%}{Na^+(aq)} + H_2O(l) + OH^-(aq)$$

Methylamine (CH_3NH_2) is a weak base and only partially dissociates:

$$\underset{\approx 99\%}{CH_3NH_2(l)} + H_2O(l)\ C \rightleftharpoons \underset{\approx 1\%}{H_3NH_3^+(aq)} + OH^-(aq)$$

A simple way to differentiate between strong and weak acids and bases is to compare their electrical conductivity values. A solution's ability to conduct electricity is determined, to a large extent, by the number of ions it contains. The more ions, the greater the conductivity.

From the equilibrium equations above, it can be seen that a strong acid such as hydrochloric acid will have many more ions in solution than a weak acid such as ethanoic acid. The same can be said for strong and weak bases.

A simple way to differentiate between a strong acid (or base) and a weak acid (or base) is to measure their relative electrical conductivities using the simple apparatus shown below. A strong acid solution contains more ions and so will have a higher electrical conductivity than a weak acid.

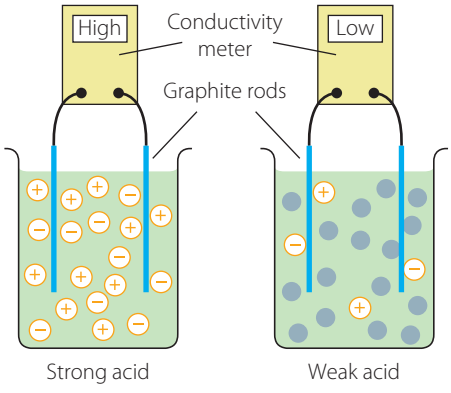


FIGURE 4.2.4 Apparatus for measuring the conductivity of strong and weak acids

SCIENCE AS A HUMAN ENDEAVOUR

SUPERACIDS

Faster at corroding than sulfuric acid, 231 019 times more powerful; unlike other acids, able to react with hydrocarbons, breaking down raw petroleum, and worthy of a Nobel Prize (1994). Look, it's a superacid!

The alchemists thought that vinegar (ethanoic acid) was a strong acid. Sulfuric acid (oil of vitriol) was the strongest acid known for centuries. With a better definition of acids, chemists were able to develop superacids that are a million times stronger than earlier acids. In 1927, the first superacids were made by reacting sulfuric acid with fluorosulfuric acid and fluoroantimonic acid. Superacids are widely used in industry, and have applications in fuel cells and batteries. They also have the potential to clean up the pollution in exhausts.

SECTION REVIEW 4.2

REMEMBERING

1 Define:

- **a** strong acid
- **b** weak acid
- **c** concentrated acid
- **d** dilute acid.

UNDERSTANDING

2 Write equilibrium equations to show the dissociation of the following substances in water.

- **a** Nitric acid $HNO_3(l)$
- **b** Propylamine, $CH_3CH_2CH_2NH_2(l)$

APPLYING

3 Sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3) are diprotic acids. If we measured the conductivity of solutions of both with equal concentrations, which acid would have the higher conductivity? Justify your answer with equilibrium equations.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

a polyprotic

b amphiprotic

c hydrogen salt

CATEGORY QUESTIONS

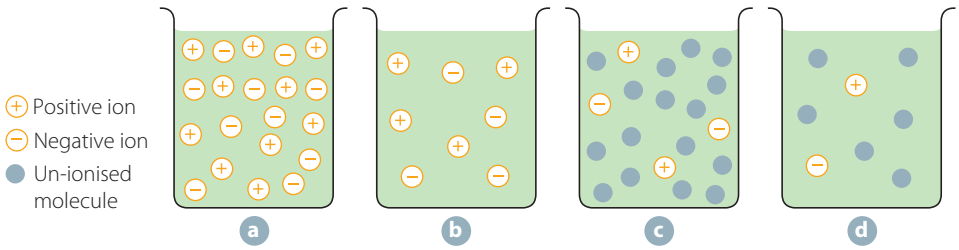
2 Write equilibrium equations to show the dissociation of the following substances in water.

a Barium hydroxide, $Ba(OH)_2(s)$

b Benzoic acid, $C_6H_5COOH(l)$

ELABORATION QUESTIONS

3 Identify the strengths of the acid solutions in the diagram below.



4 Explain the difference between concentrated and dilute solutions of a weak and a strong acid.

EVIDENCE QUESTIONS

5 The table below shows relative conductivity values for a number of substances, all of 1 mol L^{-1} concentration. The substances tested were, in no particular order, carbonic acid (H_2CO_3), hydrochloric acid (HCl), ethanoic acid (CH_3COOH), phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4).

From the results, match the substance letter with the appropriate acid. Explain your reasoning in each case.

SUBSTANCE	RELATIVE CONDUCTIVITY
A	8.0×10^{-4}
B	2.0
C	9.2×10^{-4}
D	1.7×10^{-3}
E	1.0

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END-OF-CHAPTER EXAM

End-of-chapter test

1 Which of the following could be categorised as a strong, diprotic acid?

A H_2SO_3

B $H_2C_2O_4$

C H_2SO_4

D H_2S

2 Which of the following bases would have the highest electrical conductivity?

A NH_3

B CH_3NH_2

C RbOH

D PH_3

3 Which of the following shows the correct dissociation products in the correct order for arsenic acid, H_3AsO_4?

A $AsO_4^{3-} \rightarrow HAsO_4^{2-} \rightarrow H_2AsO_4^-$

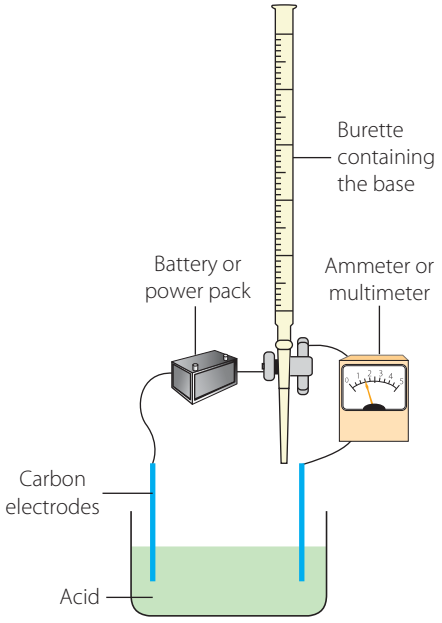
B $AsO_4^{3-} \rightarrow H_2AsO_4^- \rightarrow HAsO_4^{2-}$

C $HAsO_4^{2-} \rightarrow AsO_4^{3-} \rightarrow HAsO_4^{2-}$

D $H_2AsO_4^- \rightarrow HAsO_4^{2-} \rightarrow AsO_4^{3-}$

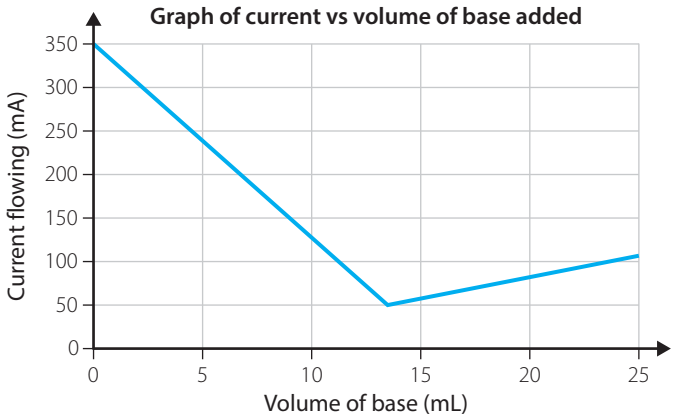
4 Two solutions, X and Y, are 100% dissociated and are known to be acidic. Solution Y has an electrical conductivity approximately twice that of solution X. Suggest an identity for solution X.

5 Conductimetric titrations are very useful in analytical chemistry. The diagram below shows the apparatus used.

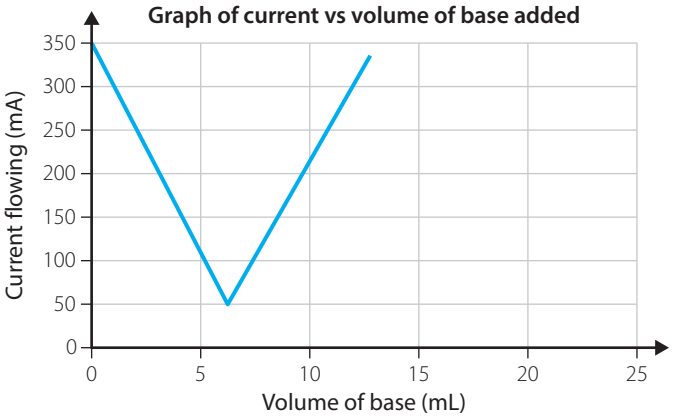


When a titration is carried out, a graph of current flowing against volume of base added is produced. The following page shows graphs produced from titrations using various acids and bases.

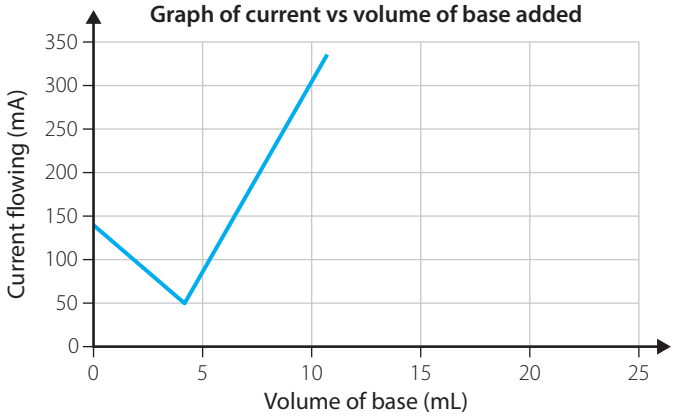
a



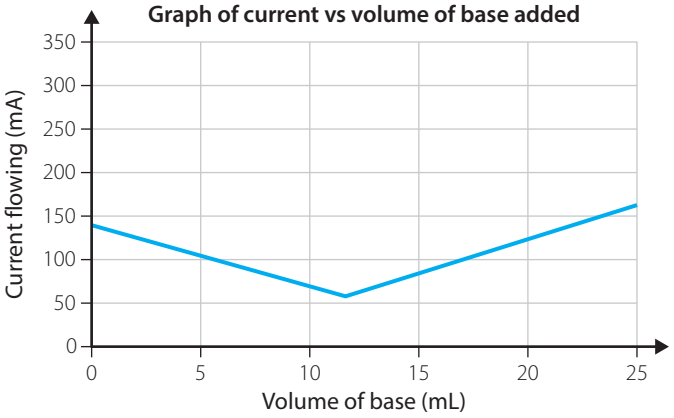
b



c



d



The solutions used in these titrations were: ammonia (NH_3), potassium hydroxide (KOH), hydrochloric acid (HCl) and ethanoic acid (CH_3COOH).

For each titration a–d, suggest an acid and a base from the above list that best matches the shape of the graph. Explain your choice in each case.

5 pH SCALE

Introduction

The pH scale is a useful way of comparing substances of varying degrees of acidity and basicity depending on the number of hydrogen ions they release into solution. While this gives us an idea of the amount of H^+ ions involved, it is important to be able to determine definitively and quantitatively the concentrations of hydrogen ions and hydroxide ions present in solutions.

An appreciation of the concepts of chemical equilibria and Le Chatelier's principle can be useful in our understanding of the interaction of acids and bases.

Stimulus questions

Why is water a weak electrolyte?

Can scientists use the concentration of hydrogen ions to calculate the pH of a solution?

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5.1 Self-ionisation of water

There is experimental evidence to show that in extremely pure water, some water molecules react with each other to produce hydronium ions ($H_3O^+(aq)$) and hydroxide ions ($OH^-(aq)$). This is shown in Figure 5.1.1. This is an equilibrium reaction.

FIGURE 5.1.1 Water reacts with itself in an equilibrium reaction to form hydronium and hydroxide ions.

Water conducts electricity as it undergoes self-ionisation according to the equation:

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

This reaction occurs only to a very small extent; it is reversible and the equilibrium constant is small. The concentration of water is very large (approximately 55 M) and so effectively does not change significantly in the reaction, so $[H_2O]$ can be removed from the equilibrium expression. To represent this, we use the **self-ionisation constant, K_w**, the ionic product constant for water:

self-ionisation constant (K_w) the equilibrium expression that shows water ionising into two ions

$$K_w = [H^+]\,[OH^-], \text{ where } K_w = 10^{-14}\ M^2 \text{ at } 25°C$$

In pure water, the concentration of H^+ equals the concentration of OH^-:

$$[H^+] = [OH^-]$$

This means that:

$$K_w = [H^+]\,[OH^-] = 10^{-14}\ M^2 \text{ at } 25°C$$

$$\text{Therefore } [H^+]^2 = 10^{-14}$$

$$\text{Therefore } [H^+] = \sqrt{10^{-14}}$$

$$= 10^{-7}\ M$$

So, at 25°C, when water is neutral, $[H^+] = [OH^-] = 10^{-7}$ M. This is true *only* when the temperature is 25°C (298 K).

When $[H^+] > [OH^-]$, the solution is considered acidic. At 25°C, this is when $[H^+] > 10^{-7}$ M. When $[H^+] < [OH^-]$, the solution is considered basic or alkaline. At 25°C, this is when $[H^+] < 10^{-7}$ M.

5.1.1 Self-ionisation of water and the pH scale

5.1.2 Self-ionisation of water

5.1.3 Water autoionisation and K_w

WORKED EXAMPLE 5.1.1

Calculate the concentrations of H^+ ions and OH^- ions in a 3.48 M solution of HCl.

ANSWER

Write the dissociation equation:

$$HCl(l) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

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Determine the $[H^+]$ from the acid concentration – HCl is a strong acid and so every HCl molecule will dissociate.

So, if the [HCl] is 3.48 M, then the $[H^+] = 3.48$ M

Use $K_w = [H^+]\,[OH^-] = 10^{-14}$ to determine the $[OH^-]$

$$K_w = [H^+]\,[OH^-] = 10^{-14}\ M^2$$

$$3.48 \times [OH^-] = 10^{-14}$$

$$[OH^-] = \frac{10^{-14}}{3.48} = 2.87 \times 10^{-14}\ M$$

It is clear that the concentration of OH^- in this HCl solution is *very* small. We would expect this for a solution of a strong acid.

WORKED EXAMPLE 5.1.2

A solution of potassium hydroxide (KOH) is prepared by dissolving 150 g of KOH in 250.00 mL of water. Calculate the concentrations of the H_3O^+ ions and OH^- ions in this solution.

ANSWER

Determine the concentration of the potassium hydroxide solution:

$$c = \frac{n}{v}$$

$$n = \frac{m}{M} = \frac{150}{56.1} = 2.674\ \text{mol}$$

$$c = \frac{2.674}{\frac{250.00}{1000}} = 10.696\ M$$

Write the dissociation equation:

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

Determine the $[OH^-]$ from the KOH concentration – KOH is a strong base and so every KOH molecule will dissociate.

So, if the [KOH] is 10.696 M, then the $[OH^-] = 10.696$ M

Use $K_w = [H^+]\,[OH^-] = 10^{-14}$ to determine the $[H^+]$

$$K_w = [H^+]\,[OH^-] = 10^{-14}\ M^2$$

$$[H^+] \times 10.696 = 10^{-14}$$

$$[H^+] = \frac{10^{-14}}{10.696} = 9.35 \times 10^{-16}\ M$$

Again, this is a *very* small number, which is to be expected in a concentrated alkaline solution.

SECTION REVIEW 5.1

REMEMBERING

1 **a** Explain what is meant by the self-ionisation of water.

b Define K_w.

APPLYING

2 Calculate the concentrations of the H^+ ions and OH^- ions in the following solutions.

a 1.45 M HNO_3

b 0.89 M NaOH

c 1.50 M H_2SO_4

d 0.89 M $Ba(OH)_2$

5.2 pH scale

5.2.1 Definition of pH

The pH scale is a measure of the concentration of hydronium ions. The concentration can vary widely, generally from 10 M to 10^{-15} M. Because this range is so large, chemists introduced the pH scale to measure the concentration. The pH scale can indicate the acidic or basic nature of substances.

The pH of a solution is defined as the negative logarithm (to the base 10) of the hydronium ion concentration:

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

KEY FORMULA

The square brackets around a species mean 'molar concentration of', so $[H^+]$ is read as the molar concentration of hydronium ions.

A change of 1 unit of pH is the same as changing the concentration of the solution by a factor of 10. This is due to the logarithmic pH – a change in concentration of H_3O^+ ion in solution by a factor of 10.

- For a solution in which $H^+ = 0.1$ M (or 10^{-1}), the pH is 1.0.
- For a solution in which $H^+ = 0.01$ M (or 10^{-2}), the pH is 2.0.
- For a solution in which $H^+ = 0.000\,0001$ M (or 10^{-7}), the pH is 7.0.
- Notice that $H^+ = 10^{-pH}$.

It is relatively straightforward to work out the pH when the concentration is 0.1 or 0.01, or any factor of 10. When the concentration is 0.015, which is between 0.1 and 0.01, you need a calculator. Use the following formula:

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

For $[H^+] = 0.015$ M, the pH is 1.82.

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

A change in pH of one unit corresponds to a tenfold change in $[H^+]$.

WORKED EXAMPLE 5.2.1

A Calculate the pH, given $[H^+] = 1.0 \times 10^{-5}$ M

B Calculate the $[H^+]$ when pH = 8.5

ANSWER

A Choose the correct formula and insert numbers.

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

$pH = -\log_{10}(1.0 \times 10^{-5})$

$pH = 5.0$

B Choose the correct formula and insert numbers.

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

$[H^+] = 10^{-8.5}$

$[H^+] = 3.2 \times 10^{-9}$ M

pH of polyprotic acids

KEY FORMULA

When determining the significant figures in pH values, only the mantissa (the digits after the decimal place) is significant; for example, a pH of 3.14 has only two significant figures. The '3' is called the characteristic and is a 'place holder'.

The pH of a 0.1 M solution of sulfuric acid (H_2SO_4) is around 0.69, not 1.0, which means it is a more acidic solution. The pH indicates that there are more hydronium ions than 0.1 M. The pH value can be used to calculate the concentration of hydronium ions $[H_3O^+]$ as almost 0.2 M. This is because sulfuric acid reacts with water as shown:

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

The complete dissociation of sulfuric acid occurs in two steps:

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

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

The second step involves HSO_4^-. This is a weaker acid than sulfuric acid and not all of the molecules will react with water and ionise. So the concentration of hydronium ions is not quite twice the concentration of the acid. However, in neutralisation reactions, both protons will be donated. Effectively, the diprotic acid requires twice the number of moles of base.

Le Chatelier's principle can be applied here. For each molecule of acid, the number of protons that may be donated is two. The concentration of the acid may be 0.1 M, but as two protons can be donated when reacting with strong bases, this must be taken into account. Strong diprotic acids have a hydronium ion concentration greater than a monoprotic acid.

Calculating the pH of alkaline solutions

If an alkaline solution has a known concentration of hydroxide ion, $[OH^-]$, you can calculate the pH from the relationship:

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

Once the hydronium ion concentration, $[H_3O^+]$, is known, we can calculate the pH.

In a 0.01 M solution of NaOH, $[OH^-] = 0.01$.

$$K_w = 1 \times 10^{-14} = [H_3O^+] \times 0.01$$

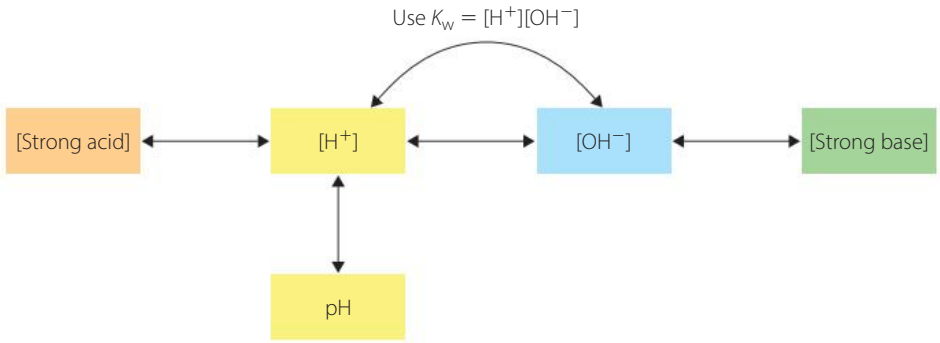

FIGURE 5.2.1 The pathway for performing pH calculations for strong acids and strong bases

$$\text{So } [H_3O^+] = \frac{10^{-14}}{0.01} = 10^{-12}$$

$$\text{So, pH} = -\log_{10}[H_3O^+] = -\log_{10} 10^{-12} = 12$$

Table 5.2.1 lists the pH values for solutions and corresponding $[H_3O^+]$ and $[OH^-]$. Notice that the pH scale 0–14 corresponds to these values. This range is due to the K_w of water, which is equal to 10^{-14} at 25°C. However, lower and higher pH values are possible for concentrated solutions of strong acids and bases; for example, 10 M KOH has a pH of just less than 15.

TABLE 5.2.1 pH values for solutions and the corresponding hydronium and hydroxide ion concentrations

pH	1.0	3.0	5.0	7.0	9.0	11.0	13.0
$[H_3O^+]$	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}
$[OH^-]$	10^{-13}	10^{-11}	10^{-8}	10^{-7}	10^{-5}	10^{-3}	10^{-1}

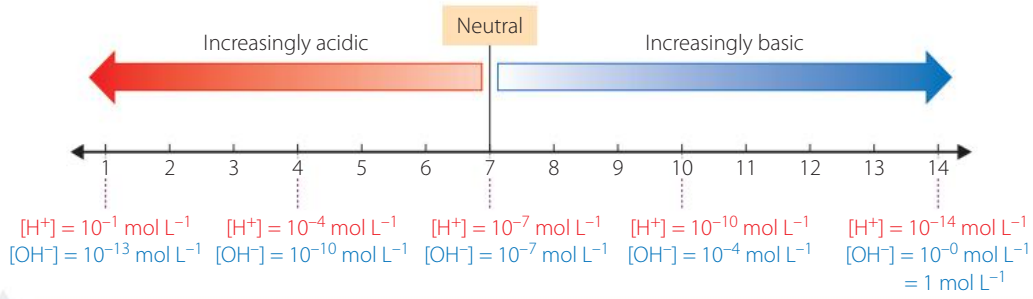

FIGURE 5.2.2 The pH scale

WORKED EXAMPLE 5.2.2

Find the pH of a 0.02 M solution of sodium hydroxide.

ANSWER

1 Determine the species present.

NaOH is a strong base and dissociates 100% in solution.

2 Determine $[OH^-]$.

$$NaOH \rightarrow Na^+ + OH^-$$

$$\text{Therefore, } [OH^-] = \text{original } [NaOH] = 0.02 \text{ M.}$$

3 Choose the correct formula and insert the correct numbers.

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

$$= [H^+][0.02] = 1 \times 10^{-14}$$

$$\text{Hence, } [H^+] = \frac{1 \times 10^{-14}}{0.02} = 5 \times 10^{-13}$$

$$pH = -\log[H^+] = 12.3$$

4 pH = 12.3

The pOH scale

The pH scale is a measure of the concentration of hydronium ions, H_3O^+ and is determined using

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

In the same way, it is possible to produce a scale that is a measure of the concentration of hydroxide ions, OH^-. This is called the pOH scale and is determined using

$$pOH = -\log_{10}[OH^-]$$

So, if a strong acid has a low pH, then a strong base has a low pOH.

$$\text{For } [OH^-] = 0.02 \text{ M, the pOH} = 1.70.$$

5.2.2 pH and pOH of strong acids and bases

5.2.3 The pH and the pOH scales

WORKED EXAMPLE 5.2.3

A Calculate the pOH, given $[OH^-] = 1 \times 10^{-5}$ M

B Calculate the $[OH^-]$ when the pOH = 8.5

ANSWER

A Choose the correct formula and insert numbers:

$$pOH = -\log_{10}[OH^-]$$

$$pOH = -\log_{10}(1.0 \times 10^{-5})$$

$$pOH = 5.0$$

B Choose the correct formula and insert numbers:

$$[OH^-] = 10^{-pOH}$$

$$[OH^-] = 10^{-8.5}$$

$$[OH^-] = 3.2 \times 10^{-9} \text{ M}$$

pH of acid–base reactions

Neutralisation is the reaction of an acid and a base to form a salt and water. According to this definition, if we mix the correct amounts of acid and base, then the resultant solution is **neutral** – neither acidic nor basic. If the solution is not neutral – that is, it does not have a pH of 7 – it is because one reactant was in excess. However, this is only true when strong acids are reacted with strong bases.

neutral
neither acidic or basic; has a pH of 7

WORKED EXAMPLE 5.2.4

If 25 mL of a 0.50 mol L^{-1} solution of NaOH was added to 75 mL of a 0.3 mol L^{-1} solution of H_2SO_4, then what would the pH of the final solution be?

ANSWER

1 Write a balanced equation:

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\,H_2O(l)$$

$$\text{or } H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l) \text{ (but remember that } H_2SO_4 \text{ is diprotic)}$$

2 Calculate the number of moles of H_2SO_4 and NaOH using $c = \frac{n}{v}$.

$$c(NaOH) = 0.50 \text{ mol } L^{-1} \quad V = 25 \text{ mL} = 0.025 \text{ L} \quad n = ?$$

$$0.50 = \frac{n}{0.025}$$

$$n(NaOH) = 0.50 \times 0.025 = 0.0125 \text{ mol}$$

$$c(H_2SO_4) = 0.30 \text{ mol } L^{-1} \quad V = 75 \text{ mL} = 0.075 \text{ L} \quad n = ?$$

$$0.30 = \frac{n}{0.075}$$

$$n(H_2SO_4) = 0.30 \times 0.075 = 0.0225 \text{ mol}$$

3 If the solution was neutral, then $[H_3O^+] \times [OH^-]$. Determine which reactant is in excess.

$$n(NaOH) = 0.0125 \text{ mol}$$

$$n(H_2SO_4) = 0.0225 \text{ mol}, \; n(H_3O^+) = 0.0450 \text{ mol}$$

$$H_2SO_4 \text{ is in excess by } 0.045 - 0.0125 = 0.0325 \text{ mol}$$

4 Calculate $[H_3O^+]$.

$$\text{Using } c = \frac{n}{v}, \; V = 25 \text{ mL} + 75 \text{ mL} = 0.100 \text{ L}$$

$$[H_3O^+] = \frac{0.0325}{0.100} = 0.325 \text{ mol } L^{-1}, \; [H_3O^+] \text{ is in excess.}$$

5 Calculate the pH.

$$pH = -\log [H^+] = 0.488$$

6 pH = 0.488

SECTION REVIEW 5.2

APPLYING

1 Determine the pH of a solution, given $[H^+] = 0.001$ M.

2 Determine the pH of a solution, given $[H^+] = 1.2 \times 10^{-5}$ M.

3 Barium hydroxide is a strong base. Determine the pH of a 0.02 M barium hydroxide solution.

4 If the pH of the NaOH solution was 9.5, what was the concentration of the solution?

5 Determine the pOH of a solution, given $[OH^-] = 0.001$ M.

6 Determine the pOH of a solution, given $[OH^-] = 1.2 \times 10^{-5}$ M.

7 What is the resultant pH when 50 mL of 0.1 M NaOH is added to 100 mL of 0.1 M HCl?

8 How many grams of barium hydroxide is required to neutralise 500 mL of 0.2 M nitric acid?

9 How much 0.1 M NaOH is required to neutralise 100 mL of 0.277 M ethanoic acid solution?

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:
- **a** pH
- **b** pOH
- **c** pH scale
- **d** pOH scale.

EVIDENCE QUESTIONS

2 Calculate the $[H^+]$ when the pH of the solution is 6 and when it is 11.7.

3 Determine the concentrations of H^+ and OH^- in aqueous solutions of:
- **a** black coffee, pH 5.0
- **b** oven cleaner, pH 14.0
- **c** cola drink, pH 2.5
- **d** toothpaste, pH 5.8.

4 Determine the pH of each of the following strong electrolytes:
- **a** 0.01M HNO_3
- **b** 0.005 M $Ca(OH)_2$
- **c** 1 M HCl
- **d** 0.1 M NaOH
- **e** 0.005 M H_2SO_4
- **f** 0.230 M hydrochloric acid
- **g** 0.0175 M nitric acid
- **h** 1.27 M hydrochloric acid

ELABORATION QUESTIONS

5 What is the resultant pH when:
- **a** 50 mL of 0.2 M HCl is added to 100 mL of 0.1 M NaOH?
- **b** 100 mL of a solution of pH 6 is diluted with 100 mL of water?

END-OF-CHAPTER EXAM

End-of-chapter test

1 Sulfuric acid (H_2SO_4) is a strong acid. In an aqueous solution of 0.0034 M H_2SO_4, the $[H_3O^+(aq)]$ would be:

A 1.7×10^{-3} M

B 6.8×10^{-3} M

C 3.4×10^{-3} M

D 0.034 M

2 Rubidium hydroxide (RbOH) is a strong base. Calculate the pH of a solution if the concentration of RbOH is 2.45×10^{-3} M.

A 11.39

B 2.61

C 13

D 11.34

3 A solution containing nitric acid (HNO_3 – a strong acid) has a pH of 2.3. What is the $[OH^-]$?

A 2.0×10^{-12} M

B 5.0×10^{-3} M

C 2.3×10^{-7} M

D 1.0×10^{-12} M

4 What is the term given to the scale that measures the concentration of hydroxide ions?

5 Calculate the $[OH^-]$ when the pOH of the solution is 6 and when it is 11.7.

6 25 mL of a 1.087 M solution of hydrochloric acid is placed into a 250.00 mL volumetric flask. Enough distilled water is added to the flask to make the volume up to 250.00 mL. 20.00 mL of this solution was transferred to a 100.00 mL volumetric flask and made up to the mark with distilled water. What is the pOH of this solution?

7 What will the pH be of a solution produced by mixing 38.95 mL of 0.108 M barium hydroxide, $Ba(OH)_2$ and 44.86 mL of 0.116 M nitric acid, $HNO_3(aq)$?

8 Estimate the number of $H^+(aq)$ ions in a single drop of:

a Water

b 1.0 mol L^{-1}HCL

c 1.0 mol L^{-1}NaOH

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6 BRØNSTED–LOWRY MODEL

Introduction

Work carried out independently by chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry in 1923 led to some important insights in acid–base chemistry, including the recognition of the reversibility of acid and base reactions and the quantification of the strength of acids and bases.

An appreciation of this theory enables a clearer understanding of the role of buffer solutions in many important biological systems.

Stimulus questions

What is the relationship between amphiprotic species and the Brønsted–Lowry model?

What is a buffer?

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6.1 Brønsted–Lowry model

The ammonia dilemma

Ammonia, the weak base, challenged early chemists' definition of a base. The dilemma facing chemists was that either ammonia was not a base or that their definition was inaccurate or incomplete. Some chemists argued that the definition was acceptable because when ammonia reacts with water, the following reaction occurs:

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

But ammonia gas reacts with hydrochloric acid fumes to form ammonium chloride. There is no water and no OH^- or O^{2-} ions involved, as shown in the reaction:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

This reaction showed that the original definition of an acid and a base needed to be redefined.

PRACTICAL ACTIVITY 6.1.1

White smoke (teacher demonstration only)

Bases, such as ammonia, were originally described by their reaction with water. They produced hydroxide ions (OH^-) and, by definition, the hydroxide ions gave the basic nature to the substance. When water is not present, will ammonia still act as a base? In this reaction, fumes from hydrochloric acid react with the gaseous ammonia, forming a white smoky substance when they meet.

AIM

To demonstrate that acid and base reactions can occur without water

EQUIPMENT

- 50 mL concentrated ammonia solution (15 M)
- 50 mL concentrated hydrochloric acid (10 M)
- Glass tubing at least 500 cm long and 2 cm wide
- Retort stands with bosses and clamps
- Forceps
- Cotton wool wads
- Bungs with small hole to hold cotton wool
- Universal indicator paper may also be used

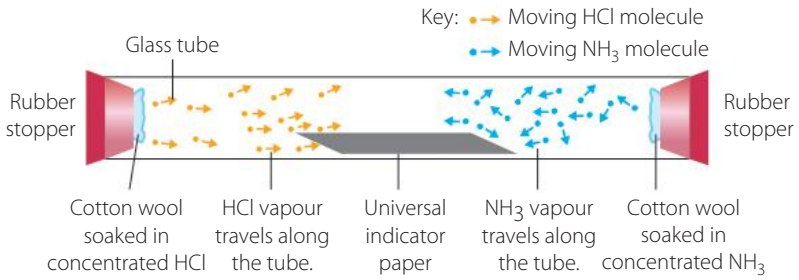

FIGURE 6.1.1 The reaction between ammonia gas and hydrogen chloride gas

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WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Concentrated ammonia solution (15 – 16 M or 28 – 30% w/w) is highly toxic and irritating to the lungs because of the ammonia gas evolved. It is corrosive to skin and eyes and may cause asthma attacks.	This is a teacher demonstration only. Avoid inhaling the extremely pungent vapour. Do not mix it with halogens or materials that release halogens. The teacher should wear gloves and safety glasses and perform the demonstration in a fume hood.
Concentrated hydrochloric acid (variable 10 – 12 M, 32 – 37% w/w; density 1.16 – 1.18 g mL^{-1}) is highly irritating to the lungs because of the HCl gas evolved. It is highly corrosive to skin and eyes, and toxic if ingested.	As above, wear gloves and safety glasses and perform the demonstration in a fume hood. Do not breathe the vapour. Avoid splashes in eyes or on skin.
Glassware may be cracked or broken.	Handle glass with care. Inspect beakers and discard any that are chipped or cracked, no matter how small the damage. Sweep up broken glass with a dustpan and brush; do not pick up glass with your hands.

RISK ASSESSMENT

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Use the clamps and retort stand to ensure that the glass is secure and horizontal, and placed in a functioning fume hood. Ensure that the bottles are also in the fume cupboard. If you are using universal indicator paper, place it in the glass tube.
2. Ensure that the mouth of the bottle is not facing anyone. Open the bottle of ammonia solution cautiously.
3. Use the forceps to dip one of the cotton wool wads into the ammonia solution and then quickly place the wad in the glass tube and put the lid back on the ammonia bottle.
4. Repeat steps 2 and 3 with the other cotton wool wad and the hydrochloric acid solution.

RESULTS

Observe what occurs in the glass tube. You could record what occurs using a digital video camera.

ANALYSIS

1. What substance was the most likely to form?
2. If the teacher used a strip of universal indicator paper, what colour did it turn?

DISCUSSION

1. Write the equation for the reaction that occurred between ammonia and hydrochloric acid.
2. Which reactant acted as a base? Which one acted as an acid?
3. Is the definition of a base a substance that produces OH^- or O^{2-} ions justified by this experiment?

INQUIRING FURTHER

Based on the white smoke experiment, investigate one of the following.

1. Why is it important that only the vapours are used?
2. Explore how the vapours travel in the tube. Explain the white smoke.
3. Where does the smoke form in the tube? Use the particle theory of matter and your understanding of temperature to explain your observations.

6.1.1 Brønsted–Lowry acid–base theory

6.1.2 Brønsted–Lowry definition of acids and bases

Redefining acids: Brønsted–Lowry acids

Chemists such as Lavoisier, Davy, von Liebig and Arrhenius each took their turn to define acids and bases. But it was the Danish chemist Brønsted and the English chemist Lowry who refined the definition of acids and bases by taking ammonia into account.

- An acid is a substance that donates one or more protons or hydrogen ions (H^+).
- A base is redefined as a substance that accepts one or more protons.

The hydrogen ion (proton), H^+

When discussing the Brønsted–Lowry model of acids and bases, the terms proton donor and proton acceptor are used frequently. Note that a proton is simply a hydrogen ion, as Figure 6.1.2 shows.

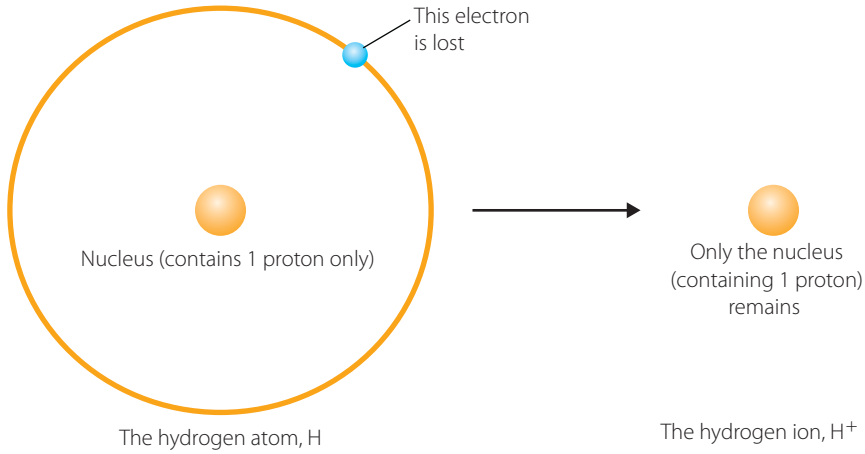


FIGURE 6.1.2 The formation of the proton (H^+ ion)

The Brønsted–Lowry definition of acids and bases is broader than the original definition. In the reaction between ammonia gas and fumes of hydrochloric acid $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$, ammonia accepts a proton to form an ammonium ion (NH_4^+) and is acting as a base. HCl is acting as an acid, as it donates a proton to form a chloride ion (Cl^-).

When hydrochloric acid molecules react with water, the HCl molecules are acting as an acid and the water molecules are acting as a base. The hydrochloric acid ionises to form hydronium ions (H_3O^+) and chloride ions (Cl^-). The water molecules are acting as a base because they accept H^+ ions:

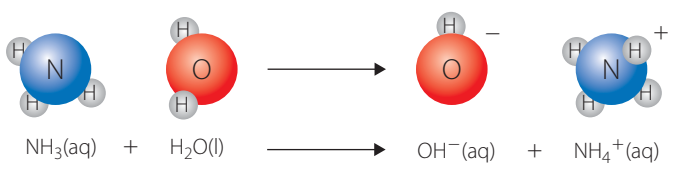
$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

In the reaction of ammonia with water:

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

sodium hydroxide is still categorised as a strong base in this definition. According to the Brønsted–Lowry definition of acids and bases, it is more correct to say that NaOH is an ionic compound that is the source of the strong base OH^-. In this example, ammonia is acting as a base and water is acting as an acid.

FIGURE 6.1.3 The ammonia molecule reacts with water to form a hydroxide ion and an ammonium ion.



Smith et al. 2010 Chemistry in use. Book 2

Mirror companions and conjugate pairs

The Brønsted–Lowry definition of a base as the mere receptor of a proton allows us to generalise about the reactions of acids. The reactions can be considered reversible, as shown in the following equation, where HA denotes an acid molecule:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For the forward reaction, HA is an acid because it is donating a proton to the water. The water is a base as it accepts a proton from HA. The reverse reaction is a reaction between the hydronium ion and the A^- ion. H_3O^+ is an acid because it is donating a proton to the A^- ion. The A^- ion is a base that accepts a proton from the H_3O^+. This reversible reaction contains *two* acids and *two* bases. The pairs are called **conjugate pairs**.

conjugate pairs
acid–base pairs that differ from each other by one proton

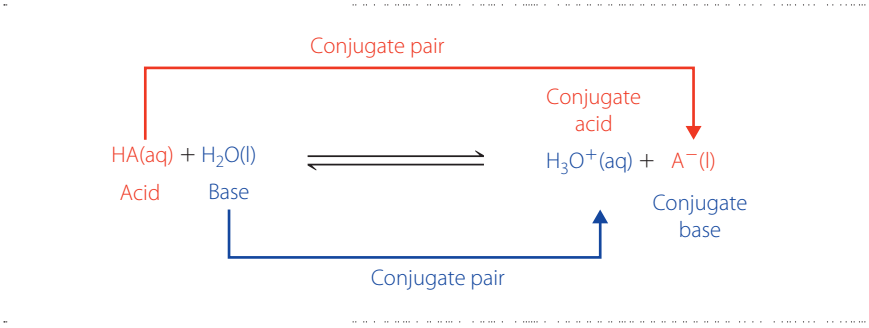


FIGURE 6.1.4
The relationship between conjugate acid–base pairs

When the acid, HA, loses a proton, it forms a base, A^-. The base, A^-, accepts a proton back again to reform the acid, HA. HA and A^- are a conjugate pair, like an object and its mirror image, except here the HA and the A^- are on either side of the arrows and are not identical.

Members of a conjugate acid–base pair differ from each other by the presence or absence of the transferable H^+ (hydrogen ion).

For example, HCl donates a proton to form its **conjugate base**, Cl^-. Water is acting as the base and forms its **conjugate acid**, H_3O^+.

conjugate base
the base that is formed when an acid donates a proton to a base

conjugate acid
the acid that is formed when a base accepts a proton from an acid

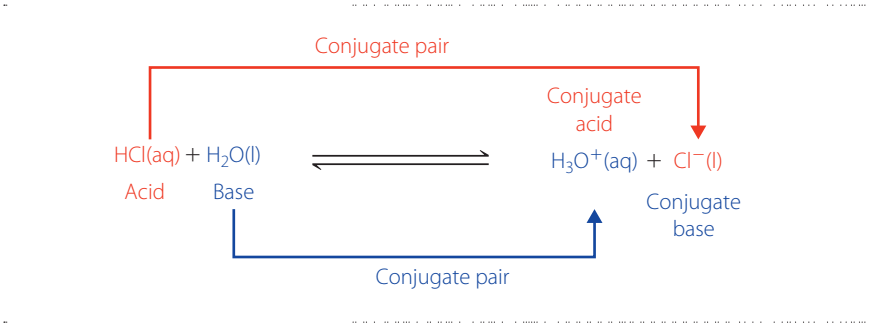


FIGURE 6.1.5
Forming a conjugate base and a conjugate acid

SECTION REVIEW 6.1

REMEMBERING

1 What was the earliest definition of acids and bases?

UNDERSTANDING

2 Can an acid be both a strong acid and a dilute acid?

3 Carbonates are bases. The earlier definitions could not account for the behaviour of carbonates but the Brønsted–Lowry definition can. Explain why.

APPLYING

4 Identify the strong acids and strong bases in the following list.

- **a** Ammonia solution, $NH_3(aq)$
- **b** Carbonic acid, $H_2CO_3(aq)$
- **c** Nitric acid, $HNO_3(aq)$
- **d** Hydrochloric acid, $HCl(aq)$
- **e** Sodium hydroxide, $NaOH(aq)$

5 Identify the two conjugate acid–base pairs in each of the following equations:

- **a** $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$
- **b** $NH_4^+(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NH_3(aq)$
- **c** $HSO_4^-(aq) + O^{2-}(aq) \rightarrow SO_4^{2-}(aq) + OH^-(aq)$
- **d** $H_2PO_4^-(aq) + CO_3^{2-}(aq) \rightarrow HPO_4^{2-}(aq) + HCO_3^-(aq)$
- **e** $HC_2H_3O_2(aq) + HS^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2S(aq)$

6 Write the conjugate acids of the following bases.

- **a** HCO_3^-
- **b** OH^-
- **c** HPO_4^{2-}

6.2 Amphiprotism

amphiprotic a substance that can gain or lose a hydrogen ion to act as an acid or a base

Many substances have the ability to act as an acid or a base, that is, they can donate a proton to a base or they can accept a proton from an acid. Such substances are called **amphiprotic** substances.

Water, H_2O, is a good example of an amphiprotic substance. Consider the self-ionisation of water:

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

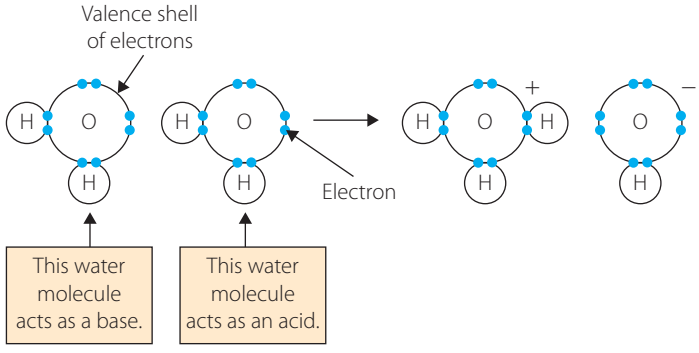


FIGURE 6.2.1 The amphiprotic nature of water: water can act as an acid and as a base, depending on what species are present.

Consider the dihydrogen phosphate ion ($H_2PO_4^-$). This has the potential to act as an acid by donating one of its protons:

$$\underset{\text{acid}}{H_2PO_4^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate base}}{HPO_4^{2-}(aq)} + \underset{\text{conjugate acid}}{H_3O^+(aq)}$$

The $H_2PO_4^-$ ion also has the potential to act as a base by accepting a proton:

$$\underset{\text{base}}{H_2PO_4^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate base}}{H_3PO_4(aq)} + \underset{\text{conjugate acid}}{OH^-(aq)}$$

APPLYING

1 Explain, with the aid of equations, why the hydrogen carbonate ion (HCO_3^-) is amphiprotic.

2 Explain, with the aid of equations, why the hydrogen sulfate ion (HSO_4^-) is amphiprotic.

SECTION REVIEW 6.2

6.3 Buffers

Buffers are solutions that can maintain a pH within a certain range, despite an acid or a base being added. These chemicals play an important role in maintaining the pH of the body within a narrow range. Buffers enable enzymes to continue to function effectively by protecting them from being denatured because of changes in acidity.

Buffers are solutions in which both a weak acid and its conjugate base are present, or in which a weak base and its conjugate acid are present. An example is a solution of carbonic acid and sodium hydrogen carbonate H_2CO_3/HCO_3^-.

The pH of a buffer is determined by the:

- degree to which the acid dissociates (how weak it is)
- ratio of weak base $[A^-]$ to weak acid [HA] in solution.

If a buffer has more acid than base, more H^+ ions are present and the pH is lower.

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

If a strong acid is added, the extra H_3O^+ pushes the equilibrium reaction to the left to partially reduce the concentration of H_3O^+. The pH increases to near the original value. Addition of a strong base (OH^-) will result in the added OH^- reacting with the H_3O^+. The system will try to oppose this change and move to produce more H_3O^+, shifting to the right. The pH is decreased to near the original value.

The pH is maintained by manipulating the proportion of weak base (A^-) and weak acid (HA) in solution. As long as $\frac{[A^-]}{[HA]}$ is between $\frac{1}{10}$ and 10, the pH is within is 1 unit and the solution is therefore buffered.

Acidic buffer solutions

$$\underset{\text{weak acid}}{HA(aq)} + H_2O(l) \rightleftharpoons \underset{\text{conjugate base}}{A^-(aq)} + H_3O^+(aq)$$

For example, the H_2CO_3/HCO_3^- buffer:

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

If a small amount of acid (H_3O^+) is added:

- Initially the pH decreases slightly because of the increased number of H_3O^+ ions present.
- Then, the HCO_3^- ions react with the excess H_3O^+. The equilibrium is restored and the pH increases to close to its original value.

If a small amount of base (OH^-) is added:

- Initially the pH increases slightly because of the increased number of OH^- ions present.
- But, according to Le Chatelier's principle, the forward reaction is favoured and H_2CO_3 dissociates, producing more H_3O^+ ions that neutralise the excess OH^- ions. The equilibrium is restored and the pH decreases to close to its original value.

Basic buffer solutions

$$\underset{\text{weak base}}{B(aq)} + H_2O(l) \rightleftharpoons \underset{\text{conjugate acid}}{BH^+(aq)} + OH^-(aq)$$

For example, the NH_3/NH_4Cl buffer:

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

If a small amount of acid (H_3O^+) is added:

- Initially the pH decreases because of the increased number of H_3O^+ ions.
- Then, more $NH_3(aq)$ reacts, producing more OH^- ions that neutralise the excess H_3O^+ ions. The equilibrium is restored and the pH increases to close to its original value.

If a small amount of base (OH^-) is added:

- Initially the pH increases slightly because of the increased number of OH^- ions present.
- The conjugate acid (NH_4^+) reacts with the excess OH^- ions. The equilibrium is restored and the pH decreases to close to its original value.

6.3.1 How buffers work
6.3.2 Buffer capacity

INQUIRING FURTHER

The pH of many biological systems is maintained within narrow ranges by buffers. The pH range for human blood is 7.35–7.45. The main buffer system in blood is the carbonic acid/hydrogen carbonate ion system:

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

If blood becomes too acidic, then the reverse reaction occurs to reduce the excess H_3O^+. If the blood becomes too basic, then the forward reaction occurs to increase the H_3O^+ to neutralise the excess base.

This buffer is also involved in transporting waste carbon dioxide from the cells. Carbon dioxide is a clear, odourless gas, which is produced in every cell in the body. The carbon dioxide has to dissolve in blood, which is an aqueous medium, in accordance with reaction (1).

$$CO_2(g) \rightleftharpoons CO_2(aq) \qquad (1)$$

In enzyme-catalysed reactions, the dissolved carbon dioxide then reacts with water in the blood to form carbonic acid, as shown in reactions (2) and (3). The majority of the carbon dioxide is transported in the blood to the lungs as the hydrogen carbonate ion.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad (2)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \qquad (3)$$

The acidity of the blood increases as more carbon dioxide is dissolved.

Once the blood reaches the lungs, the reverse series of reactions occurs with the carbon dioxide gas diffusing into the air space in the lungs. Carbon dioxide is breathed out. The concentration of carbon dioxide in the lungs is lower than in blood. The first reaction (1) proceeds to the left, which reduces the concentration of $CO_2(aq)$. Reducing $[CO_2(aq)]$ has the effect of pushing reaction (2) to the left. This reduces $[H_2CO_3]$ so that reaction (3) is also pushed to the left. Overall, $[H_3O^+]$ decreases. The amount of CO_2 in the blood is maintained within a narrow band, which helps prevent blood from becoming too acidic.

FIGURE 6.3.1 The Australian seal Is able to stay underwater for extended periods, in part because it can tolerate high levels of carbon dioxide in its blood.

Sea-diving animals such as whales, seals and dolphins can stay under water for more than an hour. These organisms have adapted to have a higher tolerance for carbon dioxide in their blood compared to humans. Humans can generally only hold their breath for a couple of minutes. It is the high level of carbon dioxide, not the low level of oxygen, that causes the breathing reflex when holding one's breath.

Research why animals such as the Australian seal have a high tolerance for carbon dioxide in their blood and the relationship between this tolerance and their ability to dive for extended periods.

SECTION REVIEW 6.3

REMEMBERING

1 Define the term buffer.

2 Give an example of a buffer.

UNDERSTANDING

3 Which of the following could be used to make an acidic buffer solution?

- **a** HCl and NaCl
- **b** CH_3COOH and CH_3COONa
- **c** NH_3 and NH_4Cl
- **d** HCl and CH_3COONa

4 What would be a suitable substance to mix with methanoic acid to make a buffer?

APPLYING

5 What kind of buffer solution is made by mixing propylamine ($CH_3CH_2CH_2NH_2$) and propyl ammonium chloride ($CH_3CH_2CH_2NH_3Cl$)?

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** amphiprotic
- **b** buffer solution
- **c** acidic buffer
- **d** basic buffer.

CATEGORY QUESTIONS

2 Explain how you would prepare an acidic buffer solution and a basic buffer solution.

3 A buffer solution has been prepared using a mixture of ethylamine ($CH_3CH_2NH_2$) and ethyl ammonium chloride ($CH_3CH_2NH_3Cl$).

- **a** Suggest a rough pH value for this system.
- **b** Write the equation for the buffer system.
- **c** With the aid of equations, explain what would happen if a small amount of hydrochloric acid was added to this system.

ELABORATION QUESTIONS

4 Explain how buffers can keep pH within a narrow range despite the addition of small amounts of acids.

5 The pH of seawater has fallen from 8.2 to 8.1 over the last 200 years.

- **a** Calculate the percentage change in [H3O+].

One main concern arising because of the lower pH is the ability of marine organisms to build calcium carbonate structures such as shells. Sea water is basic because it is naturally saturated with carbonate ion (CO_3^{2-}), which is a base.

- **b** Explain how this base is buffering the increase in acidity and how this is also causing the reduction of calcium carbonate-based structures such as shells.

Use the following series of reactions (K_a represents a weak acid in an aqueous solution.):

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O(aq) \quad K_a = 4.5 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \quad K_a = 4.7 \times 10^{-11}$$

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END-OF-CHAPTER EXAM

End-of-chapter test

1 In the reaction shown below, which is the Brønsted–Lowry acid?

$$CH_3CH_2CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + OH^-(aq)$$

A $CH_3CH_2CH_2NH_2(aq)$

B None of these

C H_2O

D $CH_3CH_2CH_2NH_3^+(aq)$

2 Identify the conjugate acid–base pair in the reaction below:

$$HSO_4^-(aq) + CH_3NH_2(aq) \rightleftharpoons SO_4^{2-}(aq) + CH_3NH_3^+(aq)$$

A $CH_3NH_3^+$ and CH_3NH_2

B HSO_4^- and SO_4^{2-}

C HSO_4^- and CH_3NH_2

D CH_3NH_2 and SO_4^{2-}

3 The hydrogen citrate ion can undergo the following reactions:

$$C_6H_7O_7^-(aq) + H_2O(l) \rightleftharpoons C_6H_6O_7^{2-}(aq) + H_3O^+(aq)$$

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

What kind of substance is the hydrogen citrate ion?

4 25 mL of a 1.087 M solution of hydrochloric acid is placed into a 250.00 mL volumetric flask. Enough distilled water is added to the flask to make the volume up to 250.00 mL. 20.00 mL of this solution was transferred to a 100.00 mL volumetric flask and made up to the mark with distilled water. What is the pH of this solution?

5 What will the pH be of a solution produced by mixing 40.0 mL of 0.200 mol L^{-1} hydrochloric acid solution with 20.0 mL of a 0.100 mol L^{-1} sodium hydroxide solution?

7 DISSOCIATION CONSTANTS

Introduction

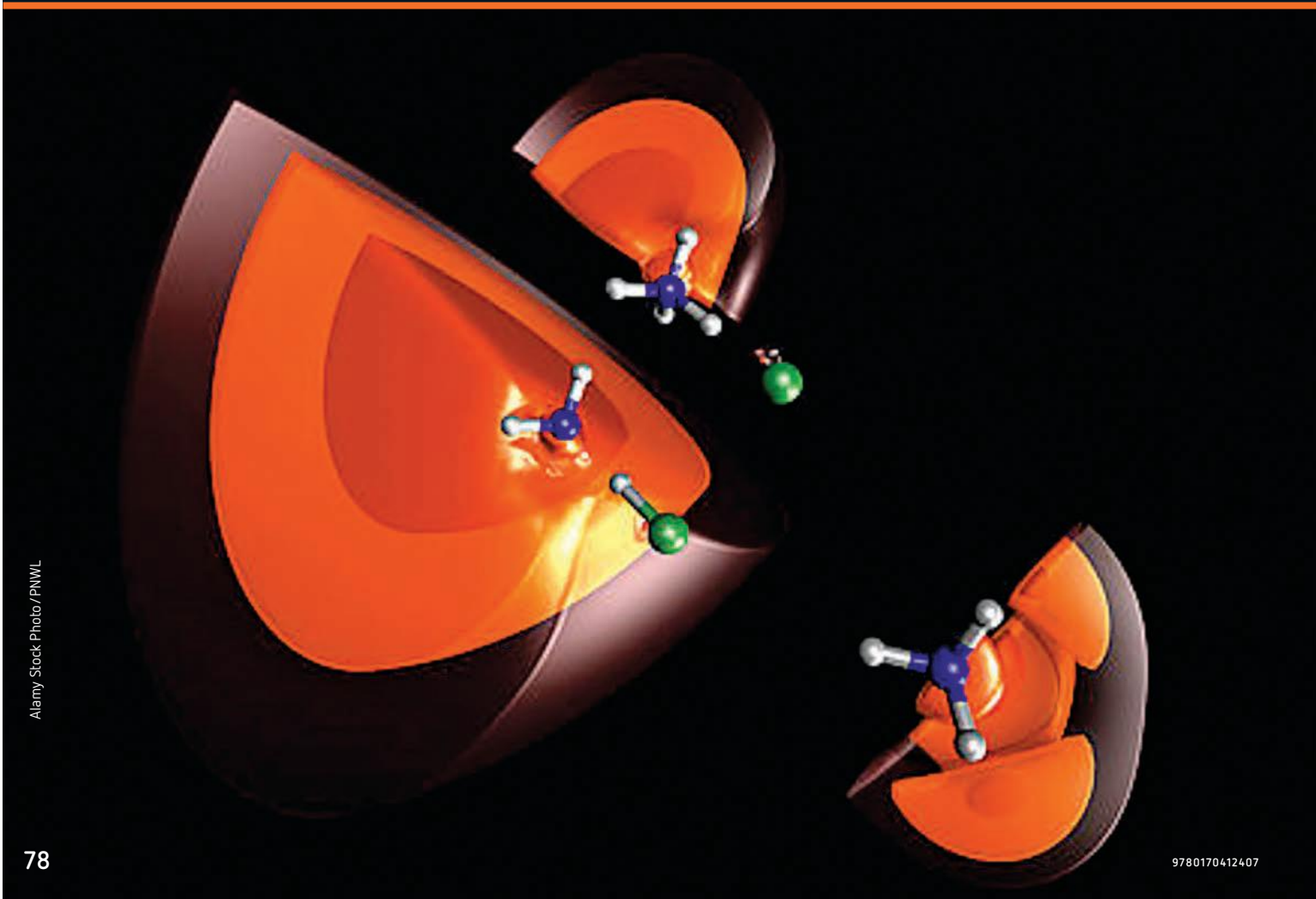
The qualitative information concerning the relative strengths of acids and bases available from a pH scale can be useful, but many important situations require a more quantitative approach. Understanding the role of dissociation constants is useful when attempting to determine the extent to which acids and bases dissociate and, hence, the strength of these acids and bases.

Stimulus questions

What is the relationship between the strength of an acid and the degree of ionisation at equilibrium?

How can data be used to determine the relative strengths of acids?

How can data be used to determine the relative strengths of bases?



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7.1 Acid dissociation constants

In a weak acid, only some of the acid molecules dissociate. This means that there is equilibrium between the acid and the conjugate base. For example, the weak acid hydrofluoric acid (HF):

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

The equilibrium expression for this reaction is:

$$K = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

Rearranging the formula gives:

$$K[H_2O] = \frac{[H_3O^+][F^-]}{[HF]}$$

Water is the solvent and the concentration of water does not alter significantly; it is effectively constant at $55.5\,mol\,L^{-1}$. This means that it can be incorporated into K. This now forms the **acid dissociation equilibrium constant**, K_a. K_a represents a weak acid in an aqueous solution.

acid dissociation equilibrium constant the equilibrium expression of a weak acid

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

When the weak acid hydrofluoric acid dissolves in water, only a small percentage of the molecules ionise. The extent of the forward reaction is very small. The K_a of hydrofluoric acid is very small.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 7.63 \times 10^{-4}$$

KEY CONCEPT

- The symbol (aq) refers to the species hydrated by water molecules. As such, HCl(aq) effectively does not exist. Rather, $H^+(aq)$ and $Cl^-(aq)$ exist. For strong acids, bases and salts, the ionised form is the best representation.

Generally, for the dissociation of a weak acid, such as hydrofluoric acid:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

When a strong acid such as hydrochloric acid dissolves in water, almost 100 per cent of the acid reacts to form hydronium and chloride ions:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

The K_a of a strong acid is very large. The reverse reaction only occurs to a very small extent. The conjugate base Cl^- is very weak and does not readily react in the reverse reaction. It is not necessary to use the equilibrium arrows for the reactions of strong acids as they effectively go to completion.

The pH will determine the concentration of hydronium ions. For strong acids, the concentration of hydrochloric acid molecules at equilibrium is negligible, so pH will give a direct measurement of the concentration of the acid. For weak acids, the pH does not give a direct measurement of the acid concentration.

KEY CONCEPT

- K_a is a measure of the strength of acids. Strong acids ionise completely in water; therefore, K_a is very large. Weak acids do not ionise completely in water; therefore, K_a is small.

An advantage of the Brønsted–Lowry model is that it shows how the strength of a conjugate acid or base can be related to the strength of the original acid or base.

For example, the reaction below proceeds virtually to completion:

$$HNO_3(aq) + H_2O \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

This means that HNO_3 is a strong acid and so the equilibrium lies well over to the right. Therefore, the conjugate base of HNO_3, the nitrate ion (NO_3^-) is a very weak base.

The reverse of the equilibrium system shown above could be written as:

$$NO_3^-(aq) + H_3O^+(aq) \rightleftharpoons HNO_3(aq) + H_2O(l)$$

The K_a expression for this would be:

$$K_a = \frac{[HNO_3]}{[H_3O^+][NO_3^-]}$$

If the NO_3^- is very weak, the concentration of HNO_3 will be very small and the value for K_a will also be very small.

In contrast, ethanoic acid (CH_3COOH) is quite weak and only dissociates to a small extent:

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

Therefore, the conjugate base (CH_3COO^-) is also quite weak.

SCIENCE AS A HUMAN ENDEAVOUR

WINE ACIDITY

The acidity of wine is one of the main factors that contribute to its taste. The acidity balances the residual sugar and alcohol content. A wine high in sugar will taste sickly sweet unless it is balanced with a high acid level (low pH). Low acidity (high pH) reduces the amount of subtle flavours in the grapes and wine. Grapes grown in very warm climates are often too sweet. This is why most wine regions are in temperate climates.

Research the acids commonly found in or added to wine. Copy and complete Table 7.1.1 by writing a short summary of the role of each acid in wine production.

7.1.1 Dissociation constant

TABLE 7.1.1 Common acids found in wine

ACID	NOTES	ACIDS IN GRAPES	ACIDS IN WINE
Tartrates H_2T (tartaric acid) KHT (potassium hydrogen tartrate) K_2T (dipotassium tartrate)			
Malic acid H_2M			
Citric acid H_3C			
Lactic acid HL	Arises due to conversion from malic acid, post-fermentation		
Acetic acid HA (ethanoic acid)			
Succinic, pyruvic acids	Small amounts during alcoholic fermentation		
Ascorbic acid (vitamin C)			
Carbonic acids	Produced by CO_2 reacting with water		
Sulfurous acid			

The acids found in the grapes remain throughout the process and so are also found in wine. Other acids are added during the process or are by-products of the production of wine.

TABLE 7.1.2 Examples of weak acids and their K_a

ACID	FORMULA	K_a
Ammonium ion	NH_4^+	5.6×10^{-10}
Ethanoic	CH_3COOH	1.7×10^{-5}
Hydrocyanic	HCN	6.3×10^{-10}
Hydrofluoric	HF	7.6×10^{-4}
Lactic	$HC_3H_5O_3$	1.4×10^{-4}
Methanoic	HCOOH	1.8×10^{-4}

Base dissociation constants

According to the Brønsted–Lowry model of acids and bases, when a base reacts with water it *accepts* a proton from water:

$$\underset{\text{base}}{B(aq)} + H_2O(l) \rightarrow \underset{\text{conjugate acid}}{HB^+(aq)} + OH^-(aq)$$

KEY FORMULA

K_a only applies when the acid is dissolved in water. It is temperature dependent and is usually quoted at 25°C.

For a strong base, such as sodium hydroxide, dissociation is complete and the equilibrium constant will be very large.

For a weak base, such as ammonia (NH_3), only some of the NH_3 molecules will dissociate:

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

The equilibrium expression for this reaction becomes:

$$K_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The equilibrium lies well to the left, meaning that there is very little $NH_4^+(aq)$ or $OH^-(aq)$. The equilibrium constant is very small.

Because this equilibrium constant refers to the dissociation of a base, it is referred to as the **base dissociation equilibrium constant**, K_b.

base dissociation equilibrium constant the equilibrium expression of a weak base

TABLE 7.1.3 Examples of weak bases and their K_b

ACID	FORMULA	K_b
Ammonia	NH_3	1.8×10^{-5}
Methylamine	CH_3NH_2	4.4×10^{-4}
Ethylamine	$CH_3CH_2NH_2$	5.4×10^{-4}
Phenylamine	$C_6H_5NH_2$	4.2×10^{-10}
Phosphine	PH_3	1.0×10^{-14}
Hydrazine	H_2NNH_2	1.3×10^{-6}

Generally, for the dissociation of a weak base, B:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

WORKED EXAMPLE 7.1.1

Dimethylamine, $(CH_3)_2NH$, is a weak base. Write the dissociation equation for dimethylamine and write the K_b expression.

ANSWER

1 According to the Brønsted–Lowry model of acids and bases, if dimethylamine is a weak base then it will accept a proton from water.

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

2 The equilibrium expression then becomes:

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

PRACTICAL ACTIVITY 7.1.1

Investigating the electrical conductivity of strong and weak acids and bases

The strength of acids and bases is a measure of the degree of dissociation of these substances. If there are more ions in solution, then the electrical conductivity will be greater.

AIM

To measure the electrical conductivity of various acids and bases, and relate this to acid or base strength

EQUIPMENT

- 0.1 mol L^{-1} solutions of hydrochloric acid, nitric acid, sulfuric acid, ethanoic acid, citric acid, ascorbic acid, sodium hydroxide, potassium hydroxide, barium hydroxide and ammonia solution
- Test tubes and test-tube rack
- Battery or power pack
- Small beaker (100 mL)
- Electrical leads
- Ammeter or multimeter
- Carbon rod electrodes
- pH meter

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THE RISKS TO STAY SAFE?
Dilute solutions of hydrochloric, sulfuric and nitric acid can cause irritation to skin and eyes.	Wear safety glasses and protective clothing. Do not allow contact with skin or clothing. If contact with skin occurs, wash with water.
Household chemicals can burn the skin.	Wear safety glasses and protective clothing. Take care when handling chemicals and tell your teacher when there is a spill.

PROCEDURE

Part A: Testing the substances with the indicator

1. Set up the test tubes in the rack and label each one with the name of the acid. Place a few millilitres of each acid into its corresponding test tube. If the acid is a solid (such as aspirin), add a little distilled water.
2. Add a drop of universal indicator to each substance and record the colour change.
3. Compare the colour of each test tube with the indicator colour chart to confirm whether the substance is an acid or a base. Note the pH of the solution if you have a pH meter.

Part B: Conductance test of each acid

1. Set up the apparatus as shown in Figure 7.1.1.
2. Half fill the beaker with the acid to be tested.
3. Switch on the power pack and set to 4 V or connect the battery.
4. Record the current reading.

RESULTS

Draw a data table to record the colour, pH value using the indicator colour chart, pH reading (if completed) and the current for each substance.

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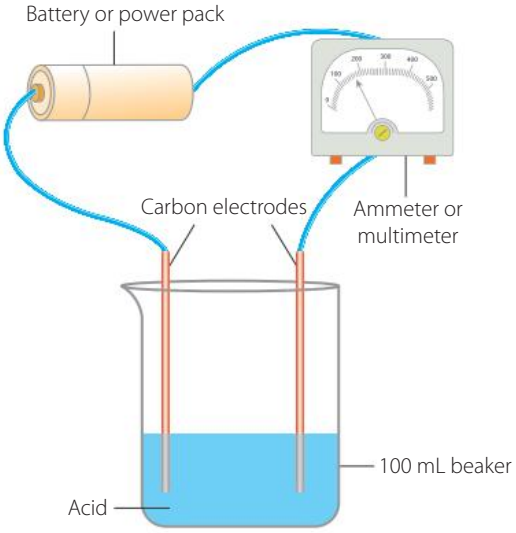

FIGURE 7.1.1 Apparatus set up for conductance test

DISCUSSION

1. Was there a trend linking the pH with the current? If so, what was it?
2. Do the current readings support the hypothesis that a stronger acid or a base will have a higher conductivity? Note that the strength of an acid or a base is related to its K_a or K_b value.

SECTION REVIEW 7.1

REMEMBERING

1. Define 'dissociation equilibrium constant'.
2. What are the differences between a strong and a weak acid? Provide three examples of strong acids and three examples of weak acids.

APPLYING

3. Write the dissociation equations and K_a or K_b expressions as appropriate for the following acids and bases.
   - **a** Carbonic acid, H_2CO_3
   - **b** Pyridine, C_5H_5N
   - **c** Hydroxylamine, NH_2OH
   - **d** Hypochlorous acid, HOCl

7.2 Calculations involving dissociation constants

Calculating a dissociation constant from a given pH value

The K_a of an acid can be determined by measuring the pH of the sample. Using HA to represent any acid and A^- to represent the conjugate base, the reaction of a weak acid with water can be represented as:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

And the equilibrium expression is:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

As $[A^-]$ must equal $[H_3O^+]$, then:

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

The following assumptions are made:

1. At equilibrium, [HA] is the same as the initial concentration; the weak acid only ionises to a small degree in water.
2. $[H_3O^+]$ produced by the self-ionisation of water is negligible and has no effect on the calculations.

WORKED EXAMPLE 7.2.1

A 0.1 M solution of hypobromous (HOBr) acid has a pH of 4.80. Determine K_a for this acid.

ANSWER

1. Write the equation for the ionisation of the acid:

$$HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OBr^-(aq)$$

2. Write the expression for K_a:

$$K_a = \frac{[OBr^-][H_3O^+]}{[HOBr]}$$

3. Choose the correct formula and insert the numbers:

$$pH = -\log_{10}[H_3O^+]$$
$$4.80 = -\log_{10}[H_3O^+]$$
$$\text{Therefore } [H_3O^+] = 1.58 \times 10^{-5}\text{ M}$$

4. Insert numbers into the formula and calculate the answer:

$$K_a = \frac{[OBr^-][H_3O^+]}{[HOBr]}$$
$$= \frac{[H_3O^+]^2}{0.1}$$
$$= \frac{[1.58 \times 10^{-5}]^2}{0.1}$$
$$= 2.5 \times 10^{-9}$$

5. $K_a = 2.5 \times 10^{-9}$

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Percentage ionisation

Percentage ionisation is the percentage of acid that has ionised in water. The general reaction for weak acids with water is:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O + (aq) + A^-(aq)$$

percentage ionisation
the percentage of acid that has ionised in water

KEY FORMULA

Important information

Once the percentage ionisation is known, a more accurate calculation for K_a can be determined.
Some weak acids may have significant ionisation (not much less than 100%), so the assumption that $[HA]_{initial} = [HA]_{equil}$ for K_a calculations may not be valid.

For each proton that is donated to water, one A^- ion is formed (provided the acid is monoprotic). By measuring the pH, the $[H_3O^+]$ can be determined and this is equal to $[A^-]$:

$$A^- = H_3O^+$$

This can then be used to calculate the percentage of the original acid that has been ionised. Note that [HA] here refers to the initial concentration and not the concentration at equilibrium:

$$\text{Percentage ionisation} = \frac{[A^-]}{[HA]} \times 100\%$$

WORKED EXAMPLE 7.2.2

Hydrofluoric acid reacts with water as shown by:

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

Determine the percentage ionisation of HF(aq) in a 0.1 mol L^{-1} hydrofluoric acid solution that was found to have a pH of 2.1.

ANSWER

1 Choose the correct formula and insert the numbers. The concentration of hydronium ions is:

$$10^{-pH} = 10^{-2.1}$$
$$= 0.008 \text{ mol } L^{-1}$$

2 Determine $[F^-]$:

The concentration of F^- is also 0.008 mol L^{-1}.

3 Calculate the percentage ionisation of hydrofluoric acid:

$$\frac{[F^-]}{[HF]} \times \frac{100}{1}$$
$$\frac{0.08}{0.1} \times \frac{100}{1}$$
$$= 8\%$$

4 Percentage ionisation = 8%

WORKED EXAMPLE 7.2.3

Determine the pH of a 0.01 M solution of hydrofluoric acid ($K_a = 6.8 \times 10^{-4}$).

ANSWER

1 Choose the correct formula and insert the numbers:

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = 6.8 \times 10^{-4}$$

$$= \frac{[H_3O^+]^2}{[HF]}, \text{ as } [F^-] = [H_3O^+]$$

$$[H_3O^+]^2 = 6.8 \times 10^{-4} \times [HF]$$

$$[H_3O^+] = \sqrt{(6.8 \times 10^{-4} \times 0.1)}$$

$$= 8.2 \times 10^{-3}$$

2 Determine pH:

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

$$= -\log_{10}[2.6 \times 10^{-3}]$$

$$= 2.58$$

3 pH = 2.58

K_a of polyprotic acids

A separate equation can be written for each step of the ionisation of a polyprotic acid. Each step has its own equilibrium expression and K_a. These are generally labelled K_{a1}, K_{a2} and so on, with the first K_a usually being the largest value. Sulfuric acid is a diprotic acid; it can release two protons and the first proton is very easily donated to water. Sulfuric acid (H_2SO_4) is a strong acid with a conjugate base, HSO_4^-.

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq) \quad K_{a1} = 10^9$$

K_a for the strong acid is very large. The second reaction is:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq) \quad K_{a2} = 10^{-2}$$

The conjugate base HSO_4^- is now donating a proton and acting as a weak acid by reacting with water to form SO_4^{2-}. The weaker an acid, the stronger its conjugate base, so the reverse reaction occurs to a higher degree. The species HSO_4^- is amphiprotic. In a solution of sulfuric acid, the main species present are HSO_4^-, H_3O^+ and water.

Diprotic weak acids such as sulfurous acid (H_2SO_3) have two ionisable protons:

$$H_2SO_3(l) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq) \quad K_{a1} = 1.7 \times 10^{-2}$$
$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq) \quad K_{a2} = 6.4 \times 10^{-8}$$

Sulfurous acid is a weak acid. In the first reaction it is in equilibrium with the conjugate base. While K_{a1} is bigger than K_{a2}, all three species would be present in an aqueous solution of sulfurous acid.

Dissociation constants for conjugate acid–base pairs

If we consider the dissociation of a weak acid, HA, in water to give its conjugate base:

$$\underset{\text{acid}}{HA(aq)} + H_2O(l) \rightleftharpoons \underset{\text{conjugate base}}{A^-(aq)} + H_3O^+(aq)$$

The reaction of the conjugate base with water is given by:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

Using these equations, the acid dissociation expression is given by:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The base dissociation expression is given by:

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

The relationship between K_a and K_b is given by:

$$K_a \times K_b = \frac{[H_3O^+]\cancel{[A^-]}}{\cancel{[HA]}} \times \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}$$

This leaves:

$$K_a \times K_b = [H_3O^+][OH^-]$$

On page 58, the self-ionisation of water is given by:

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

Therefore, it can be seen that:

$$K_w = K_a \times K_b$$

This is a significant relationship and it enables the K_a or K_b of a conjugate acid or base to be determined given the K_a or K_b value of the acid or base.

WORKED EXAMPLE 7.2.4

If the K_a value for propanoic acid (CH_3CH_2COOH) is 1.35×10^{-5}, determine the K_b value for the propanoate ion ($CH_3CH_2COO^-$).

ANSWER

1 Choose the correct formula and insert the numbers:

$$K_w = K_a \times K_b$$
$$K_w = 1.0 \times 10^{-14}$$
$$K_a = 1.35 \times 10^{-5}$$
$$1.0 \times 10^{-14} = 1.35 \times 10^{-5} \times K_b$$

2 Calculate K_b:

$$K_b = \frac{[1.0 \times 10^{-14}]}{[1.35 \times 10^{-5}]}$$
$$= 7.4 \times 10^{-10}$$

3 $K_b = 7.4 \times 10^{-10}$

SECTION REVIEW 7.2

APPLYING

1 A 0.1 mol L^{-1} solution of methanoic acid (HCOOH) has a pH of 2.37 ($K_a = 1.8 \times 10^{-4}$). Provide the:
- **a** concentration of hydronium ions
- **b** concentration of methanoate anions
- **c** percentage ionisation.

2 Determine the pH of a 0.010 M methanoic acid solution.

3 The pH of a 0.050 M solution of nitrous acid (HNO_2) is measured as 2.22. Determine K_a.

4 Determine the pH of a 0.2 M ethanoic acid solution ($K_a = 1.7 \times 10^{-5}$).

5 The ascorbate ion ($C_6H_7O_6^-$) is the conjugate base of ascorbic acid (vitamin C).
- **a** Write the equation showing the ascorbate ion acting as a base when mixed with water.
- **b** Given that the K_a value for ascorbic acid is 7.9×10^{-5}, determine the K_b value for the ascorbate ion.

6 The pyridinium ion ($C_5H_6N^+$) is the conjugate acid of pyridine.
- **a** Write the equation showing the pyridinium ion acting as an acid when mixed with water.
- **b** Given that the K_b value for pyridine is 1.7×10^{-9}, determine the K_a value for the pyridine ion.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** acid dissociation constant
- **b** base dissociation constant
- **c** percentage ionisation
- **d** polyprotic acid.

CATEGORY QUESTIONS

2 Write the dissociation expressions (K_a or K_b) for the following substances in water.

- **a** Ethanoic acid, CH_3COOH
- **b** Propylamine, $CH_3CH_2CH_2NH_2$
- **c** Hydrocyanic acid, HCN

ELABORATION QUESTIONS

3 Determine the pH of a 0.2 M ethylamine solution ($K_b = 4.3 \times 10^{-4}$).

4 Carbonic acid (H_2CO_3) is a diprotic acid, which means that it dissociates to the carbonate ion (CO_3^{2-}) in two stages.

- **a** Write the equations for both stages of the dissociation.
- **b** Write the K_a expressions for both stages of the dissociation.
- **c** If the K_a value for the hydrogen carbonate ion (HCO_3^-) is 4.7×10^{-11}, calculate the value of K_b for the carbonate ion.

5 A 0.1 mol L^{-1} solution of ammonia (NH_3) has a pH of 11.1 ($K_b = 1.8 \times 10^{-5}$). Calculate each of the following.

- **a** Concentration of hydroxide ions
- **b** Concentration of ammonium ions
- **c** Percentage ionisation

END-OF-CHAPTER EXAM

End-of-chapter test

1 Which of the following is the weakest acid?

A Hypochlorous acid (HClO) $K_a = 3.0 \times 10^{-8}$

B Benzoic acid (C_6H_5COOH) $K_a = 6.5 \times 10^{-5}$

C Ammonium ion (NH_4^+) $K_a = 5.6 \times 10^{-10}$

D Nitrous acid (HNO_2) $K_a = 4.6 \times 10^{-4}$

2 The conjugate bases of the acids in Question 1 are given below. Which has the lowest value for K_b?

A Hypochlorite ion (OCl^-)

B Benzoate ion ($C_6H_5COO^-$)

C Ammonia (NH_3)

D Nitrite ion (NO_2^-)

3 What is the pH of a 0.1 M chloroacetic acid ($CH_2ClCOOH$) solution? ($K_a = 1.4 \times 10^{-3}$)

A 3.1

B 1.9

C 3.8

D 1.5

4 Write the equation for the reaction of the base trimethylamine, $(CH_3)_3N$, with water.

5 Write the K_b expression for the reaction in Question 4.

6 If the K_b value for aniline ($C_6H_5NH_2$) is 4.3×10^{-10}, what is the K_a value for the conjugate acid of aniline?

7 Phosphoric acid, H_3PO_4, is a triprotic acid.

a Write the dissociation equations in water for each stage.

b Given that the K_a values for each dissociation stage are 7.52×10^{-3}, 6.23×10^{-8} and 4.0×10^{-13}, respectively, determine the pH of a 0.1 M phosphoric acid solution.

c Why would only K_{a1} be required to determine the pH?

8 A 0.5 M solution of phenol, C_6H_5OH, has a pH of 5.1. Determine its percentage ionisation.

8 ACID–BASE INDICATORS

Introduction

Most of the acids and bases encountered in everyday life and in the laboratory are colourless solutions. Therefore, it is important to have a way to distinguish between acids and bases, and to determine the strength of the acid or base.

Fortunately, we have acid–base indicators. An indicator is a substance that consists of a weak acid in equilibrium with its conjugate base. What makes indicators so useful is that the weak acid has a different colour from its conjugate base.

Stimulus questions

What are the common acid–base indicators that can be found in the home and garden?

What common household acids and bases can be used to characterise common acid–base indicators?

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8.1 Acid–base indicators

Indicators are molecular substances that are used because they change colour depending on the pH of the solution. An indicator is a weak acid and its conjugate base pair. The weak acid has a different colour from its conjugate base. Table 8.1.1 lists some common acid–base indicators, the pH ranges over which they change colour and their K_a values.

8.1.1 Acid–base indicators

TABLE 8.1.1 Acid–base indicators

INDICATOR	pH RANGE	COLOUR CHANGE		K_a
		ACID	BASE	
Thymol blue	1.2–2.8	Red	Yellow	2×10^{-2}
Methyl orange	3.1–4.4	Red	Yellow	2×10^{-4}
Bromophenol blue	3.0–4.6	Yellow	Blue	6×10^{-5}
Methyl red	4.2–6.3	Red	Yellow	8×10^{-6}
Litmus	5.0–8.0	Red	Blue	1×10^{-7}
Bromothymol blue	6.0–7.6	Yellow	Blue	1×10^{-7}
Phenol red	6.8–8.4	Yellow	Red	1×10^{-8}
Phenolphthalein	8.3–10.0	Colourless	Red	5×10^{-10}

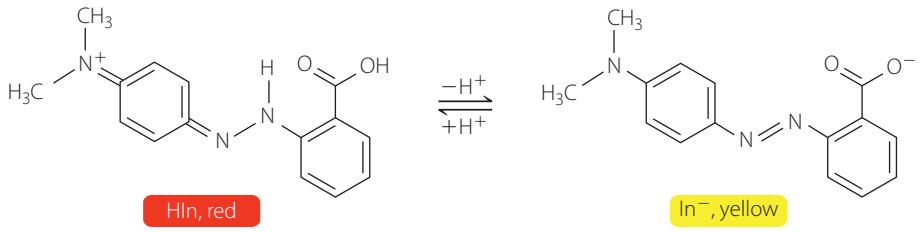

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FIGURE 8.1.1 Methyl red indicator has a bright red colour (HIn) in acidic solution, which changes to the yellow conjugate base (In^-).

When methyl red is added to an acidic solution in which the concentration of H_3O^+ is high, the red form predominates because the system attempts to partially oppose the increase in H_3O^+. By favouring the formation of HIn, the amount of hydronium ions is reduced. When methyl red is added to a basic solution in which the concentration of H_3O^+ is low, the forward reaction is favoured and the yellow form predominates. The system attempts to partially oppose the decrease in H_3O^+ by shifting the reaction forward to produce more H_3O^+ ions.

$$\underset{\text{Red}}{HIn} + H_2O \rightleftharpoons \underset{\text{Yellow}}{In^-} + H_3O^+ \qquad K_a = 8 \times 10^{-6}$$

When methyl red is added to a 0.01 M hydrochloric acid solution, the pH is 2. Substituting this into the expression for K_a gives:

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$
$$= \frac{[In^-] \times 10^{-2}}{[HIn]}$$
$$= 8 \times 10^{-6}$$

Andrew Lambert/Science Photo Library

FIGURE 8.1.2 Common indicators in acidic and alkaline solutions

$$\text{Therefore, } \frac{[In^-]}{[HIn]} = 8 \times 10^{-4} \quad [HIn] \gg [In^-]$$

In this example, [HIn] is much larger than $[In^-]$ and therefore the solution is red. Most of the indicator is present as HIn(aq).

When methyl red is added to a solution of 0.01 M sodium hydroxide, the pH is 12 and the concentration of H_3O^+ is 10^{-12}.

Substituting this into the same expression for K_a gives the following for the basic solution.

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$
$$= \frac{[In^-] \times 10^{-12}}{[HIn]}$$
$$= 8 \times 10^{-6}$$

$$\text{Therefore, } \frac{[In^-]}{[HIn]} = 8 \times 10^{-6} \quad [HIn] \ll [In^-]$$

In this example, [HIn] is much smaller than $[In^-]$ and the solution is yellow.

equivalence point the point when the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction

end point the physical sign that indicates that the equivalence point has been reached; achieving the correct end point depends on using an appropriate method that will undergo a physical change at the appropriate point

When the concentration of [HIn] = $[In^-]$, the ratio $\frac{[HIn]}{[In^-]} = 1$.

So $H_3O^+ = K_a$. The forms are present in the same amount, so the colour is between the two forms and the solution is orange. This occurs over a range of pH values (Table 8.1.1).

8.1.2 Equivalence points

KEY FORMULA

Acid–base indicators are a conjugate pair with at least one of the pair being intensely coloured. In titrations, the **end point** is when the colour changes. K_a at this point equals:

$$[H_3O^+] \text{ as } \frac{[A^-]}{[HA]} = 1$$

Indicators are chosen so that the colour change occurs at or near the **equivalence point** of the reaction. Therefore, the end point (colour change) is equal or close to the equivalence point and errors are reduced.

How an acid–base indicator works: Le Chatelier's principle

Consider the indicator methyl orange. In acidic solution it is red, in basic solution it is yellow.

In a neutral solution such as pure water the following equilibrium is present:

$$HIn + H_2O \rightleftharpoons In^- + H_3O^+$$

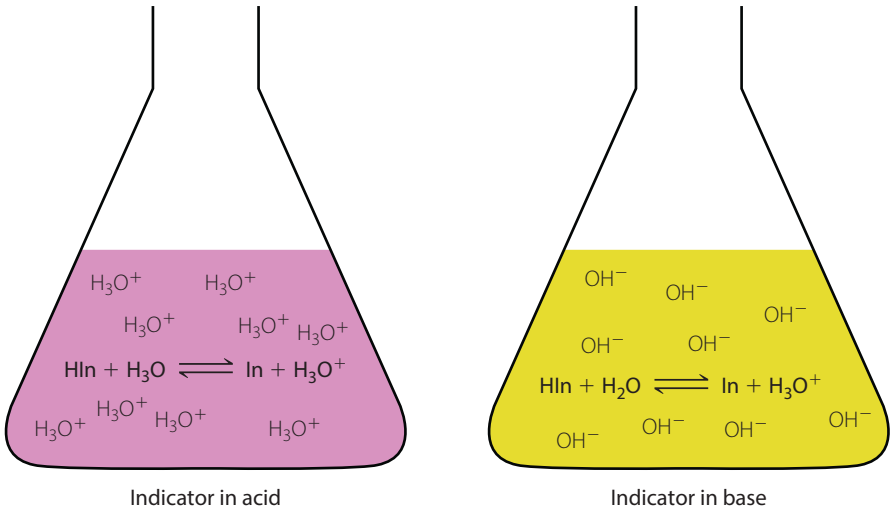


FIGURE 8.1.3 How an acid–base indicator works

In acid solution the indicator is surrounded by a large excess of H_3O^+ ions from the acid. In other words, a very large excess of H_3O^+ ions has been added to the indicator system. According to Le Chatelier's principle, the equilibrium system will shift to the left in order to decrease the concentration of H_3O^+ ions. Because there is a large excess of H_3O^+ ions, the system is firmly shifted to the left, the red form of the indicator.

In basic solution the indicator is surrounded by a large excess of OH^- ions from the base. These OH^- ions neutralise the H_3O^+ ions produced by the indicator equilibrium system. According to Le Chatelier's principle, the equilibrium system will shift to the right in order to replace the H_3O^+ ions that have been neutralised. Because there is such a large excess of OH^- ions, the system is firmly shifted to the right, the yellow form of the indicator.

SECTION REVIEW 8.1

REMEMBERING

1 Define:
   - **a** indicator
   - **b** indicator (acid form)
   - **c** indicator (basic form).

2 Write the general equation for an indicator, HIn, reacting with water to give the Ind^- ion

3 Write the K_a and K_b expressions for the acid and base forms of the indicator in Question 2.

UNDERSTANDING

4 The indicator phenolphthalein (HP) changes from pink in basic solution to clear in acidic solution. This indicator has a K_a of 5×10^{-10}. The reaction in water is:

$$HP(aq) + H_2O(l) \rightleftharpoons P^-(aq) + H_3O^+(aq)$$

Determine the magnitude of the ratio $[P^-]/[HP]$ for phenolphthalein and the dominant species present in the following pH solutions.

a 6

b 11

8.2 The relationship between pH and pK_a

The concentration of H_3O^+ ions is conveniently expressed by the term pH using the equation:

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

Chapter 7 describes how the strengths of acids and bases are represented by their dissociation constants, K_a or K_b. However, as with acids and bases, the values for these dissociation constants can be very small. Fortunately, these small numbers can be converted to convenient terms using the equation:

$$pK_a = -\log_{10} K_a$$

An acid such as nitrous acid, HNO_2, has a K_a value of 5.6×10^{-4}, while hydrocyanic acid, HCN, has a K_a value of 6.3×10^{-10}. These are not easy numbers to deal with. When they are converted to pK_a values they become more manageable:

$$HNO_2: pK_a = -\log_{10} 5.6 \times 10^{-4}$$

$$= 3.25$$

$$HCN: pK_a = -\log_{10} 6.3 \times 10^{-10}$$

$$= 9.21$$

Similarly, for bases,

$$pK_b = -\log_{10} K_b$$

A base such as ammonia, NH_3, has a K_b value of 1.8×10^{-5}, while hydroxylamine, NH_2OH, has a K_b value of 9.1×10^{-9}. Converting to pK_b gives:

$$NH_3: pK_b = -\log_{10} 1.8 \times 10^{-5}$$

$$= 4.74$$

$$NH_2OH = pK_b = -\log_{10} 9.1 \times 10^{-9}$$

$$= 8.04$$

8.2.1 pH and pK_a relationships for buffers

TABLE 8.2.1 The K_a and pK_a values of some weak acids

ACID	FORMULA	K_a	pK_a
Ammonium ion	NH_4^+	5.6×10^{-10}	9.25
Ethanoic	CH_3COOH	1.7×10^{-5}	4.77
Hydrocyanic	HCN	6.3×10^{-10}	9.20
Hydrofluoric	HF	7.6×10^{-4}	3.12
Lactic	$HC_3H_5O_3$	1.4×10^{-4}	3.85
Methanoic	HCOOH	1.8×10^{-4}	3.74

TABLE 8.2.2 The K_b and pK_b values of some weak bases

BASE	FORMULA	K_b	pK_b
Ammonia	NH_3	1.8×10^{-5}	4.75
Aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13
Methylamine	CH_3NH_2	4.6×10^{-4}	3.34
Hydroxylamine	NH_2OH	9.1×10^{-9}	8.05
Hydrazine	N_2H_4	1.3×10^{-6}	5.90
Pyridine	C_5H_5N	1.7×10^{-9}	8.77

The weaker the acid or base, the smaller its *K* value. Because the p*K* value is derived from a negative log function, then the *smaller* the *K* value, the *larger* the p*K* value and the weaker the acid or base.

pK_a of indicators

The general equation for the dissociation of an acid– base indicator is given by:

$$HIn + H_2O \rightleftharpoons In^- + H_3O^+$$

As with other weak acids, the equilibrium constant, K_a or K_{ind} in this case, can be expressed by:

$$K_{ind} = \frac{[In^-][H_3O^+]}{[HIn]}$$

At the equivalence point in a titration, the indicator is halfway through its colour change (assuming the correct indicator has been chosen). That is, the indicator equilibrium lies precisely in the middle.

At this point:

$$[HIn] = [In^-]$$

The expression above becomes:

$$K_{ind} = \frac{\cancel{[In^-]}[H_3O^+]}{\cancel{[HIn]}}$$

Therefore,

$$K_{ind} = [H_3O^+]$$

Also,

$$pK_{ind} = pH$$

The indicator will change colour when the solution it is in has the same pH as its pK_{ind} value. For example, methyl orange indicator has a pK_a value of 3.7. It will change colour when the solution it is in has a pH of 3.7.

Phenolphthalein has a pK_a value of 9.3 and it will change colour at a pH of 9.3.

It should be noted that indicators do not change colour at the precise pH governed by their pK_a value. The colour change occurs over a narrow pH range. Generally, an indicator will change colour over a range that is approximately ± 1 of their pK_a value. For example, methyl orange indicator has a pK_a of 3.7 and its useful range is between pH 3.1 and 4.4; phenolphthalein has a pK_a value of 9.3 and has a useful range between pH 8.2 and 10.0.

SECTION REVIEW 8.2

REMEMBERING

1 Define:

- **a** pK_a
- **b** pK_b
- **c** pK_{ind}
- **d** indicator pH range.

2 Using the acids and bases in Tables 8.2.1 and 8.2.2:

- **a** order the acids from strongest to weakest.
- **b** order the bases from weakest to strongest.

UNDERSTANDING

3 Chlorophenol red is a common acid–base indicator. The reaction of chlorophenol red with water is:

$$HClr(aq) + H_2O(l) \rightleftharpoons Clr^-(aq) + H_3O^+(aq) \quad pK_a = 6.2$$

- **a** Calculate K_a for chlorophenol red.
- **b** Estimate the useful pH range of chlorophenol red.

4 The pK_b of pyridine, C_5H_5N, is 8.77.

- **a** Write the equation for the dissociation of pyridine in water.
- **b** Calculate the K_b of pyridine.
- **c** Calculate the pH of a 1.00 $molL^{-1}$ solution of pyridine.

APPLYING

5 Table 8.2.3 shows some acid–base indicators and their useful pH ranges. Determine the K_a value for each indicator and write them in order of decreasing acid strength.

TABLE 8.2.3 Acid–base indicators and their useful pH ranges

INDICATOR	USEFUL pH RANGE
Congo red	3.0 – 5.0
Bromothymol blue	6.0 – 7.6
Indigo carmine	11.6 – 13.0
Methyl orange	3.1 – 4.4
Phenolphthalein	8.2 – 10.0
Alizarin yellow	10.2 – 12.0
Bromocresol green	3.8 – 5.4
Thymolphthalein	9.3 – 10.5

8.3 Indicator colour change

Earlier in this chapter it was shown that indicators are chosen so that the colour change occurs at or near the equivalence point of the reaction to be indicated. This is very important in volumetric analysis, where errors have to be kept to a minimum.

During a titration, the point at which an indicator changes colour is called the end point. An indicator must be chosen such that the equivalence point of the titration is as close as possible to the end point of the indicator.

Consider the titration of hydrochloric acid with sodium hydroxide. The reaction is given by the equation:

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

The equivalence point of this titration occurs when the precise amount of sodium hydroxide solution has been added to neutralise all of the hydrochloric acid.

The pH of the resulting sodium chloride solution is 7 because neither the $Na^+(aq)$ ions nor the $Cl^-(aq)$ ions have any acid or base properties.

Table 8.3.1 shows that the indicator with the pK_a value closest to the pH of the equivalence point is bromothymol blue, with a pK_a of 7.0.

TABLE 8.3.1 Common indicators with their pK_a values, useful pH ranges and colour changes

INDICATOR	pK_a	USEFUL pH RANGE	COLOUR CHANGE
Methyl orange	3.4	3.1 – 4.4	red → yellow/orange
Congo red	4.1	3.0 – 5.0	blue → yellow/orange
Bromocresol green	4.7	3.8 – 5.4	yellow → blue
Bromothymol blue	7.0	6.0 – 7.6	yellow → blue
Phenolphthalein	9.3	8.2 – 10.0	colourless → red/violet
Alizarin yellow	11.2	10.2 – 12.0	yellow → red
Thymolphthalein	9.9	9.3 – 10.5	colourless → blue
Indigo carmine	12.2	11.6 – 13.0	blue → yellow

WORKED EXAMPLE 8.3.1

An ethanoic acid solution ($CH_3COOH(aq)$) is titrated with a sodium hydroxide solution. Using Table 8.3.1, suggest a suitable indicator for this titration. Explain the choice of indicator and state the colour change at the end point. The equation for the reaction is given below:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

ANSWER

1 Remember, at the equivalence point there is no CH_3COOH or NaOH. Inspect what remains:
$CH_3COO^-(aq)$
$Na^+(aq)$
$H_2O(l)$

2 Identify the remaining substances for acid–base properties:
$Na^+(aq)$ has no acid or base properties
$H_2O(l)$ is neutral
$CH_3COO^-(aq)$ is the conjugate base of a weak acid

3 Write the equation for the reaction between ethanoate ion ($CH_3COO^-(aq)$) and water:

$$CH_3COO^-(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + OH^-(aq)$$

The conjugate base, the ethanoate ion, produces some $OH^-(aq)$ ions. It is, therefore, a weak base.

4 Estimate the pH of the solution. Since the ethanoate ion ($CH_3COO^-(aq)$) is the conjugate base of a weak acid, it is a weak base. It should have a pH of about 9.

5 Choose the indicator from Table 8.3.1 that has a pK_a value closest to a pH of 9: Phenolphthalein, with a pK_a of 9.3, is closest to a pH of 9.

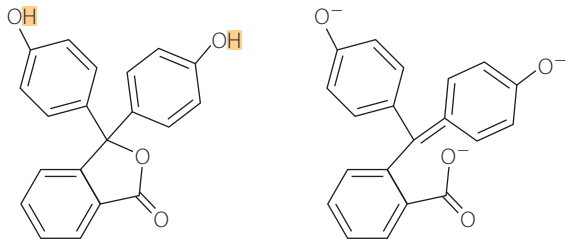
At the end point, phenolphthalein will change colour from colourless to red/violet.

The structure of indicators

Indicators generally have very complex structures, whether in their acid form or their conjugate base form.

Consider phenolphthalein as shown in Figure 8.3.1.

FIGURE 8.3.1 The acid and conjugate base form of phenolphthalein



Acid form HIn
Colourless

Base form In^-
Red/violet

The acid form is readily identified because of its extra H atoms (highlighted) compared to the base form.

SECTION REVIEW 8.3

UNDERSTANDING

1 Congo red is an acid–base indicator that consists of a weak acid in equilibrium with its conjugate base. The K_a value for the acid is 7.9×10^{-5}. In an acid solution the indicator appears blue; in a basic solution it appears red. At what pH will the solution appear violet?

APPLYING

2 The table below shows the colours of three acid–base indicators in solutions containing 10 mL samples of nitric acid at various concentrations.

	NITRIC ACID CONCENTRATION ($mol\,L^{-1}$)						
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
Methyl red	red	red	red	orange	yellow	yellow	yellow
m–cresol purple	red	orange	yellow	yellow	yellow	yellow	yellow
Alizarin red s	yellow	yellow	yellow	yellow	red	red	violet

Solutions of three different weak acids with a concentration of $1.0\,mol\,L^{-1}$ are prepared. The table below shows the colours of the different indicators in these weak acid solutions.

	METHYL RED	M–CRESOL PURPLE	ALIZARIN RED S
Solution A	red	yellow	yellow
Solution B	red	red	yellow
Solution C	yellow	yellow	red

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The three acid solutions, in no particular order, are:

- bromoacetic acid ($BrCH_2COOH$, $K_a = 1.25 \times 10^{-3}$)
- hypochlorous acid ($HOCl$, $K_a = 3.0 \times 10^{-8}$)
- hypoiodous acid (HOI, $K_a = 2.3 \times 10^{-11}$)

Determine the identities of Solutions A, B and C, justifying your answers with appropriate equations and calculations

3 Choose a suitable indicator from Table 8.3.1 for the titration between the following.

a Nitric acid and aniline ($C_6H_5NH_2$)

b Hydrocyanic acid (HCN) and potassium hydroxide (KOH)

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** indicator
- **b** indicator (acid form)
- **c** indicator (basic form)
- **d** pK_a
- **e** pK_b
- **f** pK_{Ind}

CATEGORY QUESTIONS

2 In acid solution the indicator bromothymol blue is yellow, in basic solution it is blue. Write the general equation for the indicator, represented by HIn, reacting with water to give the ind^- ion. Label the HIn and Ind^- with the appropriate colours.

3 Alizarin yellow (HAly) is a common acid–base indicator. Write the K_a and K_b expressions for this indicator.

ELABORATION QUESTIONS

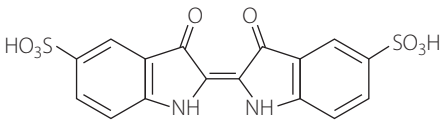
4 Using Table 8.3.1, choose an appropriate indicator for the titration between sodium hydroxide and butanoic acid:

$$CH_3CH_2CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2CH_2COONa(aq) + H_2O(l)$$

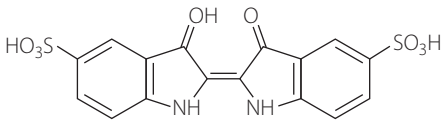
5 The pK_b of methylamine is 3.34. Calculate the pH of a 1 M solution of methylamine.

EVIDENCE QUESTIONS

6 Indigo carmine is an acid–base indicator with a pK_a of 12.2. Below are the two forms of the indicator:



Yellow



Blue

- **a** During an acid–base titration, what colour change would you expect as the acid is run into the base at the end point? Explain your decision.
- **b** Suggest an acid–base combination for which this indicator would be most suitable.

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END-OF-CHAPTER EXAM

End-of-chapter test

1 An indicator changes colour in the pH range between 9 and 11. What is the value of K_a for the indicator?

A 1×10^{-7}

B 1×10^{-13}

C 1×10^{-10}

D 1×10^{-9}

2 Which of the following always applies at the equivalence point (colour change) for the indicator HIn?

A $[HIn] = H_3O^+]$

B $[HIn] = [Ind^-]$

C $[Ind^-] = [OH^-]$

D $[Ind^-] = [H_3O^+]$

3 What is the pH at the equivalence point for an indicator with a K_a value of 1.26×10^{-3}?

A 11.1

B 4.1

C 2.9

D 1.26×10^{-3}

4 The indicator bromothymol blue can be represented by the following general equation:

$$\underset{\text{yellow}}{HIn} + H_2O \rightleftharpoons \underset{\text{blue}}{In^-} + H_3O^+$$

At a pH of 6.9 it is a greenish colour.

If sodium hydroxide is added to this indicator solution, what is the equilibrium change and resulting indicator colour change?

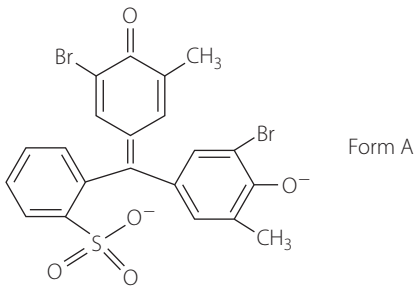
A Change: Decrease in $[H_3O^+]$ Indicator colour change: blue → yellow

B Change: Increase in $[H_3O^+]$ Indicator colour change: yellow → blue

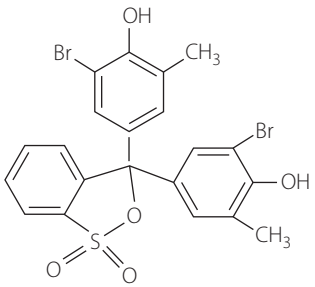
C Change: Increase in $[H_3O^+]$ Indicator colour change: blue → yellow

D Change: Decrease in $[H_3O^+]$ Indicator colour change: yellow → blue

5 Bromocresol purple is a common acid–base indicator. It exists predominantly in two forms shown below:



Form A



Form B

FIGURE 8.4.1 The two structures of bromocresol purple

In order to determine the colour changes of this indicator in acidic and basic conditions, an experiment is performed in which the indicator is mixed with solutions of known pH. These solutions are then placed in a colorimeter which accurately measures the colour of light transmitted by these solutions. Figure 8.4.2 shows a graph of these results.

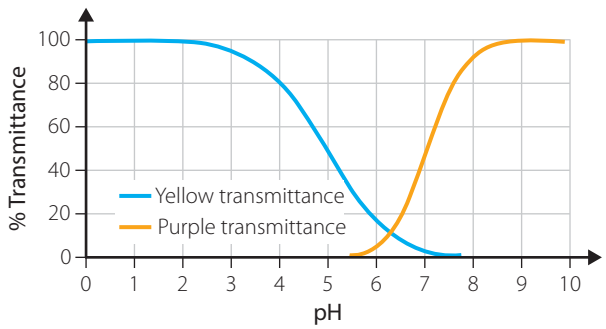


FIGURE 8.4.2 Graph showing the colour of bromocresol purple at varying pH values (note: 100% transmittance of, for example, yellow light, means that the solution is yellow).

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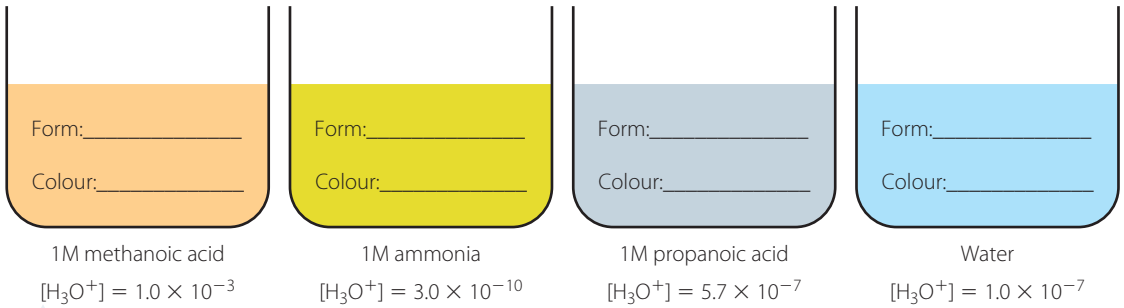
In the experiment, four beakers are filled with various substances. A few drops of bromocresol purple indicator are added to each beaker.



1M methanoic acid	1M ammonia	1M propanoic acid	Water
$[H_3O^+] = 1.0 \times 10^{-3}$	$[H_3O^+] = 3.0 \times 10^{-10}$	$[H_3O^+] = 5.7 \times 10^{-7}$	$[H_3O^+] = 1.0 \times 10^{-7}$

FIGURE 8.4.3 Beakers filled with various substances into which a few drops of bromocresol purple indicator are added.

a Use the graph in Figure 8.4.2 and the structures for bromocresol purple indicator to decide in what form, A or B, the indicator is in each of the four beakers, and what colour each solution becomes.

b Using equations and calculations, justify your decisions for each beaker.

9 VOLUMETRIC ANALYSIS

Introduction

Determining whether or not a chemical reaction has occurred is a form of qualitative analysis; it gives a 'yes' or 'no' answer. However, there are times when chemists not only want to know whether a chemical reaction occurs, but also to quantify the reaction. For this, they need to be able to perform quantitative analyses. Volumetric analysis is one type of quantitative analysis. Volumetric analysis determines the concentration of a sample by measuring the volume of this sample that reacts with a known volume of another substance of known concentration.

Stimulus question

How do you determine the difference between the end point and the equivalence point?

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9.1 End point and equivalence point

Acid–base indicators and how they operate are an important part of volumetric analysis. Most acids, bases and their reaction products are colourless, so it can be difficult to assess when an acid–base reaction is complete. Indicators show when neutralisation has occurred because they change colour when the reaction is complete.

Consider the neutralisation of hydrochloric acid by sodium hydroxide:

$$\underbrace{HCl(aq) + NaOH(aq)}_{\text{colourless}} \rightarrow \underbrace{NaCl(aq) + H_2O(l)}_{\text{colourless}}$$

When this reaction occurs, there is no obvious sign when the hydrochloric acid has been neutralised by the sodium hydroxide.

If a few drops of phenolphthalein indicator are added to the acid:

$$\underbrace{\text{phenolphthalein} + HCl(aq)}_{\text{colourless}} + \underbrace{NaOH(aq)}_{\text{colourless}} \rightarrow \underbrace{NaCl(aq) + H_2O(l)}_{\text{pink}}$$

The acid/phenolphthalein indicator mixture is colourless. As sodium hydroxide is added, it begins to neutralise the hydrochloric acid. Eventually enough sodium hydroxide is added that all of the hydrochloric acid has been neutralised. If one more drop of sodium hydroxide is added the solution turns pink.

For volumetric analysis to be meaningful, we need to know the precise point at which neutralisation occurs; that is, when the number of moles of acid equals the number of moles of base:

$$n H_3O^+(aq) = n OH^-(aq)$$

As discussed, this is called the equivalence point. The acid and base have an equivalent (or balanced) number of moles.

It was demonstrated in Chapter 8 that indicators change colour over a wide range of pH values, so it is important to choose an indicator that will change colour at, or close to, the expected pH of the equivalence point. The pH value when the indicator changes colour is called the end point.

When choosing an indicator for an acid–base reaction, it is important to pick one whose end point is as close as possible to the equivalence point of the reaction.

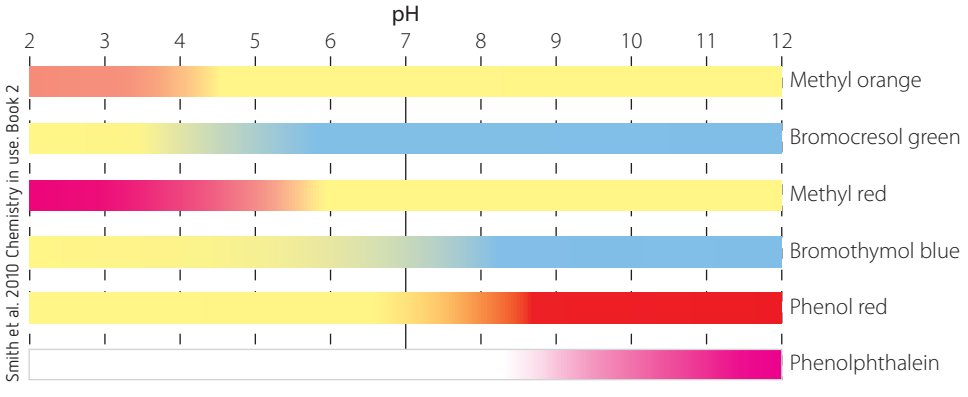

FIGURE 9.1.1 Colours of common indicators over ranges of pH

9.1.1 Acid–base reactions
9.1.2 Acid–base reaction

Types of acid–base reaction

The choice of an indicator for an acid–base reaction is complicated by the type of acid–base reaction being studied. The type of reaction is based on the *strength* of the acid and the base involved.

It is important to consider what is left in the flask once the equivalence point has been reached.

Strong acid–strong base

Example: Hydrochloric acid and sodium hydroxide

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

At the equivalence point, *just enough* sodium hydroxide has been added to neutralise the hydrochloric acid. All that is left is the sodium chloride and water. These must be inspected for acidic or basic properties:

- $Na^+(aq)$ ions have no acidic or basic properties
- $Cl^-(aq)$ ions are the conjugate base of a strong acid and, though technically a base, have no basic properties
- $H_2O(l)$ is neutral.

Therefore, the solution remaining after the equivalence point has a pH of 7. From the indicator chart in Figure 9.1.1, the indicator with an end point close to a pH of 7 is bromothymol blue.

Strong acid–weak base

Example: Hydrochloric acid and ammonia solution

At the equivalence point: $HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

This leaves ammonium ions, $NH_4^+(aq)$, and chloride ions, $Cl^-(aq)$.

- $Cl^-(aq)$ ions have no acidic or basic properties.
- $NH_4^+(aq)$ is the conjugate acid of a weak base and so is a weak acid:

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

Therefore, the solution remaining after the equivalence point has a pH about 4 or 5. From the indicator chart, the indicator with an end point close to this is methyl orange.

Weak acid–strong base

Example: Ethanoic acid and sodium hydroxide

At the equivalence point: $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq) + H_2O(l)$

This leaves acetate ions, $CH_3COO^-(aq)$, Na^+, and $H_2O(l)$.

- $Na^+(aq)$ has no acidic or basic properties and $H_2O(l)$ is neutral.
- $CH_3COO^-(aq)$ is the conjugate base of a weak acid and so is a weak base:

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

Therefore, the solution remaining after the equivalence point has a pH about 8 or 9. From the indicator chart, the indicator with an end point close to this is phenolphthalein.

Weak acid–weak base

Example: Ethanoic acid and ammonia solution

$$CH_3COOH(aq) + NH_3(aq) \rightleftharpoons CH_3COO^-(aq) + NH_4^+(aq)$$

This is a complex system with no clear-cut equivalence point. An acid–base indicator would not be appropriate to monitor this type of reaction.

SECTION REVIEW 9.1

REMEMBERING

1 Define:
   a end point
   b equivalence point.

UNDERSTANDING

2 Copy and complete the table below, using the indicator chart in Figure 9.1.1.

ACID	BASE	PRODUCTS	EQUIVALENCE POINT	INDICATOR
Propanoic		Sodium propanoate	5.5	
	Ammonia	Ammonium nitrate		
Hydrochloric		Potassium chloride		
Ethanoic		Ammonium acetate	None visible	

9.2 Acid–base titrations

Consider the following reaction:

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

The mole ratio indicates that 2 moles of sodium hydroxide react with 1 mole of sulfuric acid. The equivalence point is the point at which there are twice as many moles of sodium hydroxide present as there are moles of sulfuric acid. This is because 1 mole of sulfuric acid produces 2 moles of hydrogen ions (H^+), and 2 moles of sodium hydroxide produce 2 moles of hydroxide ions (OH^-). Therefore, there are equal numbers of moles of hydrogen ions and hydroxide ions. Hence, the equivalence point is when the reactants are present in the mole ratio given in the balanced equation for this reaction.

In the reaction above, both solutions are colourless, as are the products. It is not possible to see when the equivalence point has been reached. Acid–base indicators change colour within certain pH ranges. An acid–base indicator helps with volumetric analysis, as the end point is shown by a change in colour.

Titrations using specialist glassware are able to detect the end point by a variety of methods, such as the use of acid–base indicators, conductivity and pH probes. Chemists must have an understanding of the chemistry of the specific reaction to determine the most appropriate way to determine the end point.

titration
a type of volumetric analysis that determines the end point

accuracy
dependent on the measuring instrument that is used; a mass balance that measures to 0.001 g is a more accurate instrument than a mass balance that measures to 0.1 g

parallax error
an error in measurement due to the observer's position relative to the meaningful scales; if the reading is taken at an angle to the scale, then an error is introduced

Specialised glassware

As volumetric analysis involves the measuring of volumes, glassware with accurate measuring scales is essential. The most common types of glassware are volumetric flasks, burettes and pipettes. Since accuracy is very important in this technique, parallax error must be minimised by ensuring that when reading the volume, the measuring line is directly in line with your eye level.

Volumetric flask

A volumetric flask is a flat-bottomed flask with a long narrow neck. These are often used for accurately diluting a solution. Volumetric flasks are available in a variety of sizes but the most commonly used

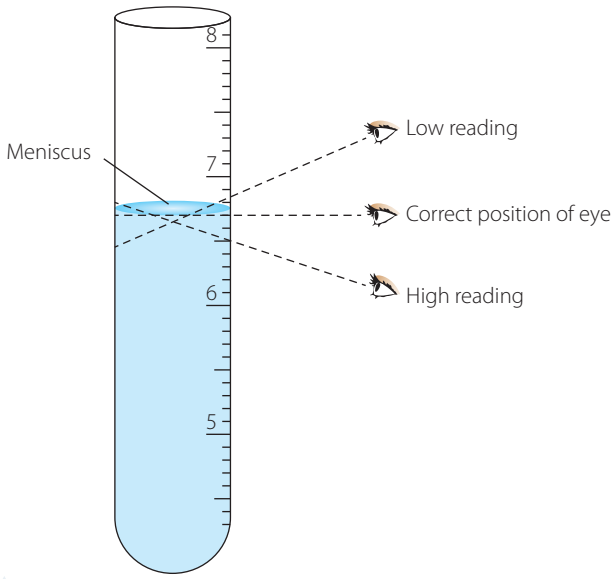

FIGURE 9.2.1 How to read a measuring cylinder and avoid parallax error

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FIGURE 9.2.2 A 250 mL volumetric flask

Shutterstock.com/141cocl2

FIGURE 9.2.3 A 50 mL burette

flasks in schools are the 100 mL and 250 mL volumetric flasks. A line on the flask indicates the volume that can be accurately measured. The volumetric flask is always rinsed with a solvent, generally water, prior to use.

Once the flask has been rinsed with the solvent, pour the solution into the flask and gradually top it up to the correct measurement line with a wash bottle or a Pasteur pipette (a dispenser with a fine tip to add small drops). The bottom of the meniscus must be just touching the line on the flask. It is important not to overfill the flask, because the volume of solution will not be accurately known. If this happens, the flask should be emptied and refilled again from the beginning.

Burette

A burette is a long, narrow glass tube with a tap at the bottom. The most commonly used burette is a 50 mL burette. The measuring scale on a burette is inverted, as it measures the volume of solution that leaves the burette through the tap. Hence, the zero position is at the top of the burette and the 50 mL position is near the bottom of the burette. The burette is always rinsed with the solution that will be placed in the burette prior to use.

To rinse the burette, pour a small volume of solution into the burette. Then, holding the burette horizontally, open the tap and turn the burette slowly in your hands so that all surfaces on the inside of the burette are rinsed with the solution. Empty this solution.

To fill the burette, place it back in the burette clamp and close the tap. Pour the solution into the burette until it is above the zero mark. Place a flask under the burette and open the tap so that the airlock below the tap is filled with solution. Adjust the volume of solution in the burette to the zero mark.

Pipette

A pipette is a thin glass tube that accurately measures a fixed volume of solution. The most common pipettes in school laboratories are 20 mL and 25 mL pipettes. A line on the pipette indicates the volume that can be accurately measured. The pipette is always rinsed with the solution that will be placed in it prior to use.

To rinse the pipette, use a pipette filler to draw up a small volume of solution. Remove the pipette filler, hold the pipette horizontally and turn the pipette in your hands so that all surfaces on the inside of the pipette are rinsed with the solution. Empty this solution.

To fill the pipette, use the pipette filler to draw the solution into the pipette. Stop when the volume of solution is above the line on the pipette. Slowly evacuate the solution until the bottom of the meniscus is just touching the line. Place the pipette over the flask into which the solution will be evacuated, remove the pipette filler and allow the pipette to empty. Tap the tip of the pipette on the inside of the flask. A small volume of solution will remain in the pipette; do not try to evacuate this solution. The pipette has been calibrated to evacuate the specified volume when it empties naturally under gravity.

Alamy Stock Photo / sciencephotos

FIGURE 9.2.4 A 25 mL pipette

PRACTICAL ACTIVITY 9.2.1

Practising rinsing and reading measurements on glassware

Volumetric flasks, burettes and pipettes are used to measure accurate volumes. Hence, you need to learn to use this equipment correctly and to read the scales correctly to benefit from using this equipment.

AIM

To use and read volumes accurately using volumetric flasks, burettes and pipettes

EQUIPMENT

- 100 mL or 250 mL volumetric flask with lid
- 20 mL or 25 mL pipette
- Pipette filler
- Burette
- Burette clamp or bosshead and retort clamp
- Retort stand
- 250 mL conical flask
- Wash bottle or Pasteur pipette and bulb
- Filter funnel
- 250 mL beaker
- 150 mL beaker

»

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Glassware may break and cut you.	Always ensure that glassware is kept away from the edge of benches. If glassware does break, inform your teacher immediately.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

Part A: Volumetric flask

1. Rinse the volumetric flask with a small volume of water, then empty it.
2. Place a filter funnel in the neck of the volumetric flask.
3. Use a 250 mL beaker to pour water through the filter funnel into the flask. Hold the filter funnel slightly above the flask so that the water will flow freely.
4. When the bulb of the flask is filled, remove the filter funnel and use a wash bottle or Pasteur pipette to fill the flask so that the bottom of the meniscus is touching the line marked on the flask.
5. Check your result with your teacher.

Part B: Burette

6. Clamp the burette to a retort stand using a burette clamp and close the tap on the burette.
7. Pour a small volume of water into the burette.
8. Remove the burette from the burette clamp, hold it horizontally, open the tap and turn the burette so that all surfaces of the burette are rinsed.
9. Empty the water into the sink.
10. Clamp the burette to the retort stand and close the tap on the burette.
11. Use a 150 mL beaker to fill the burette with water above the zero line.
12. Open the tap to allow water to flow to remove the air lock, and then close the tap.
13. Adjust the water level in the burette to the zero mark.
14. Place a flask under the burette and release exactly 26.30 mL from the burette.
15. Check your result by showing your teacher.
16. Refill your burette and adjust the water level in the burette to the zero mark.
17. Place a flask under the burette and release exactly 15.70 mL from the burette.
18. Check your result with your teacher.

Part C: Pipette

19. Attach the pipette filler to the pipette and draw up a small volume of water into the pipette.
20. Hold the pipette horizontally, remove the pipette filler and turn the pipette so that all surfaces of the pipette are rinsed.
21. Empty the pipette.
22. Attach the pipette filler to the pipette and draw water into the pipette until the volume is above the line marked on the pipette.
23. Adjust the volume until the bottom of the meniscus touches the line marked on the pipette.
24. Check your result with your teacher.
25. Place the pipette over the 250 mL conical flask and remove the pipette filler so that the pipette empties into the flask. Tap the tip of the pipette on the inside wall of the flask and rinse down the sides of the flask with water.

RESULTS

Record your results in a table, including equipment, volume and comments by your teacher.

ANALYSIS OF RESULTS

1 Compare your results with those of other students in the class.
2 Comment on the accuracy of your results.

DISCUSSION

1 Discuss any common sources of error in the class results.
2 Describe ways to overcome these sources of error.

Primary standard solutions

To be able to accurately determine the concentration of an unknown solution, it is titrated against a solution with an accurately known concentration. Accuracy is the number of significant figures to which a quantity is known. Some mass balances measure to the nearest gram, while others measure to the nearest milligram (0.001 gram). The mass balance that can measure to the nearest milligram is a more accurate measuring device than the mass balance that measures to the nearest gram. Accuracy is determined by the measuring instrument that is used.

KEY FORMULA

Accuracy is the number of significant figures to which a quantity is known. It is determined by the measuring instrument that is used.

A chemical that can be made up into a solution of accurately known concentration is called a **primary standard**. A primary standard must be stable over a long time under common laboratory conditions.

primary standard
a solution of accurately known concentration that remains stable under common laboratory conditions for extended periods of time

A primary standard must:

- have a large molar mass so that a reasonable mass is measured; hence, there is a smaller percentage error
- be cheap so that it is affordable for use
- be of high purity so that no side reactions occur
- be stable in the presence of air, so that no reaction with air occurs
- not have any water of hydration, which may change due to atmospheric conditions such as humidity
- dissolve readily in a solvent, generally water, to form a stable solution.

Anhydrous sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) are frequently used as primary standards in school science laboratories because they meet all of these criteria.

Performing volumetric analysis

The solution in the burette is called the **titrant**. The solution to be analysed, which has the unknown concentration, is called the **analyte**.

titrant
the solution in a burette

analyte
the solution of an unknown concentration that will be analysed

The most common titration conducted in a school science laboratory is the acid–base titration. The following describes the basic technique for performing a titration. Note that this procedure can only be used if one of the solutions has an accurately known concentration.

1 Rinse the burette with a small amount of the solution that it will contain. This is generally, but not always, the solution whose concentration is known (Solution A).
2 Use a pipette to transfer a known volume of the other solution (Solution B) into a conical flask that has been rinsed with water.
3 Add two drops of an appropriate acid–base indicator to Solution B.

4 Slowly add Solution A from the burette to Solution B. Make sure to swirl the flask as Solution A is added. This ensures that the reactants are adequately mixed. Stop adding Solution A when the indicator shows the first permanent colour change.

5 Record the volume of Solution A added from the burette.

6 Repeat the experiment several times until the volume of Solution A added from the burette is consistent to within about one-third of a division (0.03 mL). The second and subsequent titrations should involve slowing the rate of flow of Solution A from the burette to dropwise and parts of drops when near the end point. Use the average titre for the most accurately known titrations for your calculations.

7 Write a balanced chemical equation and use mole calculations to determine the concentration of the unknown Solution A.

WORKED EXAMPLE 9.2.1

Potassium hydrogen phthalate, $KH(C_8H_4O_4)$ (or KHP), is a good primary standard for standardising alkali solutions. It contains one acidic hydrogen per formula unit. Potassium hydrogen phthalate (0.917 g) was dissolved in water and titrated with approximately 0.2 mol L^{-1} sodium hydroxide solution; 27.2 mL hydroxide solution was needed to reach the end point. Calculate the accurate molarity of the hydroxide solution.

ANSWER

1 Write a balanced equation for the reaction:

$$KH(C_8H_4O_4)(aq) + NaOH(aq) \rightarrow Na^+(aq) + K(C_8H_4O_4)^-(aq) + H_2O(aq)$$

2 Calculate the number of moles of potassium hydrogen phthalate that reacted with the sodium hydroxide:

$$n(\text{KHP}) = \frac{m(\text{KHP})}{M(\text{KHP})} = \frac{0.917}{204.22} = 0.00449 \text{ mol}$$

3 Calculate the number of moles of sodium hydroxide that reacted with the potassium hydrogen phthalate. From the balanced equation:

$$n(\text{NaOH}) = n(\text{KHP}) = 0.00449 \text{ mol}$$

4 Calculate the molarity of the sodium hydroxide solution:

$$c(\text{NaOH}) = \frac{n(\text{NaOH})}{V(\text{NaOH})} = \frac{0.0049}{\frac{27.2}{1000}} = 0.165 \text{ mol L}^{-1}$$

5 Molarity = 0.165 mol L^{-1}

WORKED EXAMPLE 9.2.2

The acidity of a particular white wine was determined by titrating 25.0 mL of the wine with 0.0511 mol L^{-1} sodium hydroxide solution; 8.70 mL was required. Calculate the molarity of hydrogen ions in the wine. Assume that the hydrogen ions come entirely from diprotic tartaric acid, $H_2C_4H_4O_6$, and calculate the concentration of tartaric acid in the wine in grams per 100 mL.

ANSWER

1 Write a balanced chemical equation for the reaction:

$$H_2C_4H_4O_6(aq) + 2NaOH(aq) \rightarrow 2Na^+(aq) + C_4H_4O_6^{2-}(aq) + 2H_2O(l)$$

2 Calculate the number of moles of sodium hydroxide that reacts with tartaric acid:

$$n_{NaOH} = c_{NaOH} \times V_{NaOH} = 0.0511 \times \frac{8.70}{1000} = 0.000\,445\,\text{mol}$$

3 Calculate the number of moles of hydrogen ions that react with the sodium hydroxide. Using the equation and data in the question: $n_{H^+} = n(NaOH) = 0.000\,445$ mol:

Tartaric acid is diprotic; that is, each molecule of tartaric acid contains 2 hydrogen ions.

4 Calculate the molarity of hydrogen ions in tartaric acid:

$$c_{H^+} = \frac{n(H+)}{V(H_2C_4H_4O_6)} = \frac{0.000\,445}{\frac{25.0}{1000}} = 0.0178\,\text{mol L}^{-1}$$

5 Calculate the concentration of tartaric acid in g/100 mL, using equation:

$$n(H_2C_4H_4O_6) = \frac{1}{2}\, n(NaOH) = 0.000\,222\,\text{mol}$$

$$\begin{aligned} m(H_2C_4H_4O_6) &= n(H_2C_4H_4O_6) \times M(H_2C_4H_4O_6) \\ &= 0.000\,222 \times 150.088 \\ &= 0.0334\,\text{g} \end{aligned}$$

$$[H_2C_4H_4O_6] = \frac{m(H_2C_4H_4O_6)}{V(H_2C_4H_4O_6)} = \frac{0.0334}{\frac{25.0}{1000}} = 1.33\,\text{g L}^{-1} = 0.133\,\text{g/100 mL}$$

6 Concentration = 0.133 g/100 mL

MANDATORY PRACTICAL 9.2.2

Acid–base titration to calculate the concentration of a solution with reference to the standard solution

In this titration, you will be using the primary standard sodium carbonate (0.05–0.06 mol L^{-1}) solution to determine the unknown concentration of a solution of hydrochloric acid. Hydrochloric acid is a strong acid and sodium carbonate is a weak base so the equivalence point will be in the acidic region. Methyl orange is a suitable indicator for this titration.

AIM

To determine the concentration of a hydrochloric acid solution using volumetric analysis

EQUIPMENT

- 250 mL of an accurately known concentration of sodium carbonate
- 50 mL burette
- Retort stand and burette clamp
- 25 mL pipette and pipette filler
- Two 150 mL beakers

- 250 mL conical flask
- Dropper bottle containing methyl orange indicator
- 200 mL of hydrochloric acid of unknown concentration
- Two small labels for the 150 mL beakers
- Wash bottle with distilled water

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Dilute solutions of hydrochloric acid, sodium carbonate and methyl orange indicator may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Glassware could break and cut your hands.	Keep glassware away from the edge of the bench. When the pipette is not in use, leave the pipette filler on the pipette to prevent it rolling off the bench. If glassware does break, inform your teacher immediately.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Rinse one of the 150 mL beakers with a small amount of the hydrochloric acid solution, empty it, label it and fill it with about 100 mL of the hydrochloric acid solution.
2. Prepare the burette and then fill it with the hydrochloric acid solution.
3. Rinse the other 150 mL beaker with a small amount of the sodium carbonate solution, empty it, label it and fill with about 100 mL of the sodium carbonate solution.
4. Rinse the conical flask with water.
5. Prepare the pipette, then use the pipette to transfer 25 mL of the sodium carbonate solution to the conical flask.
6. Add two drops of methyl orange indicator to the conical flask and swirl to mix.
7. Place the conical flask under the burette and begin the titration.
8. When the first permanent colour change has occurred, record all results.
9. Repeat the titration several more times until the amount of titrant added is within 0.03 mL.

RESULTS

Record the following results.

- Concentration of sodium carbonate solution
- Volume of sodium carbonate used
- Volume of hydrochloric acid used

ANALYSIS

1. Calculate the average volume of hydrochloric acid used.
2. Write a balanced chemical equation for the reaction between hydrochloric acid and sodium carbonate.
3. Calculate the number of moles of sodium carbonate placed in the reaction vessel (conical flask).
4. Use the mole ratio from your balanced chemical equation to determine the number of moles of hydrochloric acid that was titrated.
5. Calculate the concentration of hydrochloric acid that was titrated.

DISCUSSION

1. Compare your value for the concentration of the hydrochloric acid with that of other students and with the value provided by your teacher.
2. Discuss any variations in the value and suggest how to improve the accuracy of your results.
3. Justify why the conical flask was rinsed with water and not the solutions that were placed in it.

Practical 9.2.2 is the simplest type of titration, where an acid and a base are titrated directly against each other using an appropriate acid–base indicator. The issues to be considered are:

- identifying the correct indicator to use
- making sure that the chemical equation is correctly balanced to ensure that the correct mole ratio is used in the calculations.

Back titrations

Sometimes, it is not appropriate to directly titrate one substance against another. In this instance, the indirect method of **back titration** is used.

back titration
a method used to determine the mass or concentration of a substance that is not able to be determined directly

A back titration is useful when:

- it is difficult to determine a definite end point because the reaction occurs too slowly
- the sample is not soluble in water but will, for example, react with an acid
- the sample is toxic
- the sample is volatile
- the sample is gaseous and in a mixture of gases
- the sample is not really reactive; that is, it is too weak to have a clearly defined end point, or is present in low concentration or in trace amounts in a mixture.

A back titration would be used to determine the percentage of calcium carbonate in a sample of limestone. Calcium carbonate is not soluble in water, so the sample cannot be dissolved to form a solution. However, the following reaction will occur with hydrochloric acid:

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

A known excess volume of a standardised hydrochloric acid solution would be added to the limestone. It is assumed that the acid only reacts with the calcium carbonate, not with any of the other impurities. The reaction would be left for a period of time and then the reaction vessel would be heated to ensure that the reaction goes to completion and all of the carbon dioxide has been released. A couple of drops of methyl orange indicator are added to the solution, and then it is titrated against a standardised sodium hydroxide solution. The excess hydrochloric acid reacts with the sodium hydroxide until the end point is reached. The equation for this reaction is:

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

WORKED EXAMPLE 9.2.3

A 2.50 g sample of limestone was dissolved in 75 mL of 0.996 mol L^{-1} hydrochloric acid. After heating to ensure that all of the carbon dioxide was expelled, the solution was cooled and diluted to 250 mL. A 25 mL sample of this diluted solution was titrated with 25.27 mL of a standardised solution of 0.1215 mol L^{-1} sodium hydroxide. Determine the percentage of calcium carbonate in the original limestone sample.

ANSWER

1 Write balanced chemical equations for all reactions:

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

2 Calculate the original number of moles of HCl that was added to the limestone:

$$\begin{aligned} n_{HCl} &= M_{HCl} \times V_{HCl} \\ &= 0.996 \times 0.0750 \\ &= 0.0747 \text{ mol} \end{aligned}$$

3 Calculate the number of moles of HCl that reacted with the NaOH:

$$n_{NaOH} = M_{NaOH} \times V_{NaOH} = 0.1215 \times 0.025\,27 = 0.00307 \text{ mol}$$
$$n_{HCl} = n_{NaOH} = 0.003\,07 \text{ mol}$$

This is the number of moles of unreacted HCl in the 25 mL sample of the diluted solution.
As the solution was 250 mL, the number of moles of HCl present in this solution is 10 times the value calculated above:

$$n_{\text{HCl in 250 mL solution}} = 10 \times 0.003\,07 = 0.0307 \text{ mol}$$

4 Calculate the number of moles of HCl that reacted with the $CaCO_3$:

$$n_{\text{HCl reacted with CaCO}_3} = 0.0747 - 0.0307 = 0.0440 \text{ mol}$$

5 Calculate the number of moles of $CaCO_3$ that reacted with HCl; this is the number of moles of $CaCO_3$ in the limestone sample.

$$n\,CaCO_3 = \frac{n\text{HCl}}{2} = 0.0220 \text{ mol}$$

6 Calculate the percentage of $CaCO_3$ in original limestone sample:

$$m_{CaCO_3} = n_{CaCO_3} \times M_{CaCO_3} = 0.0220 \times 100.09 = 2.20 \text{ g}$$

7 $$\text{Percentage of calcium carbonate} = \frac{2.20}{2.50} \times 100 = 88\%$$

SECTION REVIEW 9.2

ANALYSING

1 Oxalic acid dihydrate, $(COOH)_2.2H_2O$, can be used as a primary standard for standardising alkali solutions. 0.291 g diprotic oxalic acid required 18.2 mL of a potassium hydroxide solution for exact neutralisation. Calculate the molarity of the hydroxide solution.

2 5.267 g anhydrous sodium carbonate was dissolved in water in a volumetric flask and the volume made up to 250 mL. Using a pipette, 10 mL of this solution was transferred into a conical flask and titrated with hydrochloric acid. 21.3 mL was needed to reach the equivalence point. This solution was then used to determine the concentration of an unknown barium hydroxide solution. 25 mL of the barium hydroxide solution required 27.1 mL hydrochloric acid solution for exact neutralisation.

- **a** Calculate the molarity of the hydrochloric acid solution.
- **b** Calculate the molarity of the barium hydroxide solution.
- **c** Calculate the concentration of the barium hydroxide solution in grams per litre.

3 To calculate the percentage of calcium carbonate in a sample of limestone, a chemist dissolved 0.552 g in 50 mL of 0.121 mol L^{-1} hydrochloric acid, boiled the mixture gently to ensure complete reaction and to expel all carbon dioxide, and then titrated the excess hydrochloric acid with 21.1 mL of 0.0950 mol L^{-1} sodium hydroxide solution. Calculate the mass of calcium carbonate in the sample and hence the percentage.

4 To determine the amount of ammonium ion in a sample, a chemist dissolved 0.375 g of the sample in water, added 25 mL of 0.414 mol L^{-1} sodium hydroxide solution and boiled the mixture to drive off all of the ammonia formed. After all of the ammonium ion had been reacted, the leftover hydroxide left over required 21.2 mL of 0.161 mol L^{-1} hydrochloric acid for exact neutralisation. Calculate the mass of ammonium ion in the original sample and hence the weight percentage of ammonium ion in the sample.

9.3 Graphs

If the solution being analysed is not colourless, then it will interfere with the colour change of the indicator. Some solutions, such as malt vinegar and red wine, are so dark that the indicator colour cannot be seen at all. In this case, a pH meter would be used rather than an indicator, and the pH of the solution would be measured as the solution from the burette is added to the conical flask. The titration can be analysed by plotting a graph of pH against volume of acid or base added. This kind of graph is called a **titration curve** (or pH curve).

titration curve
a graphical representation of a titration, with the *x*-axis showing the volume of titrant added, and the *y*-axis showing the pH of the solution

When performing an acid–base titration, the pH of the solution in the reaction vessel changes. If the base is pipetted into the conical flask, then the acid is added from the burette, the pH will change from basic to acidic. The shape of the graph depends on the strength of the acid and base used; however, it is not a linear change.

Strong base–strong acid

The graph for a titration of a strong base and a strong acid shows that the pH starts at a very high value; it is in the basic region (Figure 9.3.1). It remains fairly constant until close to the equivalence point, when it suddenly decreases. The pH drops from 12–13 to 1–2. When acid is in excess, the pH stays reasonably constant again at a very low pH. The equivalence point is the midpoint of the sudden change in the pH.

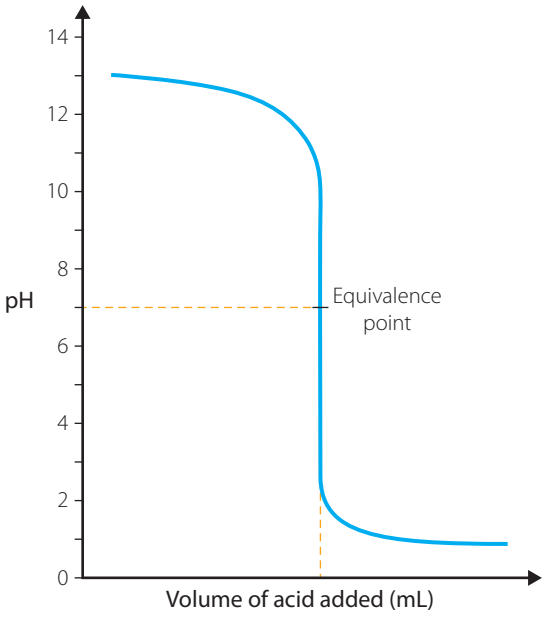
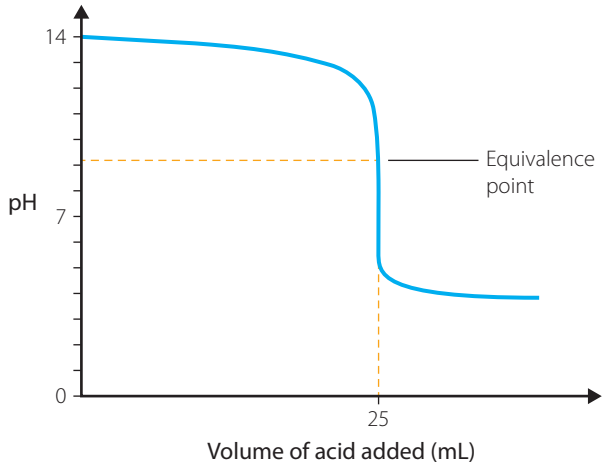


FIGURE 9.3.1
A titration curve for a strong base–strong acid titration

Strong base–weak acid

The graph for a titration of a strong base and a weak acid also begins with a very high basic pH (Figure 9.3.2). It remains fairly constant until close to the equivalence point, when it suddenly decreases, although not as much as for the strong base–strong acid titration. The pH drops from 12–13 to about 4. When acid is in excess, the slope of the pH graph changes and eventually stays reasonably constant at a low pH. The equivalence point is the midpoint of the sudden change in the pH.

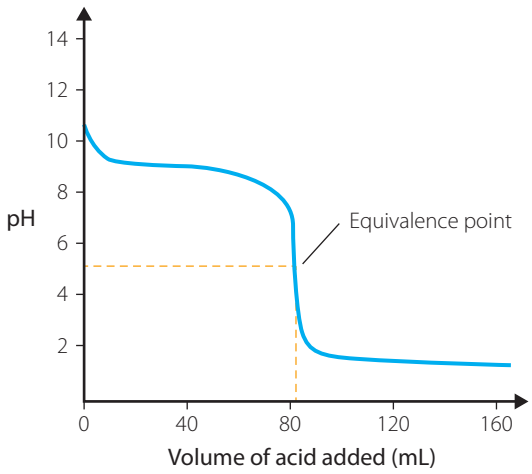
FIGURE 9.3.2 A titration curve for a strong base–weak acid titration



Weak base–strong acid

The graph for the titration of a weak base and a strong acid shows that the pH starts at a high basic value, although it is not as high as for the strong base (Figure 9.3.3). It decreases slightly, and then close to the equivalence point it suddenly decreases, although not as much as for the strong base–strong acid titration. The pH drops from 8–9 to 1–2. When acid is in excess, the pH stays reasonably constant again at a very low pH. The equivalence point is the midpoint of the sudden change in the pH.

FIGURE 9.3.3 A titration curve for a weak base–strong acid titration



Weak base–weak acid

The graph for the titration of a weak base and a weak acid shows that pH starts at a high basic value, although not as high as for the strong base (Figure 9.3.4). It remains fairly constant until close to the equivalence point, when it decreases. This change is much smaller than for the other curves. The pH drops from 8–9 to 4–5. When weak acid is in excess, the pH decreases reasonably constantly at a low pH. Generally, titrations of weak acids and weak bases are not performed directly since the curve does not show a significant change in pH at the equivalence point. It is very difficult to identify the equivalence point.

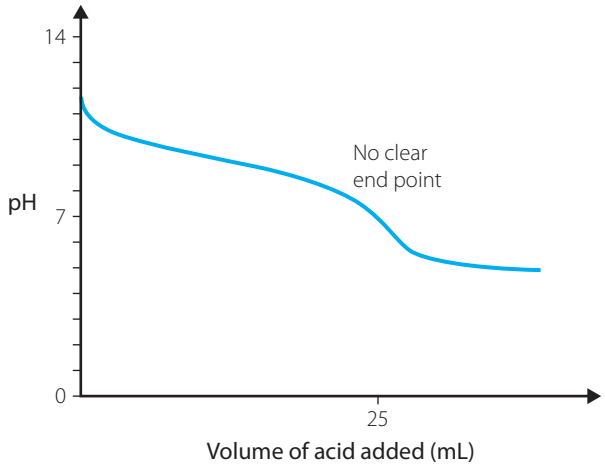


FIGURE 9.3.4
A titration curve for a weak base–weak acid titration

Features of a titration curve

Figure 9.3.5 shows a titration curve for the reaction between sodium hydroxide, in the conical flask, and ethanoic acid, in the burette. The equation for this reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

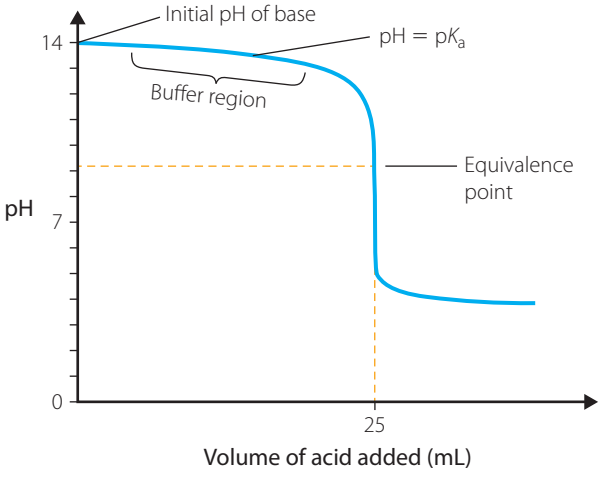


FIGURE 9.3.5
A titration curve for a strong base–weak acid titration

Initially the pH of the solution in the flask is 14, because it only contains sodium hydroxide, a strong base. As ethanoic acid is added, the pH of the solution decreases slowly. This almost horizontal part of the graph is known as the **buffer region**. It can be seen from the equation above that as ethanoic acid is added, its conjugate base, the acetate ion, is produced. This forms a buffer solution of a weak acid and its conjugate base.

buffer region
the part of a titration curve during which the pH changes little as titrant is added; occurs when one of the reagents is a weak acid or a weak base and is the result of a buffer solution being set up

The conjugate base reacts with water to produce $OH^-(aq)$ ions:

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

In this region it is reasonable to assume:

$$[\text{base}] = [\text{salt}]$$

Therefore:

$$pH = pK_a$$

In this situation, the pH is just over 13. The pK_a of sodium hydroxide is 13.8.
Sodium hydroxide is a base; therefore, we can repeat the procedure above with respect to bases:

$$pOH = 14 - pH$$

$$pOH = 14 - 13 = 1$$

The pK_b for sodium hydroxide is 0.2.

SECTION REVIEW 9.3

REMEMBERING

1 Define:

a titration curve

b buffer region.

UNDERSTANDING

2 Sketch a pH curve for a titration between potassium hydroxide and ethanoic acid. The potassium hydroxide is in the burette. On the graph identify the equivalence point and the buffer region. Estimate the value of pK_a for ethanoic acid.

9.4 Mathematical representations

The real-life applications of volumetric analysis with respect to acid–base reactions are extremely important, from quality control of domestic food to maximising efficiency of industrial chemical processes to monitoring the effects of atmospheric pollution.

Volumetric analysis can determine, with precision, the amounts of unknown substances by monitoring acid–base reactions with indicators or pH meters. The following worked examples illustrate how this is done.

WORKED EXAMPLE 9.4.1

The following data was obtained in an experiment to determine the amount of citric acid in freshly squeezed lime juice.

TABLE 9.4.1 Results of lime juice experiment

	BURETTE READING (mL)			
	ROUGH	1	2	3
Initial	0.00	23.05	0.10	22.25
Final	22.50	45.20	22.20	44.45
Titre	22.50	22.15	22.10	22.20
Average			**22.15**	

Mass of 100 mL of freshly squeezed lime juice = 101.48 g
Concentration of sodium hydroxide = 0.984 M
Which indicator would have been used in this titration?
Use the data to determine the percentage, by weight, of citric acid in freshly squeezed lime juice.

ANSWER

1 Decide which indicator to use for the titration:
Citric acid is a weak acid, so it is best to titrate it with a strong base such as sodium hydroxide. Typically, a weak acid–strong base titration has an equivalence point around pH 9. Phenolphthalein indicator has a pK_a value of 9.2. When using phenolphthalein indicator, the best results are achieved when the colour change is from colourless to pink; that is, when the acid and a few drops of the indicator are placed in the conical flask and the base is run in from the burette. The end point can clearly be seen when the faintest permanent pink colour is observed.

2 Write the balanced equation for this reaction:

$$C_6H_8O_7(aq) + 3NaOH(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O(l)$$

3 Calculate the number of moles of sodium hydroxide that have been added from the burette:

$$n = c \times V$$
$$c_{NaOH} = 0.984\,M$$
$$V_{NaOH} = 22.15\,mL \text{ (average from burette)}$$
$$n = c \times V = 0.984 \times \frac{22.15}{1000} = 0.0218 \text{ moles}$$

4 Using the mole ratio from the balanced equation, determine the moles of citric acid in the conical flask:

$$C_6H_8O_7 = 3NaOH$$
$$n(C_6H_8O_7) = \frac{n(NaOH)}{3}$$
$$= \frac{0.0218}{3}$$
$$= 0.0073 \text{ moles}$$

5 Using the molar mass of citric acid, calculate the mass of citric acid in the sample:

$$m = n \times M$$
$$= 0.0073 \times 192$$
$$1.402\,g$$

6 Calculate the percentage by mass of citric acid in the sample:

$$\% = \frac{\text{mass of citric acid in sample}}{\text{total mass of lime juice}} \times 100 = \frac{1.402}{101.48} \times 100 = 1.38\%$$

WORKED EXAMPLE 9.4.2

Balsamic vinegar is a common ingredient in salad dressings, risottos and pasta dishes. It is produced from the fermentation of certain types of grape juice. When determining the ethanoic acid content of balsamic vinegar, a major problem is encountered. It is a very dark, almost black solution. Using an indicator to determine the equivalence point is very difficult.

An experiment is conducted in which 20 mL of balsamic vinegar is transferred to a 250 mL volumetric flask. Distilled water is added up to the 250 mL mark. A 25 mL sample of this solution is transferred to a conical flask using a pipette. A sodium hydroxide solution of concentration 0.118 M is added to the flask from a burette. A pH probe in the solution in the conical flask monitors the pH changes throughout the experiment. A graph is plotted of pH against volume of sodium hydroxide added. Using this information and the titration curve in Figure 9.4.1, calculate the percentage of ethanoic acid in the balsamic vinegar.

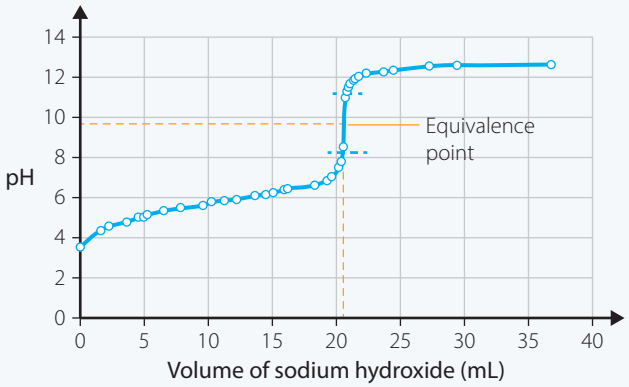


FIGURE 9.4.1 Titration curve for the reaction between balsamic vinegar and sodium hydroxide

ANSWER

1 Write the balanced equation for this reaction:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

2 Determine the equivalence point of the titration using the titration curve.
Using the dotted lines (which show the lower and upper limits of the near vertical part of the graph), measure half of this distance to find the equivalence point. Draw dotted lines from this point to the pH axis and the NaOH volume axis. This gives a volume of 20.6 mL.

3 Calculate the number of moles of sodium hydroxide added from the burette:

$$n = c \times V$$
$$c_{NaOH} = 0.118\ M$$
$$V_{NaOH} = 20.6\ mL \text{ (taken from the graph)}$$
$$n = c \times V = 0.118 \times \frac{20.6}{1000} = 0.00243 \text{ moles}$$

4 Using the mole ratio from the balanced equation, determine the moles of ethanoic acid in 25 mL vinegar solution in the conical flask:

$$CH_3COOH = NaOH$$
$$n(CH_3COOH) = n(NaOH)$$
$$= 0.00243 \text{ moles}$$

5 Determine the number of moles of ethanoic acid in the 250 mL volumetric flask:

$$25\ mL \text{ vinegar solution} = 0.002\,43 \text{ moles}$$
$$\therefore 250\ mL \text{ vinegar solution} = 0.002\,43 \times 10 = 0.0243 \text{ moles}$$

6 Calculate the mass of ethanoic acid in the 250 mL vinegar solution:

$$m = n \times M$$
$$m = 0.0243 \times 60.05 = 1.459\ g$$

7 Calculate the percentage, by mass of the ethanoic acid.
The 1.458 g of ethanoic acid came from the 20 mL sample of balsamic vinegar solution.

$$\therefore \%\text{ ethanoic acid} = \frac{\text{mass of ethanoic acid in sample}}{\text{mass of balsamic vinegar}} \times 100 = \frac{1.459}{20.0} \times 100 = 7.29\%$$

SECTION REVIEW 9.4

UNDERSTANDING

1 The active ingredient in a particular brand of antacid tablet is calcium carbonate, $CaCO_3$. The label says that each tablet contains 0.9 g of active ingredient. In order to confirm this, a back titration is carried out in which a tablet is dissolved in 10.00 mL of 3.0 M hydrochloric acid. If this mixture is titrated with 1.25 M sodium hydroxide, what will the volume of sodium hydroxide added be at the end point?

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** end point
- **b** equivalence point
- **c** titrant
- **d** analyte
- **e** back titration
- **f** titration curve
- **g** buffer region
- **h** primary standard

2 Explain why sulfuric acid, H_2SO_4, should not be used as a primary standard?

CATEGORY QUESTIONS

3 A student was required to prepare 250 mL of a 0.035 M solution of sodium oxalate, $Na_2C_2O_4$, for standardising potassium permanganate solutions.

- **a** What mass of sodium oxalate must be used?
- **b** Describe how the solution would be prepared.

ELABORATION QUESTIONS

4 A student wished to determine the percentage by weight of nitrogen in a sample of garden fertiliser. Initially, a 1.815 g sample of fertiliser was mixed with acid to convert the nitrogen into ammonia, NH_3. This ammonia was dissolved in 100.00 mL of 0.114 M hydrochloric acid.

The mixture was titrated with 0.098 M sodium hydroxide. If the end point occurs at 14.85 mL, calculate the percentage of nitrogen in the fertiliser.

EVIDENCE QUESTIONS

5 A student was asked to determine the concentration of a propanoic acid solution using 20.00 mL of a known concentration of potassium hydroxide solution.

Use the information given in the titration curve below to determine the concentration of the propanoic acid:

$$CH_3CH_2COOH(aq) + KOH(aq) \rightarrow CH_3CH_2COOK(aq) + H_2O(l)$$

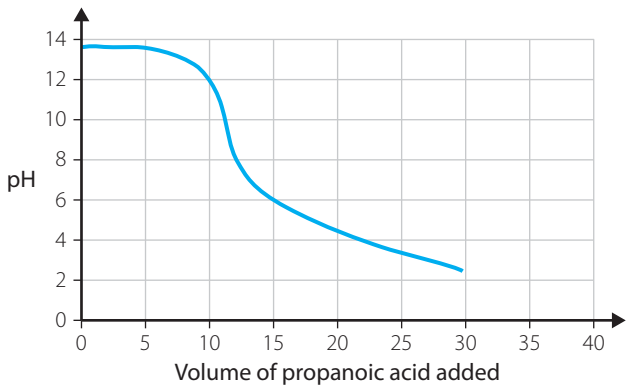


FIGURE 9.5.1 Graph of titration curve

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END-OF-CHAPTER EXAM

End-of-chapter test

1 Which of the following is not a desirable property of a substance that is to be used as a primary standard?

A Is of high purity so that no side reactions occur

B Has a low molar mass to ensure its solubility

C Is stable in the presence of air

D Has no water of hydration

2 Which piece of laboratory equipment is most suitable for transferring an accurately known volume of liquid?

A Pipette

B Burette

C Conical flask

D Measuring cylinder

3 If a 20 mL sample of nitric acid requires 28.95 mL of 0.098 M sodium hydroxide to reach the equivalence point, what is the concentration of the nitric acid?

A 0.049 M

B 0.284 M

C 0.071 M

D 0.142 M

4 Anhydrous sodium carbonate (Na_2CO_3) is dissolved in 50 mL of distilled water. This is transferred to a 250 mL volumetric flask. Distilled water is added until the solution reaches the 250 mL mark. A pipette is used to transfer 20 mL of this solution to another 250 mL flask and made up to the mark with distilled water. If the concentration of this solution was found to be 0.098 M, what mass of sodium carbonate must have been used in the beginning?

A 3.246 g

B 32.46 g

C 87.52 g

D 2.597 g

5 In a titration, what is the general term for the solution of unknown concentration?

6 What is the name of the type of volumetric analysis used when one substance cannot be titrated directly with another?

7 You are given a white, crystalline solid and told that it could be citric acid or tartaric acid. To determine which acid it is, you decide to titrate the solid with sodium hydroxide.

$$H_3C_6H_5O_7(aq) + 3NaOH(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O(l)$$

Citric acid

$$H_2C_4H_4O_6(aq) + 2NaOH(aq) \rightarrow Na_2C_4H_4O_6(aq) + 2H_2O(l)$$

Tartaric acid

A 0.956 g sample of the solid requires 29.10 mL of 0.513 M NaOH for titration to the end point. Identify the unknown acid.

8 To determine the ammonia, NH_3 concentration in a cleaning product, a chemist diluted 20 mL of the product to 500 mL. 25 mL of this solution was titrated with 0.151 M nitric acid. The end point occurred at 26.2 mL. Calculate the concentration of ammonia in the cleaning fluid.

9 Figure 9.5.2 shows a pH curve for the titration of ethanoic acid with sodium hydroxide.

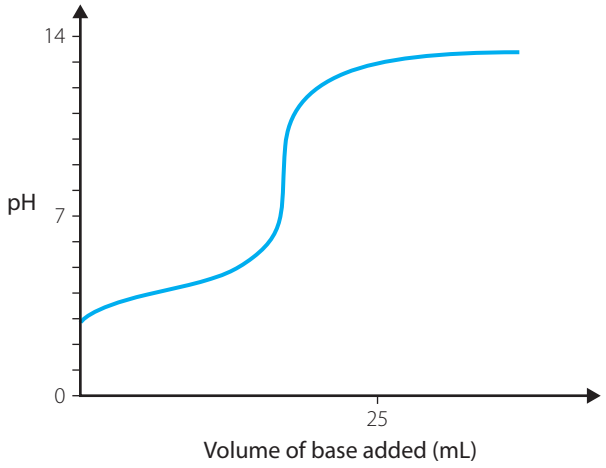

FIGURE 9.5.2 pH curve for the titration of ethanoic acid with sodium hydroxide

a Copy the graph and label the buffer region and the equivalence point.

b With the aid of equations, explain what is meant by 'buffer region'.

c With the aid of equations, explain the value of the pH at the equivalence point.

d What is the significance of the intercept of the graph with the *y*-axis?

e Estimate the value of K_a for ethanoic acid.

10 Using the table below, select suitable indicators for the reactions represented by the titration curves in Figure 9.5.3 (on the next page).

INDICATOR	pK_a	COLOUR CHANGE
Congo red	4.1	blue → yellow/orange
Thymolphthalein	9.9	colourless → blue
Bromocresol green	4.7	yellow → blue
Methyl orange	3.4	red → yellow/orange
Bromothymol blue	7.0	yellow → blue
Phenolphthalein	9.3	colourless → red/violet
Alizarin yellow	11.2	yellow → red
Congo red	4.1	blue → yellow/orange

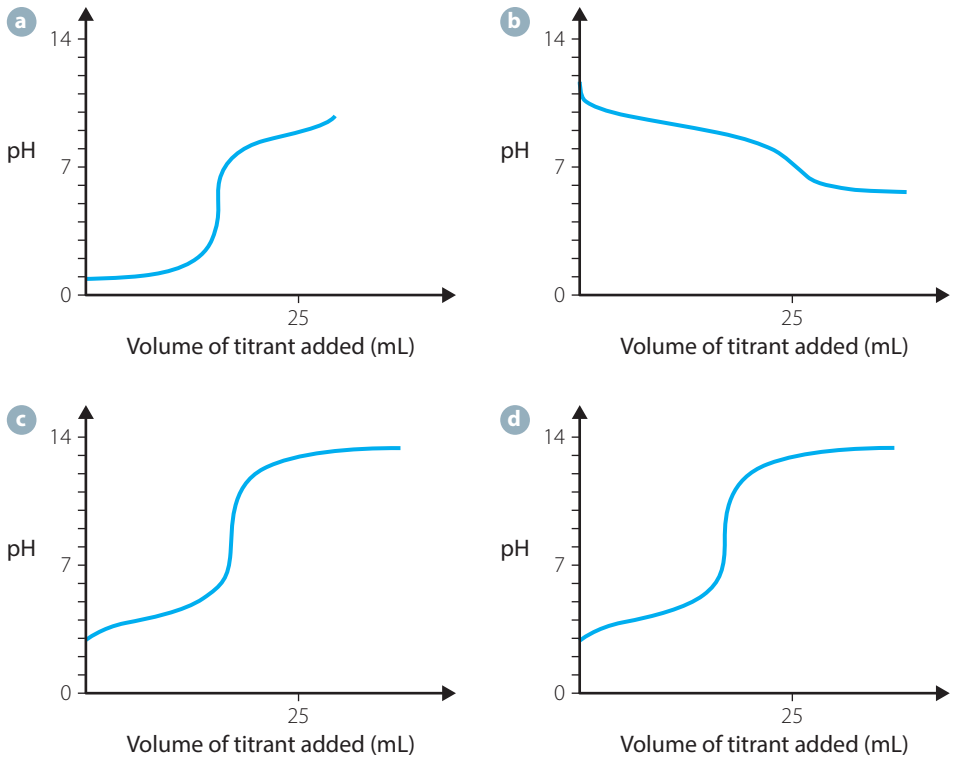

FIGURE 9.5.3 Titration curves

EQUILIBRIUM, ACIDS AND REDOX REACTIONS

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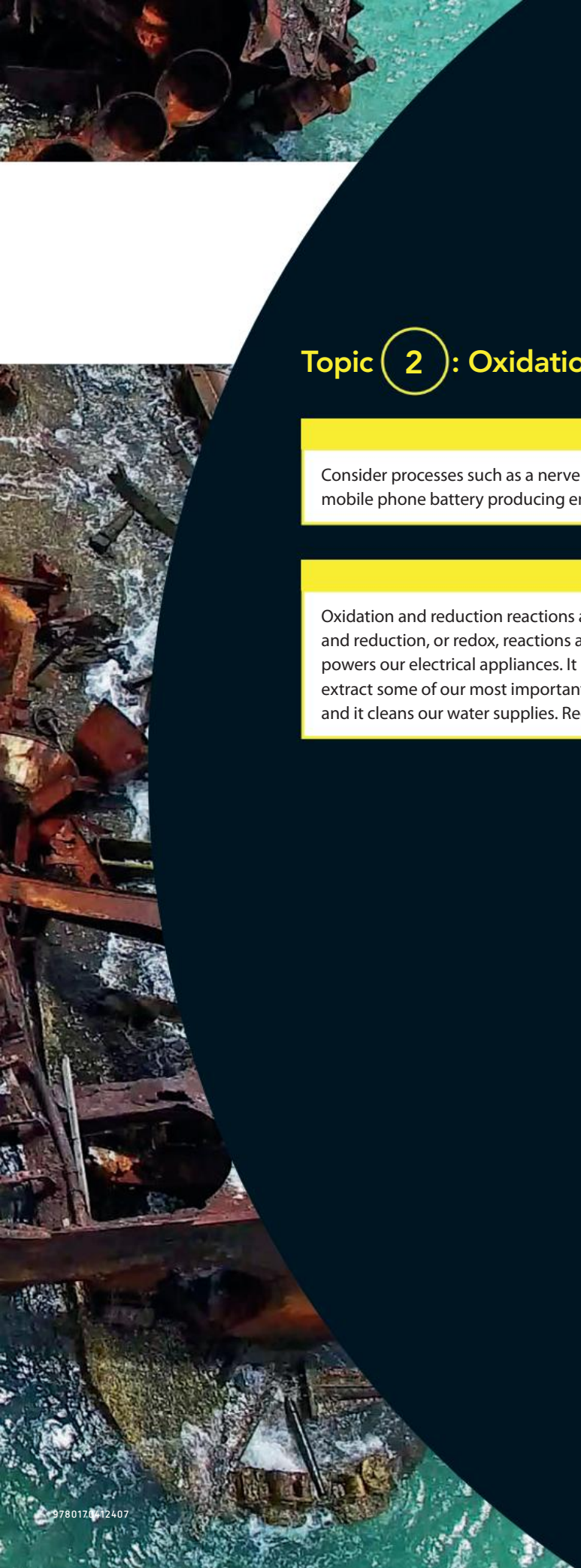

Topic 2: Oxidation and reduction

Consider processes such as a nerve impulse, burning a piece of paper, digesting potato chips and a mobile phone battery producing energy. What might these processes have in common?

Oxidation and reduction reactions are one of the largest groups of chemical reactions. Oxidation and reduction, or redox, reactions are important in many aspects of everyday life. Redox chemistry powers our electrical appliances. It is responsible for the working of our nervous system. It helps extract some of our most important metals. It enables us to extract energy from the food we eat and it cleans our water supplies. Redox chemistry is literally all around and inside us.

SCIENCE AS A HUMAN ENDEAVOUR

Students should be given opportunities to investigate:

- breathalysers and measurement of blood alcohol levels
- fuel cells and their uses
- electrochemistry for clean water.

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10 REDOX REACTIONS

Introduction

Oxidation–reduction reactions, or redox reactions, are one of the largest groups of reactions. They include reactions that power batteries, reactions that extract important metals and reactions that power our cars, aeroplanes and power stations. Redox chemistry is used in our water supplies and swimming pools to neutralise harmful bacteria and algae. The food we eat is oxidised by our bodies to provide the energy we need to live. The detection and analysis of a huge array of useful and harmful chemicals relies on redox chemistry. An understanding of redox principles relating to the corrosion of metals is vital in civil, structural and mechanical engineering.

Stimulus questions

What reactions can be modelled as a redox reaction?

How can a scientist predict if an atom will gain or lose electrons?

How can oxidation be modelled?

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10.1 The range of redox reactions

Chemical reactions can be classified in many different ways.

- Single-displacement reactions
- Double-displacement reactions
- Synthesis reactions
- Decomposition reactions
- Combustion reactions

Some reactions can be classified as, for example, displacement reactions of metals, combustion reactions, corrosion reactions and electrochemical processes.

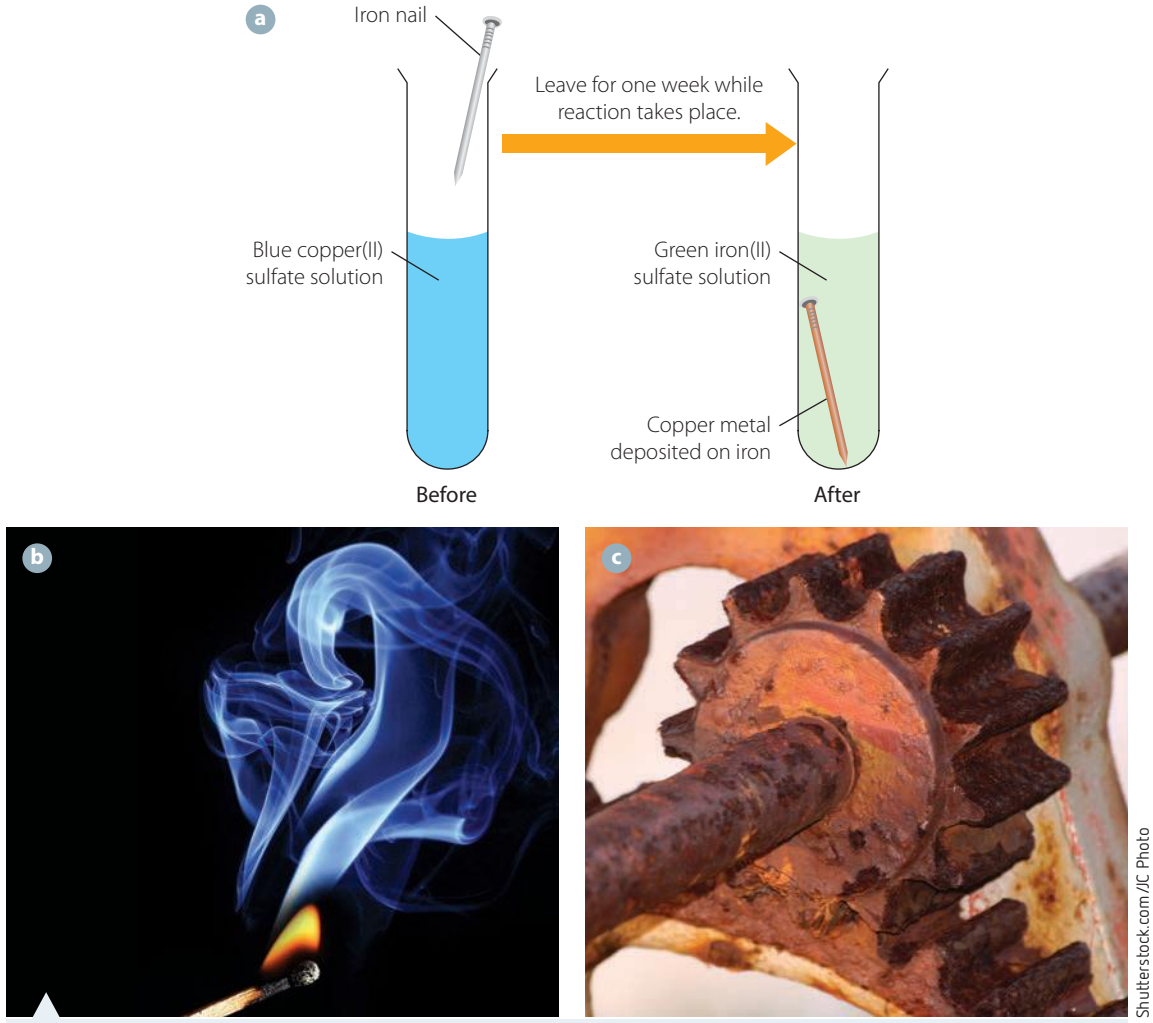

FIGURE 10.1.1 **a** Displacement reaction of metals; **b** Burning: a combustion reaction; **c** Rusting: a corrosion reaction

redox reaction
a reaction that involves the oxidation of one species and the reduction of another species

oxidation
the loss of electrons

reduction
the gain of electrons

Redox reactions are **oxidation** and **reduction** reactions (oxidation–reduction reactions) and involve the transfer of electrons. They form new substances when one species loses electrons and another species gains these electrons. Oxidation involves losing electrons, while reduction involves gaining electrons. One cannot occur without the other. A substance cannot lose electrons unless there is another substance present to accept them.

FIGURE 10.1.2
Unpacking redox

Metal displacement reactions

Metal displacement reactions are examples of redox reactions. A metal displacement reaction occurs when a metal is added to an ionic solution containing the ion of another metal. The anion in this solution is a spectator ion, as it does not take part in the chemical reaction.

For example, if a piece of zinc metal is added to a test tube containing copper sulfate solution, after a while the zinc dissolves, the solution turns from blue to colourless and a red-brown substance is deposited on the bottom of the test tube. This is an example of a metal displacement reaction. The equation for the reaction is given by:

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

KEY FORMULA

The general equation for a metal displacement reaction is written as:

$AB(aq) + C(s) \rightarrow CB(aq) + A(s)$

10.1.1 Oxidation–reduction (redox) reactions
10.1.2 Introduction to redox reactions

The sulfate ion, SO_4^{2-} is the spectator ion in this reaction.

It is useful to track what happens to the metals zinc and copper from their states as reactants to products.

Considering zinc:

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

KEY CONCEPT

- Rule 1: Charge is balanced by adding the appropriate number of electrons to the more positive side of the equation.

Although this is balanced in terms of the zinc atoms, it is not balanced in terms of charge.

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

In this case, the Zn has lost electrons. This is an example of *oxidation*.

Considering copper:

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

Balancing for charge gives:

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

half-equation
when an equation has been split into its two components: the oxidation reaction and the reduction reaction

In this case, the Cu has gained electrons. This is an example of *reduction*.

When these **half-equations** are combined, the net ionic equation for the reaction is produced:

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

MANDATORY PRACTICAL 10.1.1

Redox reactions

You will use combinations of metals and solutions of these metals to rank the metals from most reactive to least reactive; that is, most easily oxidised to least likely to oxidise.

AIM

To rank the metals from most easily oxidised to least likely to be oxidised

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EQUIPMENT

- 100 mL of 1 mol L^{-1} $AgNO_3$
- 100 mL of 1 mol L^{-1} $CuSO_4$
- 100 mL of 1 mol L^{-1} $MgSO_4$
- 100 mL of 1 mol L^{-1} acidified $FeSO_4$
- 100 mL of 1 mol L^{-1} $ZnSO_4$
- 100 mL of 1 mol L^{-1} NaCl
- Five strips of copper metal
- Five strips of magnesium ribbon
- Five ungalvanised iron nails
- Five strips of zinc metal
- 100 mL measuring cylinder
- Four 100 mL beakers
- Waste bottles for heavy metals
- 7 cm × 7 cm piece of sandpaper

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Silver nitrate can stain skin.	Be careful when pouring from the bottle to the beaker. Wipe up drips with paper towelling or a sponge.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Use the sandpaper to clean all of the pieces of metal.
2. Pour 25 mL of 1 mol L^{-1} $AgNO_3$ into four separate beakers.
3. Place one piece of each metal into different beakers.
4. Record your observations.
5. Repeat for all of the other combinations of metals and solutions. You do not need to place metals with their corresponding solution; for example, you do not need to place magnesium into the $MgSO_4$ solution.
6. Record your observations for all combinations.
7. Dispose of copper(II) sulfate and silver nitrate by pouring them into the heavy metals waste bottle. Do not pour them down the drain.

RESULTS

1. Draw a table where the metals are across the top and the solutions are down the side.
2. Record your results in the table, using either words or photos. Remember that no reaction is also a result.

ANALYSIS

1. Identify the combinations of metals and solutions where chemical reactions occurred.
2. Which metal was most reactive?
3. Which metal was least reactive?
4. Explain why $AgNO_3$ and NaCl were included in the experiment. Compare the ability of silver ions and sodium ions to oxidise, with reference to your observations.

DISCUSSION

1 Identify the metal that was most easily oxidised and relate it to its reactivity.

2 Identify the metal that was least readily oxidised and relate it to its reactivity.

WORKED EXAMPLE 10.1.1

If a piece of iron metal is placed into a solution of silver nitrate, eventually the iron is coated with small, needle-like pieces of silver.

1 Write the overall balanced equation for the reaction.

2 Write the half-equations associated with the iron and silver.

3 Identify each half-equation as oxidation or reduction.

4 Write the net ionic equation for the reaction.

ANSWER

1

$$Fe(s) + 2AgNO_3(aq) \rightarrow Fe(NO_3)_2(aq) + 2Ag(s)$$

2 and **3**

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ *oxidation*

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

4 In the oxidation reaction, two electrons are lost by the iron but only one electron is gained by the silver.

In redox reactions the number of electrons transferred *must* be the same. The number of electrons in the reduction half-equation must be multiplied by two.

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

KEY FORMULA

Rule 2: If the number of electrons in a half-equation is multiplied by a number, then *everything* in the half-equation must be multiplied by the same number.

Sodium and potassium metals react violently with water and acids, so they are not used in schools. Both of these metals are normally stored in kerosene (to prevent them reacting with water). They oxidise readily in water; hence, they are more reactive than calcium. Potassium is more reactive than sodium and its reactions are more violent. Potassium metal is banned in many educational jurisdictions across Australia, while sodium metal can be used only in teacher demonstrations.

Combustion

Combustion reactions do not, at first glance, appear to be redox reactions; however, it is possible to see how individual elements are oxidised or reduced in a combustion reaction. Consider the combustion of magnesium; that is, the reaction of magnesium with oxygen:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

Writing the two half-equations gives:

$Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$ *oxidation*

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

Multiplying the magnesium half-equation by 2 and adding the half-equations gives the net ionic equation:

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

This method illustrates that more complex combustion reactions are redox reactions, and this will be described in more detail later in this chapter.

10.1.3 What is combustion?
10.1.4 Is fire a solid, liquid or gas?

Corrosion

In its simplest form, corrosion is the oxidation of a metal in the presence of air to form the metal oxide. The reaction is between the metal and the oxygen in the air. The water vapour also present in air acts as the **electrolyte** for the transfer of the electrons from the metal to the oxygen.

electrolyte
a substance that conducts an electric current

$$\text{Metal} + \text{oxygen} \rightarrow \text{metal oxide}$$

This is a spontaneous chemical reaction. However, it is also a very slow reaction. Corrosion takes time. For example, magnesium reacts with oxygen to form magnesium oxide:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

A strip of magnesium metal that is exposed to the air for a period of time will lose some of its lustre. This is because it has oxidised to form magnesium oxide. This happens to many metals and explains why sandpaper is used to clean metals before their use in experiments: to remove the outer oxide layer and ensure that the metal is taking part in the reaction.

The most common example of corrosion is rust. Rust is hydrated iron(III) oxide, which is produced when iron corrodes. Overall, the simplified reaction is:

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

The chemistry is a little more complicated than this simplified reaction suggests. The half-equations for this reaction are:

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

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

Overall, this reaction becomes:

$$2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 4OH^-(aq) + 2Fe^{2+}(aq)$$

The products of this reaction form an iron(II) hydroxide precipitate, $Fe(OH)_2$, which further oxidises to form the hydrated iron(III) oxide, which we call rust.

$$4Fe(OH)_2(s) + O_2(g) \rightarrow 2(Fe_2O_3.H_2O)(s) + 2H_2O(l)$$

Aluminium is another commonly available metal. It is used for window frames and screen doors. It is also used in aircraft manufacture because it is strong but much lighter than steel. It oxidises to form aluminium oxide, Al_2O_3. Aluminium does not appear to corrode as much as iron. The reason for this is that aluminium is a **passivating metal**. It reacts to form aluminium oxide, but this oxide binds tightly to the surface of the metal to form a layer that is impervious to oxygen and water, which prevents the metal underneath from corroding further.

passivating metal
a metal that can become less reactive because of the addition of a less-reactive surface layer

However, iron does not form an impervious oxide layer. Rust is a red-brown colour and it flakes off the surface, allowing the metal to continue to react with oxygen and form more rust.

10.1.5 Corrosion

Electrochemical processes

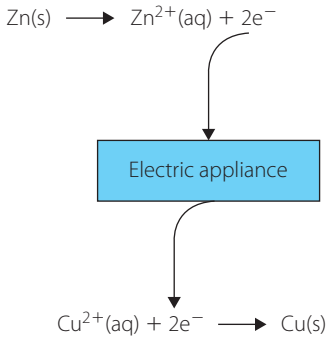
An electrochemical process is one that either causes or is caused by the movement of electric current.

Consider the earlier example of zinc reacting with copper sulfate:

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

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

FIGURE 10.1.3
Harnessing electricity from a spontaneous reaction



The electrons move from the zinc to the copper. If the two half-equations are chemically separated from one another but remain connected by a wire, it is possible to harness the moving electrons and thus provide electricity from a spontaneous chemical reaction.

This is the basis of galvanic cells, or batteries, which will be discussed in more detail in Chapter 12.

If a spontaneous redox reaction has the ability to produce an electric current, then it is also possible that the reverse can occur. That is, an electric current can enable a non-spontaneous reaction to occur, such as the decomposition of sodium chloride (the sodium chloride would have to be in its molten state in order to conduct an electric current):

$$NaCl(l) \rightarrow Na(l) + Cl_2(g)$$

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

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

This would never occur spontaneously, because the Na^+ and Cl^- ions are far too stable, but if an electric current is supplied to sodium chloride in its molten state the half-equations given above would occur. This is the basis of electrolysis, an extremely important industrial process which will be discussed in more detail in Chapter 14.

SECTION REVIEW 10.1

REMEMBERING

1 Define:
- **a** oxidation
- **b** reduction
- **c** half-equation.

UNDERSTANDING

2 Explain why oxidation and reduction must always occur as a pair.

3 Aluminium is a more reactive element than iron. Explain why iron oxidises readily to form rust while aluminium does not corrode as easily.

APPLYING

4 Write the oxidation and reduction half-equations for the following reactions.
- **a** Magnesium metal in an iron(II) solution
- **b** Copper metal in a silver solution

5 Write a balanced equation for the corrosion of zinc.

ANALYSING

6 An activity series for a number of metals is given below:

K > Na > Ca > Mg > Zn > Fe > Cu > Ag

As written, the series shows that potassium is the most reactive metal while silver is the least reactive metal. Use the activity series to justify whether a chemical reaction will occur for the following solutions.

a Zinc metal in a silver solution

b Zinc metal in a sodium solution

c Magnesium metal in a copper(II) solution

d Iron metal in a copper(II) solution

10.2 Predicting loss and gain of electrons

The periodic table can be used to determine whether elements will lose or gain electrons. The most chemically stable elements on the periodic table are the noble gases (helium to radon). Chemical stability relates to the arrangement of electrons in the atom; in particular, the valence, or outer shell of electrons. Metals become chemically stable by losing some or all of their valence electrons to form cations. For example, magnesium has a total of 12 electrons. Its electron configuration is 2, 8, 2. Neon is the nearest noble gas to magnesium on the periodic table, with an electron configuration of 2, 8. To become chemically stable, magnesium will lose two electrons so that it achieves the same stable electron configuration as neon. Hence, the magnesium ion has a 2+ charge since it has 10 electrons but 12 protons. The formula for the magnesium ion is Mg^{2+}.

Non-metals become chemically stable by gaining electrons to form anions. For example, chlorine has 17 electrons. Its electron configuration is 2, 8, 7. Argon is the nearest noble gas to chlorine on the periodic table, with an electron configuration of 2, 8, 8. To become chemically stable, chlorine gains one electron so that it achieves the same stable electron configuration as argon. Hence, the chloride ion has a 1– charge since it has 18 electrons but 17 protons. The formula for the chloride ion is Cl^-.

These general rules explain why metals tend to be oxidised to form cations while non-metals tend to be reduced to form anions. However, they do not explain why some metals are more reactive than others and can displace them from solution.

SYLLABUS LINK

The arrangement of electrons in atoms was discussed in *Nelson QScience Chemistry Units 1 & 2* Chapter 1 and the formation of ions in *Nelson QScience Chemistry Units 1 & 2* Chapter 2.

PRACTICAL ACTIVITY 10.2.1

The periodic table and reactivity

AIM

To identify simple trends between position on the periodic table and reactivity

EQUIPMENT

- Blank periodic table as shown in Figure 10.2.1
- Results of Practical activity 10.1.1.

»

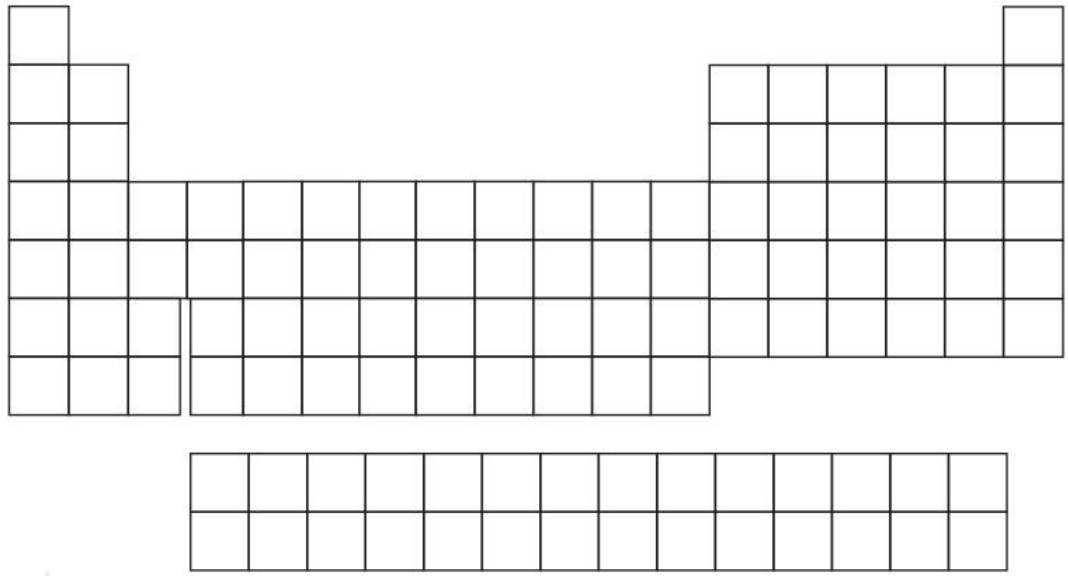


FIGURE 10.2.1 A blank periodic table

PROCEDURE

Copy and complete the periodic table shown in Figure 10.2.1 by adding the following elements.

1. All noble gases
2. Fluorine, chlorine and bromine
3. Calcium, copper, iron, magnesium, potassium, silver, sodium and zinc.

ANALYSIS

1. Compare the reactivity of the metals in groups 1 and 2 as you move down the group.
2. Compare the reactivity of the transition metals in period 4 with the period 4 metals in groups 1 and 2.

Chemical reactions involve rearranging electrons so that each chemical species present achieves an electron configuration similar to its nearest noble gas; therefore, there must be a link between the ability of a chemical species to attract electrons and its reactivity. The model of the atom indicates:

- there is a positively charged nucleus containing protons and neutrons
- electrons are arranged in distinct shells, or energy levels, around the nucleus
- the innermost shell can only contain two electrons since there is a balance between the force of attraction between the nucleus and the electrons and the force of repulsion between the electrons
- the number of electrons in a shell increases as the distance of the shell from the nucleus increases
- the valence electrons are those involved in chemical reactions.

Three factors to consider are the:

1. number of protons in the nucleus: the greater the number of protons, the greater the force of attraction between the nucleus and the valence electrons
2. distance of the valence electrons from the nucleus: the greater the distance of the valence electrons from the nucleus, the smaller the force of attraction between the nucleus and the valence electrons

3 number of shells between the valence shell and the nucleus that are shielding the valence electrons from the nucleus: the greater the number of shells of electrons between the valence electrons and the nucleus, the smaller the force of attraction between the nucleus and the valence electrons.

Ionisation energy

Ionisation energy is the energy required to remove one electron from a gaseous species. The first ionisation energy is the energy required to remove one electron from a gaseous atom to form a gaseous ion. It can be written as:

$$E(g) \rightarrow E^{+}(g) + e^{-}$$

The second ionisation energy is the energy needed to remove one more electron from the ion:

$$E^{+}(g) \rightarrow E^{2+}(g) + e^{-}$$

ionisation energy the energy required to remove one electron from an atom or ion of an element in a gaseous state

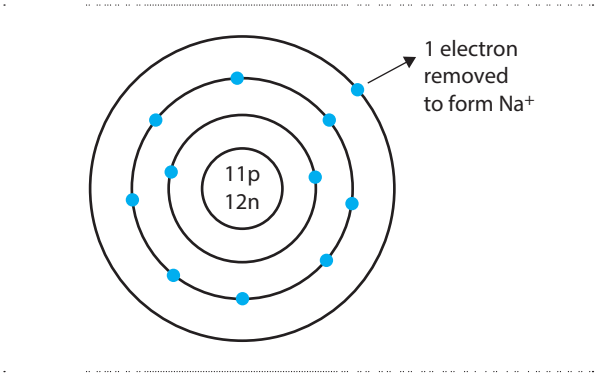


FIGURE 10.2.2 Sodium atom ionisation removes the electron in the outer shell

KEY FORMULA

Ionisation energy is the energy required to remove one electron from a gaseous species.

An element has as many ionisation energies as it has electrons. Sodium has 11 electrons, so it has 11 ionisation energies. Chlorine has 17 electrons, so it has 17 ionisation energies.

As more electrons are removed, the ratio of protons to electrons changes and a greater force of attraction occurs between the nucleus and the remaining electrons. Therefore, the energy to remove each successive electron increases. As more electrons are removed, electrons from shells closer to the nucleus are removed, so it requires more energy to overcome the force of attraction between the nucleus and the valence electrons. Table 10.2.1 shows the first four ionisation energies for sodium, magnesium and aluminium.

TABLE 10.2.1 Ionisation energies required to remove the first four electrons in Na, Mg, Al.

IONISATION ENERGY ($kJ\ mol^{-1}$)	SODIUM	MAGNESIUM	ALUMINIUM
first	486	738	576
second	4562	1451	1817
third	6910	7733	2745
fourth	9543	10 543	11 577

PRACTICAL ACTIVITY 10.2.2

Ionisation energy and valency

AIM

To identify the relationship between ionisation energy and valence

PROCEDURE

1. Draw a diagram to show the structure of each of the following. Clearly indicate the number of protons in the nucleus and the arrangement of electrons in each shell.
   - **a** Sodium atom
   - **b** Sodium ion with one electron removed
   - **c** Sodium ion with two electrons removed
   - **d** Sodium ion with three electrons removed
2. Draw a diagram to show the structure of each of the following. Clearly indicate the number of protons in the nucleus and the arrangement of electrons in each shell.
   - **a** Magnesium atom
   - **b** Magnesium ion with one electron removed
   - **c** Magnesium ion with two electrons removed
   - **d** Magnesium ion with three electrons removed
3. Draw a diagram to show the structure of each of the following. Clearly indicate the number of protons in the nucleus and the arrangement of electrons in each shell.
   - **a** Aluminium atom
   - **b** Aluminium ion with one electron removed
   - **c** Aluminium ion with two electrons removed
   - **d** Aluminium ion with three electrons removed
4. Refer to Table 10.2.1 to answer the following questions.
   - **a** Why does sodium have the lowest first ionisation energy?
   - **b** Why does sodium have a large second ionisation energy?
   - **c** Why is there a large increase between the second and third ionisation energies for magnesium?
   - **d** Why does aluminium have the lowest third ionisation energy?
   - **e** Why is there a large increase between the third and fourth ionisation energies for aluminium?

ANALYSIS AND DISCUSSION

1. Refer to Table 10.2.1 and the structure of the atom to justify the following questions.
   - **a** Why does sodium have a 1+ valence?
   - **b** Why does magnesium have a 2+ valence?
   - **c** Why does aluminium have a 3+ valence?

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PRACTICAL ACTIVITY 10.2.3

Trends in ionisation energy

AIM

To describe the trends in ionisation energies both across a period and down a group

EQUIPMENT

- Graph paper or spreadsheet program such as Microsoft Excel or Apple Numbers
- First ionisation energies for elements in period 3 (Na to Ar)
- First ionisation energies for elements in group 1 (Li to Cs)
- First ionisation energies for elements in group 17 (F to At)

PROCEDURE

1. Graph the data of first ionisation energy versus atomic number for the elements in period 3.
2. Graph the data of first ionisation energy versus atomic number for the elements in group 1.
3. Graph the data of first ionisation energy versus atomic number for the elements in group 17.
4. Compare the first ionisation energies for elements in groups 1 and 17 in the corresponding period of the periodic table.
5. Identify which of the following factors has the greatest impact on the difference in the ionisation energy as you move from left to right across a period: the number of protons, distance of valence electrons from the nucleus or the number of shells between the valence shell and the nucleus.
6. Identify which of the following factors has the greatest impact on the difference in the ionisation energy as you move down a group: number of protons, the distance of valence electrons from the nucleus or the number of shells between the valence shell and the nucleus.

ANALYSIS AND DISCUSSION

1. Use your period 3 graph to describe the general trend for ionisation energies across a period.
2. Use your data for groups 1 and 17 to describe the general trend for ionisation energies down a group.
3. Justify the trend for first ionisation energy across a period.
4. Justify the trend for first ionisation energy down a group.
5. Explain the trend for first ionisation energies for the groups 1 and 17 elements in the corresponding period of the periodic table.

The positions of the elements on the periodic table and the trends in ionisation energy help to explain the activity series of metals. The positions and ionisation energy trends explain why calcium is more reactive than magnesium and why calcium is more reactive than iron. They also explain why iron is more reactive than copper. However, they do not explain why zinc is more reactive than copper.

K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > (H) > Cu > Ag > Pt > Au

FIGURE 10.2.3 Activity series of metals

So far in this chapter, we have analysed trend data. We've looked at the trends for the reactivity of metals. However, there are slight differences when individual data points are considered. Both zinc and copper form 2+ ions. Zinc's second ionisation energy is lower than copper's. Hence, Zn^{2+} forms more readily than Cu^{2+}. Many factors must be considered to determine the reactivity of an element and it is important we don't oversimplify the chemistry involved.

SECTION REVIEW 10.2

REMEMBERING

1 Identify three factors to consider when assessing the stability of an atom.
2 Define ionisation energy.

UNDERSTANDING

3 Write the electron configuration for the following:
   a oxygen atom
   b oxide ion.
4 Explain why:
   a strontium forms a 2+ ion
   b aluminium forms a 3+ ion.
5 How many ionisation energies would bromine have? Justify your answer.

APPLYING

6 Justify the formula for the phosphide ion.
7 Justify why fluorine has a larger first ionisation energy than bromine.

ANALYSING

8 Justify whether there is a large increase in ionisation energy between the first and second ionisation energies for calcium.
9 Justify whether sulfur or magnesium would have the larger first ionisation energy.

10.3 Identification in redox reactions

Redox terminology

Redox reactions have been studied for centuries, long before the actual processes involved were completely understood. It is difficult now to think of redox reactions without understanding the role of electrons. The electron was not discovered until 1897 by J. J. Thomson, many decades after important conclusions had been made about redox reactions.

Consequently, the study of redox chemistry today is beset by many archaic ideas, definitions and terminology which must be kept in mind when studying and describing the chemical reactions.

Consider the reaction between zinc metal and copper sulfate solution:

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

As discussed at the beginning of this chapter, we can write half-equations that clearly show which substance is being oxidised and which substance is being reduced:

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

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \textit{reduction}$$

oxidant or **oxidising agent** a chemical species that causes another species to be oxidised

In this reaction the Zn(s) has been *oxidised* by the $Cu^{2+}(aq)$. The $Cu^{2+}(aq)$ is the **oxidising agent** or **oxidant**.

In turn, the $Cu^{2+}(aq)$ ions have been *reduced* by the Zn(s). The Zn(s) is the **reducing agent** or **reductant**.

reductant or **reducing agent**
a chemical species that causes another to be reduced

SECTION REVIEW 10.3

APPLYING

1 Arrange the following metals in order of decreasing reducing strength: Fe, Ca, Ag, Cu, Pb, Zn, Ba, Au, Sn, Pt and Al.

REFLECTING

2 Research definitions of oxidation and reduction and use your research to explain how the terms originated.

10.4 Oxidation

As has been stated earlier in this chapter, oxidation is the loss of electrons and reduction is the gain of electrons. The mnemonic in Figure 10.4.1 may help you to remember.

FIGURE 10.4.1 Mnemonic for redox reactions

Although some of the examples shown previously have been quite straightforward, it is possible to deal with more complex reactions by keeping track of the number of electrons lost or gained.

WORKED EXAMPLE 10.4.1

Magnesium metal reacts with chlorine gas to give magnesium chloride. Write the oxidation and reduction half-equations for this reaction and a net ionic equation.

ANSWER

1 Magnesium reacts to give the Mg^{2+} ion:

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

2 Rule 1 is used. Electrons are added to the more positive side of the equation to balance for charge:

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

The magnesium metal has lost electrons. This is the *oxidation* half-equation.

3 Chlorine reacts to give the chloride ion:

$$Cl_2(g) \rightarrow 2Cl^-(s)$$

4 Rule 1 is used again. Electrons are added to the more positive side of the equation to balance for charge:

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

The chlorine gas has gained electrons. This is the *reduction* half-equation.

5 The two half-equations are added together to give the net ionic equation. Both half-equations involve the movement of two electrons so there is no need for any multiplication of equations. The two electrons in each half-equation cancel to give:

$$Mg(s) + Cl_2(g) \rightarrow Mg^{2+}(s) + 2Cl^-(s)$$

WORKED EXAMPLE 10.4.2

Aluminium metal reacts with oxygen to give aluminium oxide. Write the oxidation and reduction half-equations for this reaction and a net ionic equation.

ANSWER

1 Aluminium reacts to give the Al^{3+} ion:

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

2 Rule 1 is used. Electrons are added to the more positive side of the equation to balance for charge:

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

3 Oxygen reacts to give the oxide ion:

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

4 Rule 1 is used. Electrons are added to the more positive side of the equation to balance for charge:

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

5 Before the half-equations are added together the electrons in each half-equation must be the same. To make the electrons equal, the $3e^-$ in the aluminium half-equation must be multiplied by 4 and the $4e^-$ in the oxygen half-equation must be multiplied by 3.

Rule 2 is used. The number of electrons in a half-equation is multiplied by a number then *everything* in the half-equation must be multiplied by the same number:

$$4Al(s) \rightarrow 4Al^{3+}(s) + 12e^-$$
$$3O_2(g) + 12e^- \rightarrow 6O^{2-}(s)$$

6 Cancelling the $12e^-$ on each half-equations and adding them together gives:

$$4Al(s) + 3O_2(g) \rightarrow 4Al^{3+}(s) + 6O^{2-}(s)$$

7 Verify this by writing an overall balanced equation.

When more complex ions are involved, things become a little more complicated. For example, in order to write the half-equation for the reduction of the permanganate ion, MnO_4, in acidic solution, a set of rules needs to be applied.

WORKED EXAMPLE 10.4.3

When more complex ions are involved, the reactions also become more complicated.

A Write the half-equation for the reduction of permanganate ion, MnO_4^-, in acidic solution.

ANSWER

1 Rule 3. Write the partial or skeleton half-equation:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

2 Rule 4. Balance for elements other than O and H: Not necessary in this case.

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

3 Rule 5. Balance for O by adding the appropriate number of H_2O molecules to the opposite side:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + \mathbf{4H_2O(l)}$$

4 Rule 6. Balance for H by adding the appropriate number of H^+ ions to the opposite side:

$$\mathbf{8H^+(aq)} + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

5 Rule 1. Add electrons to the more positive side of the equation to balance for charge:

$$8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$\mathbf{7+\ charge} \qquad\qquad \mathbf{2+\ charge}$$
$$\mathbf{5e^-} + 8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

6 The half-equation for the reduction of permanganate in acidic solution is:

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

B Write the half-equation for the reduction of dichromate, $Cr_2O_7^{2-}$, to Cr^{3+} in acidic solution.

ANSWER

1 Apply Rule 3:

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

2 Apply Rule 4:

$$Cr_2O_7^{2-} \rightarrow \mathbf{2}Cr^{3+}(aq)$$

3 Apply Rule 5:

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

4 Rule 6:

$$\mathbf{14H^+(aq)} + Cr_2O_7^{2-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

5 Rule 1:

$$14H^+(aq) + Cr_2O_7^{2-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
$$\mathbf{+12\ charge} \qquad\qquad \mathbf{+6\ charge}$$
$$\mathbf{6e^-} + 14H^+(aq) + Cr_2O_7^{2-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

6 The half-equation for the reduction of dichromate is:

$$14H^+6e^-(aq) + Cr_2O_7^{2-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Redox reactions in acidic solution

The rules followed for writing half-equations in acidic solution can be applied when determining the full equations for redox reactions.

For example, an Fe^{2+} solution is oxidised by permanganate ions to Fe^{3+} in acidic solution. The equation for this redox reaction can be determined using the rules given previously.

WORKED EXAMPLE 10.4.4

Write the equation for the redox reaction between $Fe^{2+}(aq)$ and $MnO_4^-(aq)$ in acidic solution.

ANSWER

1 Rule 3:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

2 Rule 4:

(no change)

3 Rule 5:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

4 Rule 6:

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

5 Rule 1:

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

6 Rule 2:

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

SECTION REVIEW 10.4

UNDERSTANDING

1 Write oxidation and reduction half-equations and the net ionic equations for the following reactions.

- **a** Reaction between magnesium and bromine to give magnesium bromide
- **b** Reaction between sodium and oxygen to give sodium oxide
- **c** Reaction between aluminium and nitrogen to give aluminium nitride

APPLYING

2 Write balanced half-equations for the following processes. State whether each one is oxidation or reduction.

- **a** $NO_2(g) \rightarrow NO_3^-(aq)$
- **b** $S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
- **c** $HOCl(aq) \rightarrow Cl_2(g)$
- **d** $C_2O_4^{2-}(aq) \rightarrow CO_2(g)$

3 Write balanced equations for the following reactions given their skeleton half-equations.

- **a** Reaction between dichromate, $Cr_2O_7^{2-}(aq)$, and $Sn^{2+}(aq)$

  $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

  $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq)$
- **b** Reaction between oxalate, $C_2O_4^{2-}(aq)$, and permanganate, $MnO_4^-(aq)$

  $C_2O_4^{2-}(aq) \rightarrow CO_2(g)$

  $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

c Reaction between $SO_2(g)$ and dichromate

$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

$SO_2(g) \rightarrow SO_4^{2-}(aq)$

d Reaction between nitrate, $NO_3^-(aq)$, and nickel

$NO_3^-(aq) \rightarrow NO_2(g)$

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

e Reaction of calcium with phosphorous to give calcium phosphide

f Reaction of potassium metal with fluorine to produce potassium fluoride

g Oxidation of sulfur dioxide in acidic solution to form the sulfate ion

h Chlorate, ClO_3^-, being reduced in acidic solutions to form chlorine dioxide, ClO_2

10.5 Deducing the oxidation state

KEY FORMULA

The oxidation state is an indication of the number of electrons an atom would gain or lose to get to its present state. It assumes that each species is completely ionic.

In the examples examined so far in this chapter, it is relatively easy to determine which species is being oxidised and which is being reduced. However, sometimes it is difficult to determine whether an oxidation–reduction reaction is occurring or not. To assist with this, scientists have developed oxidation states, sometimes referred to as oxidation numbers.

The oxidation state always indicates whether it has a positive or negative charge. It is straightforward to determine the oxidation states of simple ionic compounds such as sodium sulfide, Na_2S. The sodium ion is written as Na^+. It has a +1 oxidation state. The sulfide ion is written as S^{2-}. It has a −2 oxidation state.

However, in covalent molecules, electrons are shared by different species. It is more difficult to determine the oxidation states, and hence to determine if a redox reaction has occurred or not.

The following rules can be used when determining the oxidation states of various species.

1. The oxidation state of any element is zero.
2. The oxidation state of a monatomic ion is the same as the charge on that ion.
3. The oxidation state of hydrogen in compounds is always +1, except when forming metal hydrides, when it is −1.
4. The oxidation state of oxygen in any compound is always −2, except when forming peroxides, where it is −1, and in F_2O, where it is +2.
5. In a neutral compound, the sum of the oxidation states must always equal zero.
6. In ions, the sum of the oxidation states must always equal the charge on the ion.
7. The most electronegative species in a compound is assigned the negative oxidation state; the less electronegative species is assigned the positive oxidation state.

WORKED EXAMPLE 10.5.1

A Determine the oxidation state of the various species in methane, CH_4.

ANSWER

1. Rule 3 says that H must have an oxidation state of +1. Therefore, since there are 4 hydrogens, there is a total oxidation state of +4 due to the hydrogens.
2. Rule 5 says that the sum of the oxidation states on the neutral compound must equal zero. Therefore, the oxidation state of carbon must be −4.

B Determine the oxidation state of the various species in the phosphate ion, PO_4^{3-}.

ANSWER

1. Rule 4 says that oxygen has an oxidation state of –2. Since there are 4 oxygens, the total oxidation state is –8 due to the oxygens.
2. Rule 6 says that in ions, the sum of the oxidation states must equal the charge on the ion. Hence, the sum of the oxidation states for the phosphate ion, PO_4^{3-}, must equal –3. Therefore, the oxidation state of the phosphorus must be +5.

An understanding of how oxidation states are assigned can be of great assistance when recognising redox equations.

WORKED EXAMPLE 10.5.2

Use oxidation states to decide whether or not the following are redox reactions.

A $MgO(s) + HCl(aq) \rightarrow MgCl_2(s) + H_2O(l)$

ANSWER

1. Oxidation state of Mg in MgO = +2
2. Oxidation state of Mg in $MgCl_2$ = +2

   Therefore, there is no change for magnesium.
3. Oxidation state of Cl in HCl = –1
4. Oxidation state of Cl in $MgCl_2$ = –1

   Therefore, there is no change for chlorine.
5. Hydrogen and oxygen remain unchanged. This is *not* a redox reaction.

B $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow 2NaNO_3(aq) + PbSO_4(s)$

ANSWER

1. Pb in $Pb(NO_3)_2$ = +2
2. Pb in $PbSO_4$ = +2

   There is no change in lead.
3. Na in Na_2SO_4 = +1
4. Na in $NaNO_3$ = +1

   Therefore, there is no change in sodium.
5. Lead and sodium remain unchanged. This is *not* a redox reaction.

Oxidation states of transition metals

Main group metals such as sodium, magnesium and aluminium have oxidation states that are predictable. They correspond to the group in the periodic table to which they belong. Transition metals, on the other hand, have varying oxidation states. Iron can have oxidation states of +2 and +3, chromium can have +2, +3 and +6. Manganese can have +2, +3, +4 and +6.

It is meaningless, therefore, to refer to iron oxide or tin chloride. It is necessary to specify the oxidation state of the transition metal in the compound. This is done using roman numerals.

For example, FeO is called iron(II) oxide and Fe_2O_3 is called iron(III) oxide.

Manganese(IV) oxide has the formula MnO_2.

SECTION REVIEW 10.5

REMEMBERING

1 Define:
- **a** oxidation state
- **b** oxidation number.

UNDERSTANDING

2 Use the combustion of ethene to explain why a combustion reaction is an example of a redox reaction.

APPLYING

3 Identify the oxidation state of the underlined species.
- **a** $\underline{I}O_3^-$
- **b** $\underline{C}_2H_2$
- **c** $\underline{Cl}O_3^-$
- **d** $\underline{Cr}O_4^{2-}$
- **e** $H_3\underline{As}O_4$

APPLYING

4 Determine the oxidation state of chromium in the dichromate ion, $Cr_2O_7^{2-}$.

5 Determine the oxidation state of nitrogen in dinitrogen tetroxide, N_2O_4.

6 Determine the oxidation state of oxygen in hydrogen peroxide, H_2O_2.

7 Determine the oxidation state of hydrogen in aluminium hydride, AlH_3.

ANALYSING

8 Write a balanced equation for the following redox reactions.
- **a** The reaction between permanganate and chloride ions:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$
$$Cl^-(aq) \rightarrow Cl_2(g)$$

- **b** The reaction between dichromate and sulfite ions:

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$
$$SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$$

10.6 Using representations

Redox reactions comprise one of the largest groups of reactions and encompass some of the most important reactions we know, from the industrial production of vital chemicals to the production of energy in our bodies.

Accurate communication of redox processes and ideas is of the utmost importance and requires unambiguous representations. As shown in this chapter, these representations include:

- half-equations
- oxidation states
- balanced redox equations.

These representations can be used to solve problems and make predictions about reactions.

WORKED EXAMPLE 10.6.1

Explain why the reaction for cellular respiration is considered to be a redox reaction.

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

ANSWER

1 Rule 7: When an element is bonded to an element of its own kind, its oxidation state is 0. For carbon:

$$C \text{ in } C_6H_{12}O_6 = 0$$
$$C \text{ in } CO_2 = +4$$

This is an increase is oxidation state. Therefore, this is oxidation.

2 For oxygen:

$$O \text{ in } O_2 = 0$$
$$O \text{ in } CO_2 = -2$$

This is a decrease in oxidation state. Therefore, this is reduction.

3 Oxidation and reduction have taken place. This is a redox reaction.

KEY FORMULA

Oxidation is an *increase* in oxidation state.

Reduction is a *decrease* in oxidation state.

Worked example 10.6.1 has given some further useful definitions for oxidation and reduction.

WORKED EXAMPLE 10.6.2

With the aid of half-equations, explain why the corrosion of an iron object will not occur if the object is submerged in deep water.

ANSWER

1 The half-equations are:

$$4Fe^{2+}(aq) \rightarrow 4Fe^{3+}(aq) + 4e^-$$
$$H_2O(l) + O_2(aq) + 4e^- \rightarrow 4OH^-(aq)$$

2 In deep water, the pressure is such that any dissolved oxygen is forced out of solution, leaving a very low oxygen concentration.

3 Without oxygen, there will be very little corrosion, since it is required for the reduction part of the redox reaction to occur.

WORKED EXAMPLE 10.6.3

With reference to the activity series shown in Figure 10.2.3, show how zinc can be used to protect iron from corrosion.

ANSWER

1 If the zinc is attached to iron and the pair are put into water, a situation arises in which the two metals are competing to react with oxygen and water:

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

2 From the activity series, it can be seen that zinc is more reactive than iron. Therefore, the zinc will react with oxygen and water in preference to iron. As long as zinc is attached to the iron, the iron will remain free of corrosion.

SECTION REVIEW 10.6

APPLYING

1 With the aid of half-equations, show why the combustion of methane, CH_4, is a redox reaction.

2 With the aid of half-equations, explain why the decomposition of potassium chlorate is a redox reaction. The overall balanced equation is:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

3 With the aid of half-equations, explain whether or not the decomposition of calcium carbonate is a redox reaction. The overall balanced equation is:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

ANALYSING

4 Table 10.6.1 contains the first ionisation energy of five consecutive elements. Use this table to answer the questions below.

TABLE 10.6.1 First ionisation energy of five elements

ELEMENT	IONISATION ENERGY ($kJ\,mol^{-1}$)
R	1006
S	1257
T	1527
U	425
V	596

a Identify an element that would form an ionic compound with Br^-.

b Which element would be in the same group as oxygen?

c Which element is an inert gas?

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Identify whether the following statements are true or false. Correct any false statements and rewrite them to make them true.

- **a** Oxidation occurs when a species gains electrons.
- **b** A metal reacting with an acid is an example of a redox reaction.
- **c** Magnesium is more reactive than copper and reduces preferentially in the presence of copper.
- **d** A reducing agent gains electrons.
- **e** The first ionisation energy is the energy required to remove one electron from an element in its gaseous state.
- **f** A passivating metal forms an impervious oxide layer when it reacts with oxygen and this prevents further oxidation of the metal.

CATEGORY QUESTIONS

2 Explain why oxidation reactions can only occur when a reduction reaction occurs simultaneously on another species.

3 Explain why sodium is less reactive than potassium.

4 Explain why fluorine is the most reactive non-metal on the periodic table.

5 Explain why calcium's third ionisation energy is much greater than its second.

6 Justify why chlorine is more likely to be reduced than magnesium.

7 For the equations below, identify whether the underlined species is undergoing oxidation or reduction.

- **a** $Zn(s) + 2\underline{Fe}^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
- **b** $\underline{Cu}(s) + 2NO_3^-(aq) + 4H_3O^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 6H_2O(l)$
- **c** $4\underline{Mn}O_4^-(aq) + 12H_3O^+(aq) \rightarrow 4Mn^{2+}(aq) + 5O_2(g) + 18H_2O(l)$
- **d** $Mg(s) + \underline{Cl}_2(g) \rightarrow MgCl_2(aq)$
- **e** $Fe_2O_3(s) + 2\underline{Al}(s) \rightarrow Al_2O_3(s) + 2Fe(l)$
- **f** $2\underline{H}_2O(l) \rightarrow 2H_2(g) + O_2(g)$

8 Determine the oxidation state of the underlined species.

- **a** $\underline{S}O_4^{2-}(aq)$
- **b** $H\underline{Cl}(aq)$
- **c** $\underline{N}H_4^+(aq)$
- **d** $\underline{V}O^{2+}(aq)$
- **e** $Li\underline{Co}O_2(aq)$

ELABORATION QUESTIONS

9 Determine whether the following reactions are oxidation–reduction reactions. For any redox reaction, identify the species being oxidised and the species being reduced.

- **a** $2Al(s) + 3FeCl_2(aq) \rightarrow 2AlCl_3(aq) + 3Fe(s)$
- **b** $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
- **c** $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
- **d** $2Ni(OH)_3(aq) + Cd(s) \rightarrow 2Ni(OH)_2(aq) + Cd(OH)_2(aq)$
- **e** $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow 2KNO_3(aq) + PbI_2(s)$

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EVIDENCE QUESTIONS

10 The following partial periodic table shows that the elements have been replaced by their respective first ionisation energies. Use this data to indicate how the reducing strength of elements changes across the periodic table and down groups in the periodic table.

Justify your reasoning with reference to specific elements.

1312																	2372
526	905											810	1090	1410	1320	1690	2090
496	737											578	789	1012	1000	1251	1521
419	590															1140	1351
403	549															1008	1170
376	503																1037

END-OF-CHAPTER EXAM

End-of-chapter test

1 In a metal displacement reaction:

A the metal is oxidised.

B the metal ion loses electrons.

C the metal gains electrons.

D the metal ion is oxidised.

2 During a redox reaction:

A the oxidation state becomes more positive for the species being reduced.

B the oxidation state increases for the species being oxidised.

C the oxidation state becomes more negative for the species being reduced.

D there is no change in oxidation state for the species being reduced.

3 Using the reactivity series below, which statement is correct?

$$K > Na > Ca > Mg > Zn > Fe > Cu > Ag$$

A Iron will react in a solution of magnesium nitrate.

B Magnesium is more likely to be reduced than copper.

C There will be no reaction if zinc is placed in copper nitrate.

D Sodium is more likely to be oxidised than zinc.

4 Which of the following reactions is not a redox reaction?

A $2NaCl(l) \rightarrow 2Na(s) + Cl_2(g)$

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

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

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

5 When balancing the following skeletal half-equation:

$$MnO_4^- \rightarrow Mn^{2+}$$

A 4 water molecules would be written in the products.

B 4 water molecules would be written in the reactants.

C 3 electrons would be written in the products.

D 1 electron would be written in the reactants.

6 How does the reactivity of metals in groups 1 and 2 change going down the group?

7 In the equation below, identify the reductant.

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

8 What conditions must be present for the corrosion of iron to occur?

9 Using oxidation state changes, explain why the combustion of propane is a redox reaction.

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

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10 The reaction between potassium dichromate and ethanol in acidic solution used to be the basis for breathalysers used by police to determine the amount of alcohol consumed by drivers. The skeleton half-equations are given below:

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$
$$CH_3CH_2OH(aq) \rightarrow CH_3COOH(aq)$$

Write a balanced redox equation for this reaction.

11 An experiment was carried out in which an iron nail, an iron nail with copper wire wrapped around it and an iron nail with a zinc strip wrapped around it were each placed in a beaker. The beakers were filled with warm ferroxyl jelly, covered and left for a few hours for the jelly to set. The results are shown in Figure 10.7.1.

Ferroxyl jelly is made by adding a hexacyanoferrate indicator and phenolphthalein indicator to agar jelly. Hexacyanoferrate indicator turns dark blue in the presence of $Fe^{2+}(aq)$ ions. Phenolphthalein indicator turns pink in the presence of $OH^-(aq)$ ions.

a With the aid of half-equations, explain the colour changes in each beaker.

b Suggest a reason why a white deposit formed in the beaker that contained the iron nail wrapped in zinc.

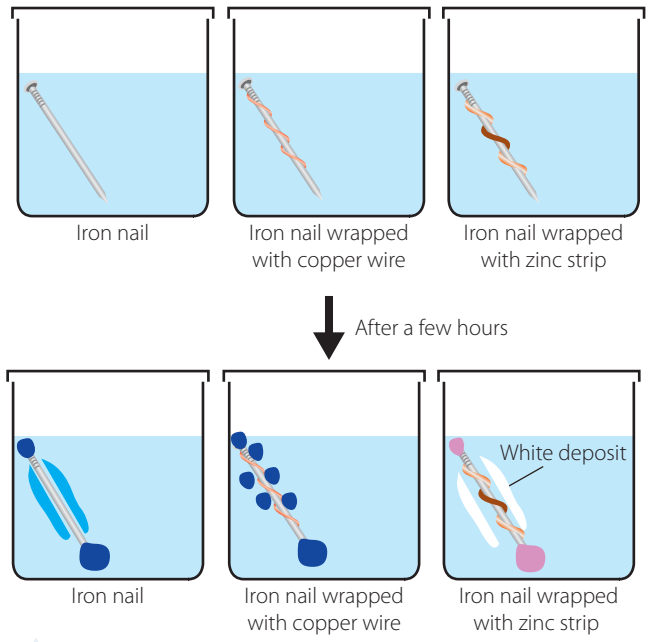

FIGURE 10.7.1 Results for experiment iron nail experiment

11 ELECTROCHEMICAL CELLS

Introduction

In Chapter 10, we introduced the concepts of oxidation and reduction. We learned that during oxidation, electrons are released and during reduction, electrons are accepted. Hence, you can see there is a movement of electrons. This chapter introduces the process by which this movement of electrons is harnessed for use in electrochemical cells.

Galvanic cells are the basis of commonly available batteries. They are also the basis of fuel cells, which are being investigated as alternatives to fossil fuels for powering cars.

The chemistry of electrolytic cells underpins rechargeable batteries. Electrolysis is used extensively in the extraction and refining of metals from their ores. Electrolysis is also used in the electroplating industry, where one metal coats another metal – usually a more expensive metal coats a less expensive metal. Electroplating is cheaper than making an object completely from the more expensive metal.

Stimulus questions

How does the famous potato clock work?

How can the almost-microscopic parts of a watch be plated with metals such as gold and platinum?

Hydrogen fuel cells are generating great excitement in industrial, commercial and domestic circles. Why?

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11.1 Electrochemical cells

Electrochemical cells allow for the transformation of energy between chemical potential energy and electrical energy. There are two types of electrochemical cells: **galvanic cells**, shown in Figure 11.1.1 and **electrolytic cells**, which are used in electroplating, see Figure 11.1.2.

electrochemical cells
transforms energy between electrical energy and chemical potential energy

galvanic cells
a type of electrochemical cell that transforms chemical potential energy to electrical energy in a spontaneous chemical reaction

electrolytic cells
a type of electrochemical cell that transforms electrical energy and chemical potential energy

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FIGURE 11.1.1 Batteries are galvanic cells.

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FIGURE 11.1.2 These copper-plated pots and the chrome-plated wheel rim were made by electroplating.

11.1.1 The electrochemical series
11.1.2 Electrochemistry
11.1.3 How batteries work

SYLLABUS LINK

In Chapter 10, we discussed metal displacement reactions and how they are linked to reactivity and oxidation and reduction reactions was discussed. This can inform how galvanic cells and electrolytic cells operate.

Metal displacement reactions and galvanic cell

When a piece of zinc metal is added to a copper(II) sulfate solution a spontaneous chemical reaction occurs:

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

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

The zinc gives up electrons to the copper ions and the products are copper metal and zinc ions. If the reacting species are put into two separate beakers and connected in a specific way, then the same reaction will occur, but the electrons can be utilised to do work in the process. This is the principle of galvanic cells. The beaker containing zinc metal and zinc solution is an electrode. The beaker containing the copper metal and the copper(II) solution is the other electrode. Oxidation will occur at one of the electrodes and reduction will occur at the other electrode. These electrodes are given specific names – the electrode where reduction occurs is called the **cathode**, and the electrode where oxidation occurs is the **anode**.

Galvanic cells are electrochemical cells in which the oxidation and reduction chemical reactions occur spontaneously. For this to occur, the electrical circuit must be complete. For the electrical energy to be harnessed, the electrons must flow from the anode to the cathode through an external circuit.

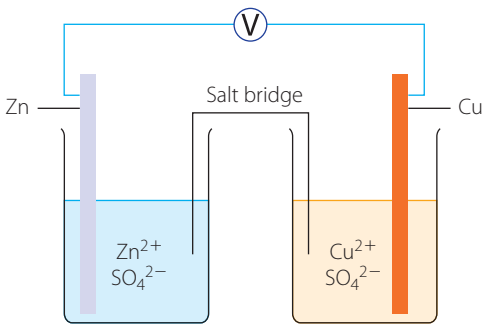
cathode
the electrode where oxidation occurs

anode
the electrode where reduction occurs

To do this, the galvanic cell is composed of two half-cells. The simplest half-cells are composed of a solid metal in a solution that contains its ions. The half-cells are in separate beakers so that the electrons can flow through an external circuit rather than transfer by direct contact.

Consider the galvanic cell between zinc and copper shown in Figure 11.1.3.

FIGURE 11.1.3
Galvanic cell between zinc and copper



The anode will consist of a solid piece of zinc in a beaker containing a 1 mol L^{-1} solution of zinc ions, such as zinc sulfate ($ZnSO_4$). The cathode will consist of a solid piece of copper in a beaker containing a 1 mol L^{-1} solution of copper ions, such as copper(II) sulfate ($CuSO_4$). To complete the circuit, a **salt bridge** and some electrical wires are added. A voltmeter is also included to measure the work done in moving the charge through the circuit. A lamp or ammeter could also be used to show that the charge is moving through the external circuit.

salt bridge
a link containing electrolyte between the oxidation and reduction half-cells of a galvanic cell

internal circuit
the internal circuit of an electrochemical cell consists of the strips of metal, solutions and the salt bridge

external circuit
the external circuit of an electrochemical cell consists of the connecting wires and the voltmeter or electrical appliance

The strips of metal, solutions and salt bridge constitute the **internal circuit** whereas the wires, voltmeter or appliance constitute the **external circuit**.

The salt bridge is used to complete the circuit. It can simply be a strip of filter paper soaked in an electrolyte such as a potassium nitrate solution. A potassium nitrate solution is commonly used for the salt bridge because it always forms soluble salts when in contact with other solutions. All potassium salts are soluble and all nitrate salts are soluble. So when one end of the filter paper with potassium nitrate is placed in the zinc sulfate solution, no precipitate forms. Similarly, when the other end of the salt bridge is in contact with the copper sulfate solution, no precipitate forms. If a precipitate formed, then the circuit would be broken because charge, electrons or ions would not be free to move through that part of the circuit.

At the anode, solid zinc loses electrons to form zinc ions. Over time, the mass of the solid zinc anode decreases. Hence, there is an excess of zinc ions at the anode. The electrons flow through the external circuit to the cathode. The electrons combine with copper ions in the solution to form solid copper. Over time, the mass of the solid copper cathode increases and there becomes an excess of sulfate ions at the cathode. The salt bridge allows for the movement of ions so that the solutions in each beaker remain neutral. Anions flow towards the anode and cations flow towards the cathode to balance charge. There is neither excess cations at the anode nor excess anions at the cathode.

Electrolytic cells

In its simplest form, a galvanic cell is made up of a spontaneous metal displacement reaction in which the anode (oxidation) is the more reactive metal and the cathode (reduction) is the less reactive metal.

If a spontaneous reaction such as this can produce energy, it follows that electricity could be used to force a non-spontaneous reaction to occur.

This is the basis of electrolysis, in which electrical energy is converted into chemical energy. In its simplest form, an electrolytic cell consists of two inert electrodes, usually carbon or platinum, dipping into a molten salt such as lithium bromide.

Lithium bromide is a stable salt. Its decomposition, even in its molten state, is a non-spontaneous reaction:

$$LiBr(l) \rightarrow Li(l) + Br_2(g)$$

The half-equations for this reaction are:

$$Li^+(l) + e^- \rightarrow Li(l) \qquad \textit{reduction}$$

$$2Br^-(l) \rightarrow Br_2(g) + 2e^- \qquad \textit{oxidation}$$

The Li^+ and Br^- ions are far too stable to spontaneously react in this way. If, however, an electric current is passed through molten lithium bromide in the apparatus shown in Figure 11.1.4, the half-equations shown above are forced to occur.

In this process, electrons are provided by an external power source such as a power pack or a battery.

These electrons flow from the power source, via the external circuit to the carbon electrode, making it negatively charged.

The positively charged lithium ions in the molten electrolyte move towards the negative electrode, where they pick up an electron:

$$Li^+(l) + e^- \rightarrow Li(l)$$

This is *reduction*, so this electrode is the *cathode*.

As Li^+ ions are reduced, more are attracted to the cathode, creating a flow of positive ions through the electrolyte towards the cathode.

The lithium metal produced melts because of the high temperature of the molten salt and forms a pool on the surface of the electrolyte around the cathode.

Completing the circuit is the other electrode, which is positively charged. Negatively charged bromide ions move towards this electrode. When they make contact with the electrode they release their extra electrons:

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

This is *oxidation*, so this electrode is the *anode*.

As Br^- ions are oxidised, more are attracted to the anode, creating a flow of negative ions through the electrolyte towards the anode. The molecular bromine that is produced vaporises because of the high temperature of the molten salt and dissipates away.

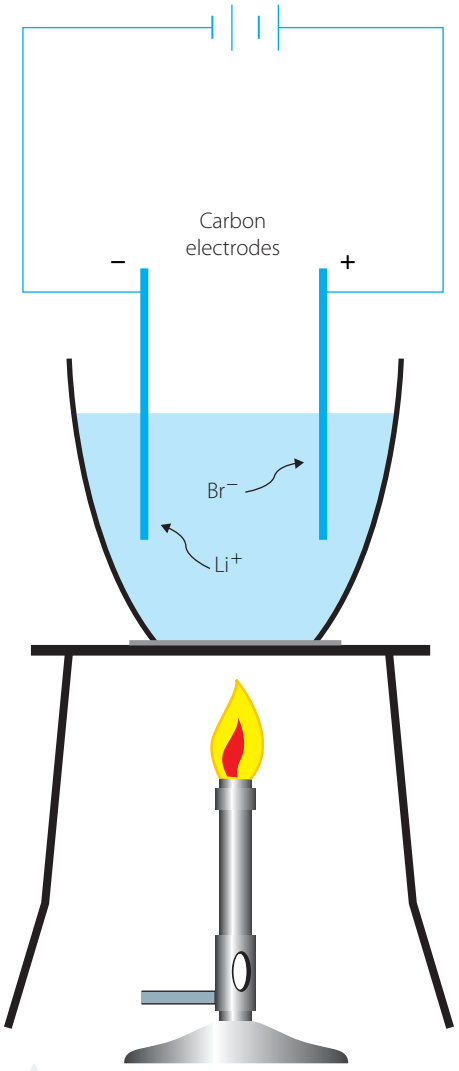


FIGURE 11.1.4 Apparatus used for the electrolysis of molten lithium bromide

Galvanic and electrolytic cells – a comparison

The fundamental difference between galvanic and electrolytic cells is the spontaneity of their cell reactions. Cell diagrams showing direction of electron and ion flow are shown in Figure 11.1.5.

GALVANIC CELL	ELECTROLYTIC CELL
Spontaneous reaction	Non-spontaneous reaction
Oxidation at anode	Oxidation at cathode
Anode is negatively charged	Anode is positively charged
Electrons flow from anode to cathode	Electrons flow from anode to cathode
Positive ions flow in opposite direction	Positive ions flow in opposite direction

Some of this can be confusing, but it can help to remember that, in both kinds of cell, *oxidation* occurs at the *anode*.

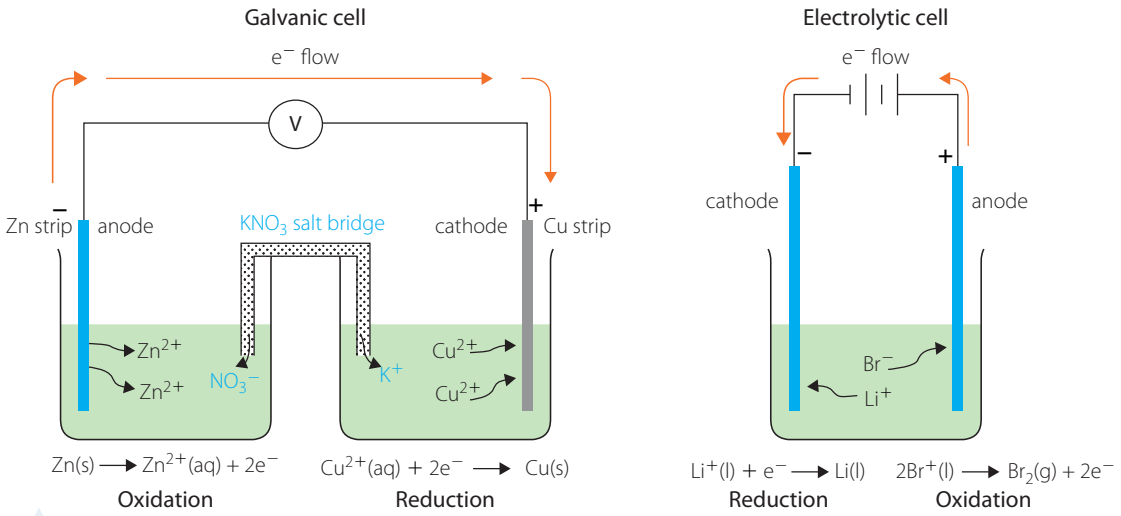


FIGURE 11.1.5 Diagram showing the similarities and differences between galvanic and electrolytic cells.

SECTION REVIEW 11.1

REMEMBERING

1 Define:

- **a** anode
- **b** cathode
- **c** electrolyte.

UNDERSTANDING

2 Copy the table below into your book, then fill in the blanks.

	CELL REACTION	ANODE	CATHODE
Galvanic	spontaneous		
Electrolytic	non-spontaneous		

APPLYING

3 Figure 11.1.6 shows a galvanic cell. On the diagram, label:

- **a** the unknown metal strip
- **b** the anode and cathode
- **c** the solution in the beaker with the lead strip
- **d** the direction of electron flow
- **e** the direction of the flow of ions from the salt bridge
- **f** the oxidant and the reductant
- **g** the direction of positive ion flow.

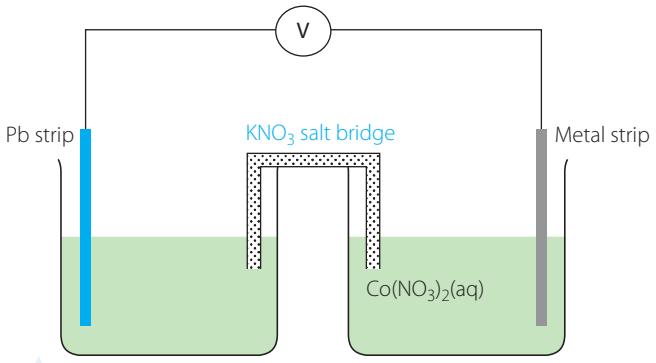


FIGURE 11.1.6 A galvanic cell

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** galvanic cell
- **b** electrolytic cell
- **c** internal circuit
- **d** external circuit.

CATEGORY QUESTIONS

2 Describe the similarities and differences between galvanic cells and electrolytic cells

ELABORATION QUESTIONS

3 Suggest a reason why the voltage produced by a galvanic cell should decrease over time.

4 Explain how the electrolysis of copper(II) sulphate solution using copper electrodes produces extremely pure copper.

EVIDENCE QUESTIONS

5 An experiment is carried out in which a student sets up an electrolytic cell and determines the thickness of chromium metal that is plated onto a piece of steel as the voltage applied to the cell is changed.

A graph of the results is shown below.

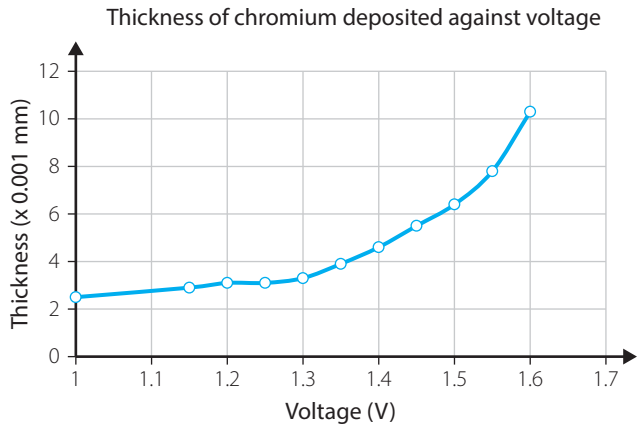


FIG 11.2.1 Graph of thickness of chromium deposited against voltage

- **a** The electrodes used in these experiments were a piece of chromium and a piece of steel. Which metal was the anode and which was the cathode?
- **b** Suggest a solution for the electrolyte.
- **c** What other important variable could be investigated in this way?
- **d** What would be the optimum value for the applied voltage?

END-OF-CHAPTER EXAM

End-of-chapter test

1 Galvanic cells transform:

- **A** electrical energy into chemical potential energy.
- **B** chemical potential energy into electrical energy.
- **C** electrical energy into kinetic energy.
- **D** elastic potential energy into chemical potential energy.

2 Batteries are an example of:

- **A** an electrolytic cell.
- **B** a chemical cell.
- **C** electrical cells.
- **D** a galvanic cell.

3 Which of the following statements is correct?

- **A** Oxidation occurs at the anode.
- **B** Oxidation occurs at the cathode.
- **C** Reduction occurs at the anode.
- **D** Reduction occurs in the salt bridge.

4 In a galvanic cell it is important that the half-cells are separated because:

- **A** oxidation and reduction are two separate reactions.
- **B** oxidation and reduction cannot happen at the same time.
- **C** this allows ions to flow through the salt bridge.
- **D** this allows electrons to flow through the external wire.

5 In an electrolytic cell, what charge does the cathode have?

6 In a galvanic cell, what is the collective term used for the wires and the voltmeter or appliance?

7 In a nickel/cadmium galvanic cell, which is the oxidant?

8 In the electrolysis of molten mercury(I) bromide, what is the product formed at the cathode?

9 Explain why a salt bridge is necessary when operating a galvanic cell and why, in most cases, it contains sodium or potassium nitrate solution.

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10 Figure 11.2.1 shows the electrolysis of molten sodium chloride.

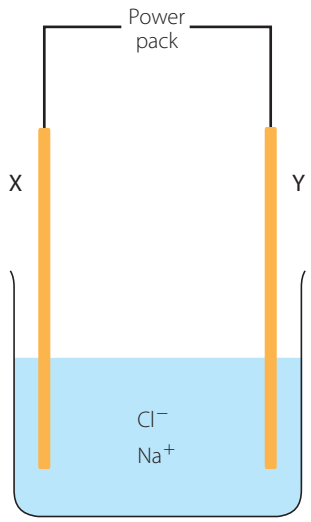

FIGURE 11.2.1 The electrolysis of molten sodium chloride

It was observed that when an electric current was applied to the molten sodium chloride, a pale green, noxious gas was produced at electrode X.

a From this information, label:

- **i** the anode
- **ii** the cathode
- **iii** the direction of electron flow
- **iv** the direction of positive ion flow
- **v** the charges of the electrodes.

b Write the oxidation and reduction half-equations.

12 GALVANIC CELLS

Introduction

Galvanic cells are a type of electrochemical cell that uses a spontaneous redox chemical reaction to generate an electric current.They are sometimes referred to as voltaic cells, but most people know them by their common name – batteries!

The importance of galvanic cells is beyond question. But as we become more aware of the dangers that using fossil fuels cause to our climate, the more we are searching for ways to make battery technology more efficient – to produce more power from smaller batteries. This chapter will discuss how galvanic cells are constructed and the role of each component in the cell.

Stimulus questions

How would we label the parts of a potato clock?

What causes a battery to go flat?

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12.1 Galvanic cells

Oxidation and reduction reactions occur where a metal is in direct contact with a solution containing the ions of a less-reactive metal, such as zinc in a copper(II) sulfate solution. The zinc gives up electrons to the copper ions and the products are copper metal and zinc ions. If the reacting species are put into two separate beakers and connected in a specific way, then the same reaction will occur but the electrons can be utilised to do work in the process. This is the principle of galvanic cells. The beaker containing zinc metal and zinc solution is an electrode. The beaker containing the copper metal and the copper(II) solution is the other electrode. Oxidation will occur at one of the electrodes and reduction will occur at the other electrode. These electrodes are given specific names – the electrode where reduction occurs is called the cathode, and the electrode where oxidation occurs is the anode.

Galvanic cells are electrochemical cells in which the oxidation and reduction chemical reactions occur spontaneously. For this to occur, the electrical circuit must be complete. For the electrical energy to be harnessed, the electrons must flow from the anode to the cathode through an external circuit. To do this, the galvanic cell is composed of two half-cells. The simplest half-cells are composed of a solid metal in a solution that contains its ions. The half-cells are in separate beakers so that the electrons can flow through an external circuit rather than transfer by direct contact.

KEY FORMULA

Galvanic cells involve spontaneous reactions. The overall cell voltage is positive.

Consider the galvanic cell between zinc and copper. This is based on the spontaneous reaction between zinc and copper (II)sulfate.

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

As this is a spontaneous reaction, it follows that zinc is the more reactive metal and so will be the anode and copper will be the cathode. The anode will consist of a solid piece of zinc in a beaker containing a 1 mol L^{-1} solution of zinc ions, such as zinc sulfate ($ZnSO_4$). The cathode will consist of a solid piece of copper in a beaker containing a 1 mol L^{-1} solution of copper ions such as copper(II) sulfate ($CuSO_4$). To complete the circuit, a salt bridge and some electrical wires are added. A voltmeter is also included to measure the work done in moving the charge through the circuit. A lamp or ammeter could also be used to show that the charge is moving through the external circuit.

Figure 12.1.1 shows the galvanic cell between zinc and copper, showing the direction of electron flow from the zinc strip to the copper strip.

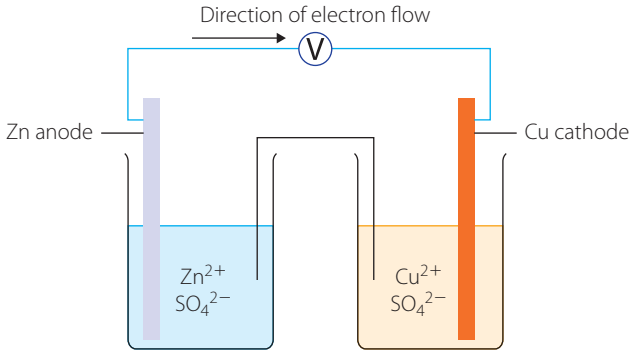


FIGURE 12.1.1 The galvanic cell between zinc and copper

The half-equations for this reaction are:

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

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

The electrons produced by the oxidation of zinc move through the wires of the external circuit and into the copper strip. Here they are added to copper ions, causing them to be reduced to copper metal.

Fuel cells

fuel cell
a galvanic cell in which a fuel, such as hydrogen or methanol, is oxidised and oxygen is reduced, releasing electrical energy

When we consider fuels as a source of energy, what comes to mind is combustion reactions where chemical energy is converted to heat energy. However, a **fuel cell** is an electrochemical device. It converts chemical energy directly into electrical energy, without the need for any combustion reactions. Since a fuel cell is a type of galvanic cell, it has the same structure as described above – an anode, a cathode, an electrolyte and the flow of electrons through an external circuit.

The most commonly used fuel in fuel cells is hydrogen, although they can also use short-chain alkanes. One way a fuel cell is different from a normal galvanic cell is that the fuel and air are continuously fed into the cell – the electrodes don't need to be replaced.

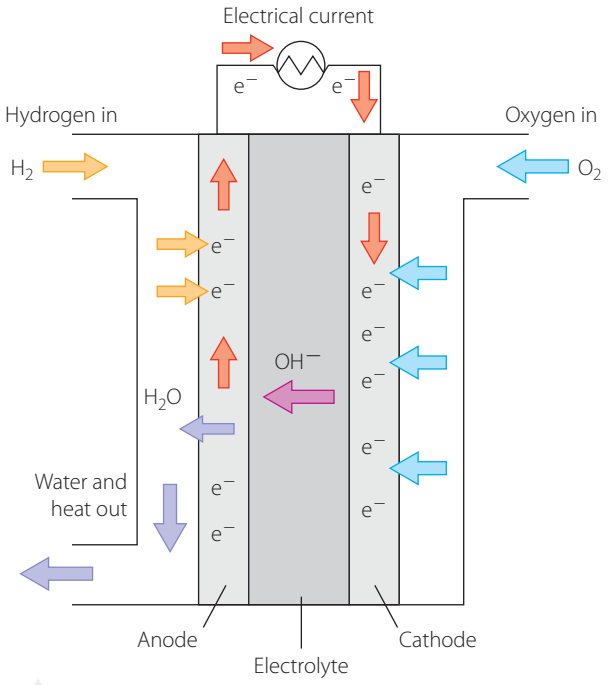
12.1.1 Chemical cells and fuel cells

In most fuel cells, hydrogen is oxidised at the anode and oxygen is reduced at the cathode. A by-product of the fuel cell is water.

The reactions in the fuel cell are:

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

$$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$$



US Department of Energy

FIGURE 12.1.2 Alkali fuel cell

Different types of fuel cells generally differ in the type of electrolyte used. For example, the alkali fuel cell uses a concentrated potassium hydroxide electrolyte.

The fuel cell is compartmentalised. The hydrogen and oxygen are on opposite sides with the electrolyte in the middle compartment. The electrodes are porous to allow the gas molecules to pass through and are lined with a catalyst that assists with breaking bonds in the gaseous molecules. The most commonly used catalyst is platinum, although rhodium and nickel are also used. The use of a platinum catalyst is one of the main costs of a fuel cell.

Fuel cells can be stacked together to increase the total cell voltage, just as batteries are added in series to increase the total voltage output. The water produced must be removed from the cell; otherwise, the electrolyte will become diluted, which will affect the cell's efficiency.

Metal nanomaterials in fuel cells

The platinum catalyst contributes significantly to the cost of developing a fuel cell. Therefore, scientists have focused their research on trying to develop more efficient and cheaper catalysts. Additionally, as surface area affects the rate of a chemical reaction, scientists have investigated ways of increasing the surface area of the fuel-cell catalyst with nanoparticles. Nanoparticles have a size of about one-billionth of a metre. Lining the electrodes with many nanoparticles instead of a larger piece of platinum increases the surface area of the catalyst. This allows the bonds of more molecules of hydrogen and oxygen to be broken at any particular time, which increases the rate of the reaction of the fuel cell.

The other area of research is the use of materials other than platinum as the catalyst in fuel cells. Scientists have investigated mixed-metal nanoparticles using a nanostructure support composed of carbon. One such mixed-metal nanoparticle is composed of platinum and ruthenium.

SYLLABUS LINK
Nelson QScience Chemistry Units 1 & 2, Chapter 21, shows that catalysts increase the rate of a chemical reaction without taking part in the reaction.

SECTION REVIEW 12.1

REMEMBERING

1 What is a fuel cell?

2 Identify the energy transformation that takes place in a fuel cell.

3 What is the most common catalyst used in fuel cells?

UNDERSTANDING

4 Explain why the blue solution decolourises when a galvanic cell is set up using a strip of copper in a copper(II) solution and a strip of lead in a lead(II) nitrate solution.

5 A fuel cell releases only a small voltage. How can this be used to provide the energy for a car?

6 Describe the chemistry of a fuel cell.

APPLYING

7 Draw a galvanic cell for each of the following, clearly indicating the anode, cathode and direction of electron flow.

- **a** A strip of tin in a solution of tin(II) chloride and a strip of zinc in a solution of zinc sulfate.
- **b** A strip of magnesium in a solution of magnesium nitrate and a strip of iron in a solution of iron(II) nitrate.

12.2 Inside the galvanic cell

The reaction between zinc and copper in a galvanic cell is rapid and releases a significant amount of heat. In order to make use of the electrons transferred in this reaction, the Zn atoms and Cu^{2+} ions must be separated, and the electrons made to travel through a wire to be detected or put to work.

This arrangement results in two compartments of **half-cells** consisting of a metal electrode and a solution of the ions of the metal. In the case of the zinc/copper galvanic cell, the oxidation half-cell consists of a strip of zinc metal dipping into a zinc sulfate electrolyte, while the reduction half-cell consists of a strip of copper dipping into a copper sulfate electrolyte. The internal circuit consists of a salt bridge containing an inert electrolyte that allows ions to flow between the two half-cells.

half-cells
the part of a galvanic cell where oxidation or reduction occurs

In the zinc half-cell, the zinc atoms at the surface of the zinc electrode are oxidised to Zn^{2+} ions, which move into solution. The electrons produced in the oxidation of zinc move up through the electrode and into the wire of the external circuit. Since negatively charged electrons are produced at this electrode, the zinc strip is the negative electrode. It is referred to as the anode because oxidation occurs here.

The electrons, having moved through the wires of the external circuit, enter the copper strip. The positively charged copper ions in solution are attracted to the negative charge build-up in the copper strip. Here, they pick up the electrons that travelled from the zinc strip and are reduced to copper atoms. The copper strip is the positive electrode. It is referred to as the cathode because reduction occurs here. Figure 12.2.1 shows how this process takes place.

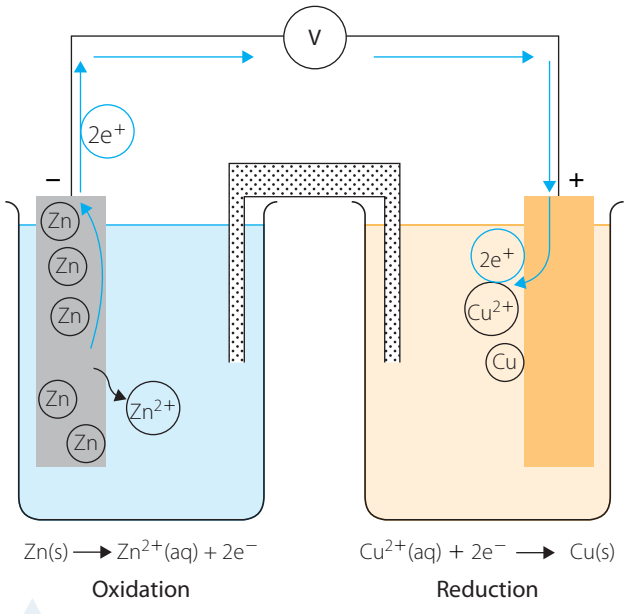


FIGURE 12.2.1 The operation of a galvanic cell

The salt bridge

In Chapter 11, we showed that in a galvanic cell, a salt bridge is necessary to complete the circuit and to maintain neutrality in each half-cell. It is important to understand how this is achieved.

Consider the oxidation half-cell:

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

Typically, the concentration of electrolyte, in this case zinc sulfate, is 1 mol L^{-1}. The positive $Zn^{2+}(aq)$ ions are balanced out by the $SO_4^{2-}(aq)$ ions.

If the cell were able to operate without a salt bridge, then as the Zn metal atoms are oxidised, the resulting Zn^{2+} ions would move into solution. This would increase the number of $Zn^{2+}(aq)$ ions, thereby creating a build-up of positive charge within the half-cell. This is not possible.

The salt bridge contains a solution of potassium ions and nitrate ions, neither of which can interfere chemically with the components of either half-cell. For every Zn^{2+} ion that moves into solution, a NO_3^- ion moves from the salt bridge into the solution. This keeps the charges balanced.

Similarly, in the reduction half-cell:

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

If the cell were able to operate without a salt bridge, then as the $Cu^{2+}(aq)$ ions are reduced, they are effectively removed from the solution, thereby creating a build-up of negative charge within the half-cell. This is not possible.

For every Cu^{2+} that is lost from the half-cell, two K^+ ions move from the salt bridge into the solution. This keeps the charges balanced.

This is shown in Figure 12.2.2

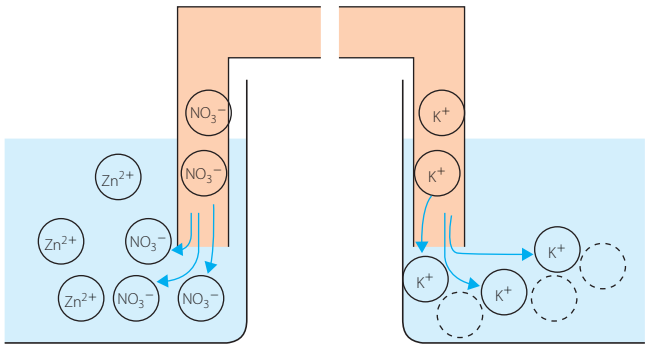


FIGURE 12.2.2 The role of the salt bridge in a galvanic cell

SECTION REVIEW 12.2

UNDERSTANDING

1. Explain why the mass of the cadmium electrode decreases during the operation of a nickel–cadmium galvanic cell.
2. Why do the reactants in a galvanic cell, such as nickel and cadmium, have to be placed in separate beakers?
3. Explain why a salt such as potassium nitrate is used in the salt bridge?

APPLYING

4. If a galvanic cell was left to run indefinitely it would go 'flat', that is, it would stop working. With reference to the zinc–copper galvanic cell, suggest a reason why this could occur.

12.3 The essential elements of a galvanic cell

A galvanic cell is based on a redox reaction. For example, the oxidation of lead(II) nitrate by magnesium:

$$Mg(s) + Pb(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + Pb(s)$$

To simplify things, the spectator ions NO_3^- are removed, since they take no part in the reaction. This gives a net ionic equation:

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

In this case, it is easy to identify the species being oxidised and the species being reduced.

The **oxidation state** of the magnesium is increasing from Mg(0) to Mg^{2+}(+2). An increase in oxidation state means that the magnesium has been oxidised:

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

The oxidation state of the lead is decreasing from Pb^{2+} (+2) to Pb(0). The lead is being reduced:

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

oxidation state the number of electrons that an atom would have gained or lost to get to its present state; it assumes that each species is completely ionic

The oxidation half-cell, then, would consist of a strip of magnesium dipping into a solution of Mg^{2+} ions – probably $Mg(NO_3)_2(aq)$. The reduction half-cell would consist of a strip of lead dipping into a solution of $Pb(NO_3)_2(aq)$.

The two metal strips are the electrodes and their respective solutions are the electrolytes. Along with the salt bridge, they make up the internal circuit of the cell. The metal strips are connected to the wires and meters/appliances that make up the external circuit. Since the Mg strip is oxidised, it is the anode and because it is the source of electrons, it is the negative electrode. The Pb strip is the cathode and is the positive electrode.

WORKED EXAMPLE 12.3.1

The displacement reaction between manganese and iron is given by the equation:

$$Mn(s) + Fe(NO_3)_2(aq) \rightarrow Mn(NO_3)_2(aq) + Fe(s)$$

From this information, draw and label the galvanic cell represented by this equation.

ANSWER

Step 1 Remove any spectator ions and separate the equation into oxidation and reduction half-equations:

$$Mn(s) \rightarrow Mn^{2+}(aq) + 2e^- \text{ oxidation}$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \text{ reduction}$$

Step 2 Sketch the basic form of the cell.

Step 3 Label the anode and the cathode and add the minus sign and plus sign.

Step 4 Add the salt bridge.

Step 5 Add an external circuit to the cell, consisting of wires and a voltmeter.

Step 6 Show the direction of electron flow through the external circuit.

Step 7 Show the direction of positive ion flow through the cell.

Step 8 Show the direction of positive and negative ion flow from the salt bridge.

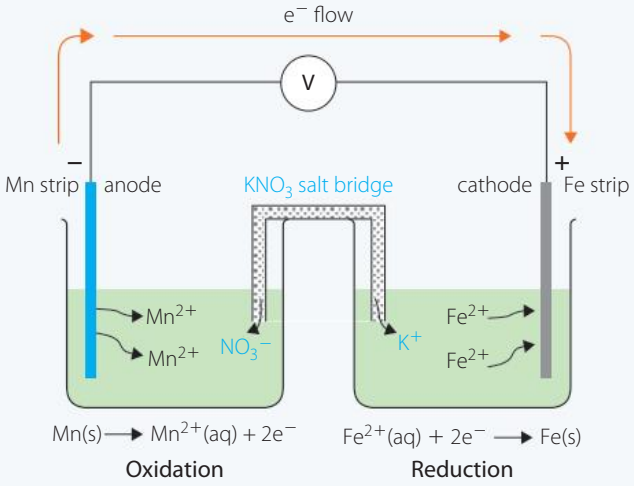


FIGURE 12.3.1 Galvanic cell for Worked example 12.3.1.

MANDATORY PRACTICAL 12.3.1

Constructing galvanic cells

Galvanic cells involve joining two half-cells by a salt bridge and an external circuit. In this experiment, you will use different combinations of half-cells.

AIM

To measure the cell voltage for a variety of galvanic cells

EQUIPMENT

- 50 mL of 1 mol L^{-1} $CuSO_4$
- 50 mL of 1 mol L^{-1} $MgSO_4$
- 50 mL of 1 mol L^{-1} acidified $FeSO_4$
- 50 mL of 1 mol L^{-1} $ZnSO_4$
- 50 mL of 1 mol L^{-1} KNO_3
- Strip of Cu metal
- Strip of Mg ribbon
- Ungalvanised iron nail
- Strip of zinc metal
- Four 100 mL beakers
- Waste bottle for heavy metals
- 7 cm × 7 cm piece of sandpaper
- Voltmeter

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- Two electrical wires with banana plugs on each end
- Two alligator clips – place one on each electrical wire
- Filter paper cut into strips
- Petri dish
- Four labels for beakers
- Small piece of Blu Tack
- Forceps

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Potassium nitrate is a moderately toxic salt.	Use forceps to handle filter paper soaked with potassium nitrate.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Pour 50 mL of each solution (except KNO_3) into separate labelled beakers.
2. Clean the metals with sandpaper.
3. Stand a piece of metal in the beaker with its corresponding solution so that it is partly submerged. It may be helpful to use a small piece of Blu Tack to hold the metal in place.
4. Soak a piece of filter paper in a petri dish containing KNO_3.
5. Place the piece of filter paper so that one end is in the copper(II) solution and the other end is in the zinc solution.
6. Connect the zinc strip and copper strip to the voltmeter with electrical wires.
7. Record the voltage. If the needle drops below zero, connect the wires to the opposite terminals of the voltmeter.
8. Repeat for all other combinations for galvanic cells: copper–magnesium, copper–iron, magnesium–zinc, magnesium–iron and zinc–iron.
9. Dispose of copper(II) sulfate by pouring it into the heavy metals waste bottle. Do not pour it down the drain.

RESULTS

Record the voltage for each galvanic cell in a table.

ANALYSIS

1. Which galvanic cell had the largest cell voltage?
2. Which galvanic cell had the smallest cell voltage?
3. For each galvanic cell, identify the anode and the cathode.
4. Construct an activity series of the metals used based on the cell voltages.

DISCUSSION

Explain why metal combinations that are further away from each other in the series have the largest cell voltages.

SECTION REVIEW 12.3

REMEMBERING

1 Define oxidation and reduction in terms of oxidation states.

2 In a galvanic cell, what name is given to the electrode that is made of the oxidant in a metal displacement reaction?

3 What two properties must a salt possess for it to be used in the salt bridge of a galvanic cell?

UNDERSTANDING

4 Which ions from the salt bridge, K^+ or NO_3^-, move into the reductant half-cell? Explain your choice.

5 If aluminium is to be used as an electrode in a galvanic cell, what preparation would you need to carry out? Explain why you would need to do this.

APPLYING

6 Draw and label the galvanic cells based on the following displacement reactions:

- **a** the reaction between lead and copper(II) nitrate
- **b** the reaction between cadmium and silver nitrate.

7 A galvanic cell was set up as shown in Figure 12.3.2 with metal electrodes **X** and **Y** dipping into solutions of $\mathbf{X}(NO_3)_2$ and $\mathbf{Y}(NO_3)_2$ respectively. The electrodes were weighed before they were placed into the cell.

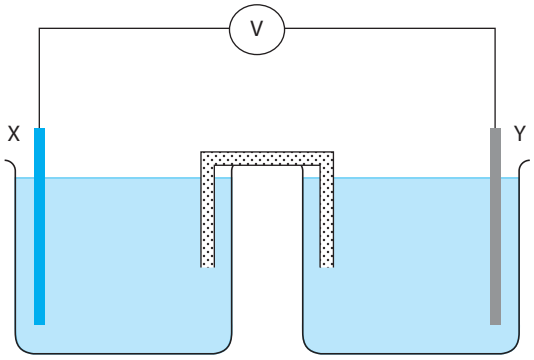

FIGURE 12.3.2 Galvanic cell

After a few minutes the electrodes were taken out and weighed again. It was found that electrode **X** had gained mass, while the mass of electrode **Y** had decreased.

Use this information to label the cell, using the labels below:

Anode, cathode, the sign (+ or –) of the electrodes, the direction of current flow, the movement of positive ions, the salt used in the salt bridge, the movement of ions from the salt bridge, and the oxidation and reduction half-equations.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** fuel cell
- **b** salt bridge
- **c** anode
- **d** cathode
- **e** oxidation half-cell
- **f** reduction half-cell
- **g** oxidation state.

CATEGORY QUESTIONS

2 Write the reactions that occur in the oxidation and reduction half-cells of a nickel–cadmium galvanic cell.

3 Identify the anode and cathode in the described in Question 2.

ELABORATION QUESTIONS

4 Explain how a salt bridge operates in a galvanic cell.

5 A student carried out a series of experiments in which she set up a galvanic cell. She varied the concentration of the solution of the metal in the anode half-cell and recorded the corresponding cell voltage.

The results are recorded in the graph in Figure 12.4.1.

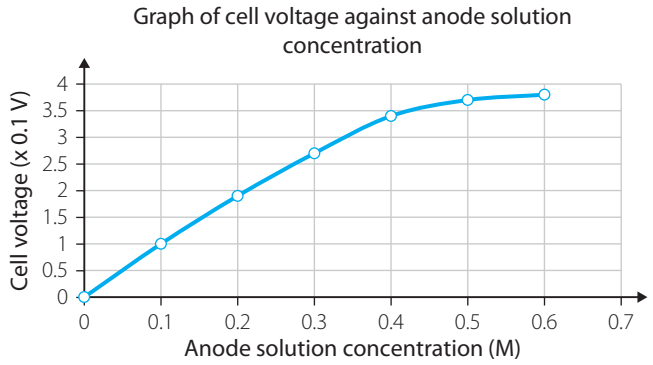

FIGURE 12.4.1 Graph of cell voltage against anode solution concentration

- **a** What general statement can be made regarding the relationship between concentration of anode solution and cell voltage?
- **b** Suggest a reason why the cell voltage should increase with increasing concentration.
- **c** Why does the graph plateau after about 0.4 M concentration?
- **d** What would the graph look like if the cathode solution concentration was varied instead?

END-OF-CHAPTER EXAM

End-of-chapter test

1 Research is being conducted into using metal nanoparticles as catalysts in hydrogen fuel cells because:

A they are more readily available.

B they are lighter and so add less mass to the fuel cell.

C the platinum catalyst slows the reaction in the fuel cell.

D their higher surface area would allow the catalyst to work more effectively.

2 In a galvanic cell, it is important that the half-cells are separated because:

A oxidation and reduction are two separate reactions.

B oxidation and reduction cannot happen at the same time.

C this allows ions to flow through the salt bridge.

D this allows electrons to flow through the external wire.

3 In a hydrogen fuel cell:

A hydrogen is oxidised at the cathode.

B water is produced.

C oxygen is oxidised at the anode.

D water is split into hydrogen and oxygen gas.

4 Which of the following is not true? The salt bridge in a galvanic cell must:

A contain ions.

B be an electrolyte.

C connect the two half-cells.

D react with the half-cells.

5 In a galvanic cell, one of the half-cells can be represented by the half-equation:

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

State whether this is the reductant or oxidant half-cell.

6 Would the reaction shown below produce a galvanic cell?

$$Sn(s) + Fe(NO_3)_2 \rightarrow Sn(s) + Fe(NO_3)_2(aq)$$

7 Identify the role of platinum in a fuel cell.

8 When a galvanic cell is set up with copper and zinc electrodes dipping into their respective nitrate solutions, what observations could be made as the cell is made to work for a long time?

9 Explain how the voltage produced by a displacement reaction in a galvanic cell could be increased.

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10 An experiment is carried out to develop an activity series for a group of unknown metals: T, Q, L and G. A number of galvanic cells are set up using the given metals dipping into solutions of their respective ions. In each cell, a galvanometer is used to measure the voltage in the cell as well as the direction of current flow. The results are shown in Figure 12.4.2.

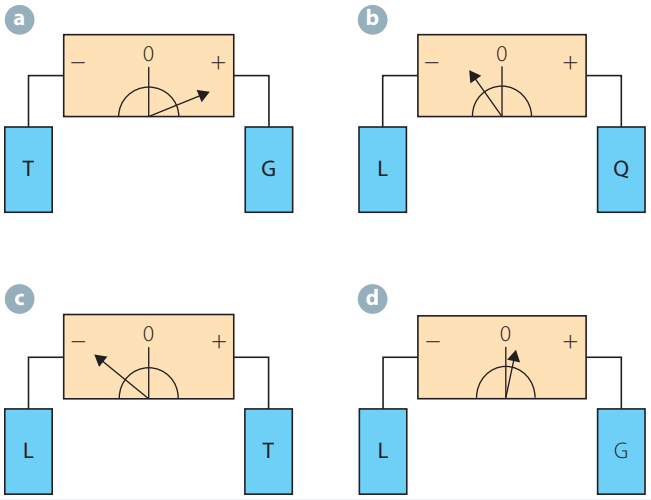

FIGURE 12.4.2 Results for Question 10

Use these results to produce an activity series for the metals. For each experiment, a–d, identify the anode and cathode and write oxidation and reduction half-equations (assume all of the metals produce 2+ ions).

13 STANDARD ELECTRODE POTENTIAL

Introduction

Galvanic cells consist of two half-cells. If a half-cell is connected to a reference cell, its standard electrode potential can be measured. The standard electrode potential of substances is a very useful property. Standard electrode potentials enable the relative strength of oxidising and reducing species to be determined, they can be used to predict whether or not redox reactions will happen and they can be used to calculate the voltage produced by galvanic cells.

Stimulus questions

Adding a piece of copper to a sodium chloride solution could be very dangerous. Is there a quantitative way to safely predict whether this will be a dangerous reaction?

How could you increase the voltage produced by your potato clock? Is there a way that you could predict the voltage?

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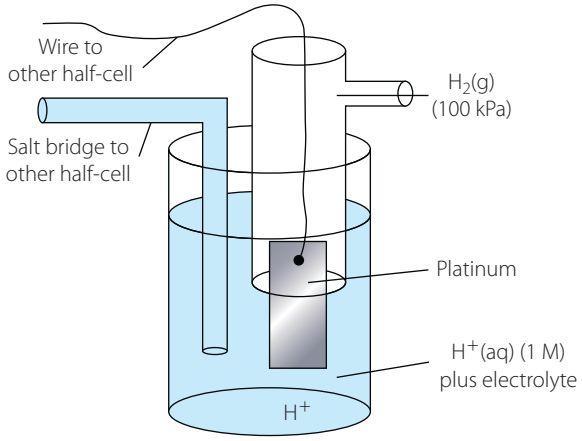
13.1 The relative strength of oxidising and reducing agents

Using a standard to rank oxidising strength

Experiment 10.1.1 on page 134 compared the oxidising strength of a variety of metals when placed in solutions containing cations of other metals. This enabled you to verify the reactivity of different metals. If chemists continued to perform experiments with different combinations of metals and solutions, they could put together a table showing the ability to be oxidised for all elements on the periodic table; however, this would be very time consuming. Instead, chemists compare all other species to a **reference cell**. The reference cell is a hydrogen cell. It contains a solution with hydrogen ions, hydrogen gas and a piece of platinum (called a platinum electrode) to connect this cell to the electric circuit. The hydrogen gas is bubbled into the solution. Platinum is used because it is a good conductor of electricity and it is relatively inert. It is also a catalyst for the dissociation of H_2 gas. Therefore, it provides a pathway for the electric charge, while not taking part in the chemical reaction, as shown in Figure 13.1.1.

reference cell electrode used for reference on half-cell potential reactions



Dr Michael Blaber http://www.mikeblaber.org/

FIGURE 13.1.1 The standard hydrogen electrode

The test cell consists of a solution containing ions of the element being tested and a metal electrode, or the non-metal with a platinum electrode. The test cell and the reference cell are connected by a and external wires to a voltmeter. The salt bridge is used to complete the circuit. The simplest salt bridge is composed of a piece of filter paper soaked in an electrolyte such as potassium nitrate, since it will not react with any of the test or reference solutions. Figure 13.1.2 shows how this equipment is set up.

Conditions for half-cells

To ensure the validity of the data being collected, we must use standard conditions:

- solutions must contain 1 mol L^{-1} of ions of the species being tested
- solutions must be at 25°C
- gases must be at 100 kPa and 25°C.

Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

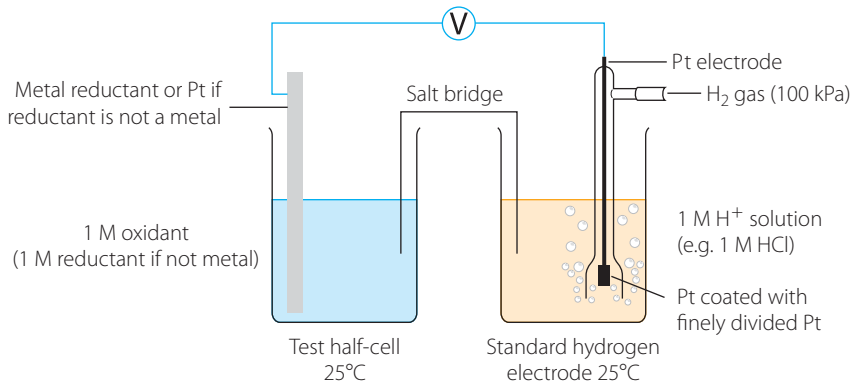


FIGURE 13.1.2 Set-up for determining the standard electrode potentials

Determining standard test half-cell potentials

All values are measured relative to the hydrogen half-cell. The hydrogen half-cell is given a value of 0.00 V. Hence, the reading on the voltmeter becomes the value of the test half-cell. This method has been used to produce a table of standard electrode potentials. Table 13.1.1 shows part of this table for common chemical species.

***E*° values**
electrode potential is a measure of the electrical potential of an electrochemical cell; the standard electrode potential is represented by *E*° values

Elements that are more likely to gain electrons than hydrogen have positive ***E*° values**. Elements that are more likely than hydrogen to lose electrons have negative $E°$ values.

The half-reactions are all written in the same format. They are all written as reduction reactions, hence, it is easy to compare their relative strengths as oxidising or reducing agents.

Table 13.1.1 can be used to compare the relative abilities of metals to be oxidised. Consider magnesium and copper:

$$Mg^{2+} + 2e^- \rightarrow Mg \qquad E° = -2.37\,V$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\,V$$

The Mg half-equation is lower in the table than the Cu half-equation. It has a smaller $E°$ value. Mg is therefore more easily oxidised than Cu.

Similarly, we can compare the relative abilities of non-metals to be reduced. Consider fluorine and bromine:

$$F_2 + 2e^- \rightarrow 2F^- \qquad E° = +2.87\,V$$

$$Br_2 + 2e^- \rightarrow 2Br^- \qquad E° = +1.09\,V$$

The F_2 half-equation is higher in the table than the Br half-equation. It has a larger $E°$ value. F_2 is more easily reduced than Br_2.

Some important generalisations can be made from the table:

- Metals 'prefer' to lose electrons to be oxidised. The most reactive metals, such as sodium, potassium and calcium, are towards the bottom of the table and have the lowest $E°$ values.
- Non-metals 'prefer' to gain electrons to be reduced. The most reactive non-metals, such as fluorine, chlorine and bromine, are towards the top of the table and have the highest $E°$ values.

TABLE 13.1.1 Standard electrode potentials at 25°C

OXIDISED FORM + ne^- → REDUCED FORM		E° (V)
$F_2 + 2e^-$	$\rightarrow 2F^-$	+2.87
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	+1.78
$Au^+ + e^-$	$\rightarrow Au$	+1.69
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	+1.51
$PbO_2 + 4H^+ + 2e^-$	$\rightarrow Pb^{2+} + 2H_2O$	+1.46
$Cl_2 + 2e^-$	$\rightarrow 2Cl^-$	+1.36
$O_3 + H_2O + 2e^-$	$\rightarrow O_2 + 2OH^-$	+1.24
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	+1.23
$O_2 + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	+1.23
$MnO_2 + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	+1.22
$Pt^{2+} + 2e^-$	$\rightarrow Pt$	+1.18
$Ag_2O + 2H^+ + 2e^-$	$\rightarrow 2Ag + H_2O$	+1.17
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	+1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO + 2H_2O$	+0.96
$NO_3^- + 3H^+ + 2e^-$	$\rightarrow HNO_2 + H_2O$	+0.93
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	+0.92
$Hg^{2+} + 2e^-$	$\rightarrow Hg$	+0.85
$NO_3^- + 2H^+ + e^-$	$\rightarrow NO_2 + H_2O$	+0.80
$Ag^+ + e^-$	$\rightarrow Ag$	+0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	+0.77
$O_2 + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	+0.70
$MnO_4^- + 2H_2O + 3e^-$	$\rightarrow MnO_2 + 4OH^-$	+0.60
$I_2 + 2e^-$	$\rightarrow 2I^-$	+0.54
$O_2 + 2H_2O + 4e^-$	$\rightarrow 4OH^-$	+0.40
$Ag_2O + H_2O + 2e^-$	$\rightarrow 2Ag + 2OH^-$	+0.34
$Cu^{2+} + 2e^-$	$\rightarrow Cu$	+0.34
$SO_4^{2-} + 4H^+ + 2e^-$	$\rightarrow H_2SO_3 + H_2O$	+0.17
$Sn^{4+} + 2e^-$	$\rightarrow Sn^{2+}$	+0.15
$S + 2H^+ + 2e^-$	$\rightarrow H_2S$	+0.14
$S_4O_6^{2-} + 2e^-$	$\rightarrow 2S_2O_3^{2-}$	+0.08
$2H^+ + 2e^-$	$\rightarrow H_2$	0.00
$Pb^{2+} + 2e^-$	$\rightarrow Pb$	−0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn$	−0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni$	−0.26
$Co^{2+} + 2e^-$	$\rightarrow Co$	−0.28
$PbSO_4 + 2e^-$	$\rightarrow Pb + SO_4^{2-}$	−0.36
$Cd^{2+} + 2e^-$	$\rightarrow Cd$	−0.40
$Fe^{2+} + 2e^-$	$\rightarrow Fe$	−0.45
$2CO_2 + 2H^+ + 2e^-$	$\rightarrow H_2C_2O_4$	−0.49
$Zn^{2+} + 2e^-$	$\rightarrow Zn$	−0.76
$2H_2O + 2e^-$	$\rightarrow H_2 + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	$\rightarrow Mn$	−1.18
$Al^{3+} + 3e^-$	$\rightarrow Al$	−1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg$	−2.37
$Na^+ + e^-$	$\rightarrow Na$	−2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca$	−2.87
$Ba^{2+} + 2e^-$	$\rightarrow Ba$	−2.91
$K^+ + e^-$	$\rightarrow K$	−2.93
$Li^+ + e^-$	$\rightarrow Li$	−3.04

Oxidising strength increases ↑

Reducing strength increases ↓

WORKED EXAMPLE 13.1.1

In the reaction between potassium dichromate solution, $K_2Cr_2O_7$, and tin(II) nitrate solution, $Sn(NO_3)_2$, which one is the oxidising agent? Write the half-equation associated with each reactant.

ANSWER

1 Identify the reactants in the form that they appear in Table 13.1.1.

$K_2Cr_2O_7$ appears as $\mathbf{Cr_2O_7^{2-}}$

$Sn(NO_3)_2$ appears as $\mathbf{Sn^{2+}}$

2 Write the reduction half-equations as they appear in the table along with their $E°$ values.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad E° = +1.23\,V$$

The $\mathbf{Sn^{2+}}$ is problematic. It could be:

$$\mathbf{Sn^{2+}} + 2e^- \rightarrow Sn \quad E° = -0.14\,V$$

or it could be:

$$Sn^{4+} + 2e^- \rightarrow \mathbf{Sn^{2+}} \quad E° = +0.15\,V$$

Both values are less than the value for the $Cr_2O_7^{2-}$.
Therefore, if the $E°$ value for $Cr_2O_7^{2-}$ is higher than either of the $\mathbf{Sn^{2+}}$ values it must be the one being reduced. $Cr_2O_7^{2-}$ is, therefore, the oxidising agent.
The $\mathbf{Sn^{2+}}$ reactant is being oxidised, so the reduction half-equation is:

$$Sn^{4+} + 2e^- \rightarrow \mathbf{Sn^{2+}} \quad E° = +0.15\,V$$

3 Write the half-equations for each reactant.

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Because the $\mathbf{Sn^{2+}}$ is being oxidised, the reduction half-equation given above must be reversed.

Oxidation: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

$K_2Cr_2O_7$ is the oxidising agent

SECTION REVIEW 13.1

REMEMBERING

1 Define:

- **a** standard electrode potential
- **b** hydrogen electrode
- **c** oxidising agent
- **d** reducing agent.

2 Identify the conditions under which standard electrode potentials are measured.

UNDERSTANDING

3 Explain why chemists have used a reference cell to develop the table of standard electrode potentials.

APPLYING

4 The $E°$ value for the reduction of species A is –1.4V, while the $E°$ value for species B is 10.70V. Justify which of species A or B is more likely to be reduced.

5 **a** In the reaction between iron(II) nitrate solution, $Fe(NO_3)_2$ and hydrogen peroxide solution, H_2O_2, which one is the oxidising agent? Write the half-equation associated with each reactant.

b In the reaction between cadmium, Cd, and lead(II) nitrate solution, $Pb(NO_3)_2$, which one is the reducing agent? Write the half-equations associated with each reactant.

13.2 Calculating standard cell potentials

Table 13.1.1 (page 179) can be used to identify the half-equations for the reactions in a galvanic cell. Remember, all of the half-equations are written as reduction reactions:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E° = +0.34\,V$$

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

However, there must always be an oxidation reaction and a reduction reaction. Hence, one of the reactions will be reversed. Galvanic cells are spontaneous reactions; hence, they have an overall positive cell voltage. In the metal displacement reactions in Chapter 10, you saw that zinc is more likely to be oxidised and copper is more likely to be reduced. This is supported by the $E°$ values for their half-equations. The reduction of zinc ions to zinc solid has a negative $E°$ value. The $E°$ value for the reduction of Cu^{2+} is bigger than the $E°$ value for the reduction of Zn^{2+}. The Cu^{2+} will be reduced, and the zinc half-equation will be reversed so that zinc solid oxidises to form zinc ions. The sign for the $E°$ is also reversed:

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

$E°$ is now positive, which indicates that this reaction will occur spontaneously.

$E°$ for the reduction of copper is positive, which indicates that it will occur spontaneously. Therefore, zinc will be oxidised at the anode and copper will be reduced at the cathode:

$$\text{Anode: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E° = +0.76\,V$$

$$\text{Cathode: } Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E° = +0.34\,V$$

The overall reaction for this galvanic cell can be determined by adding the two equations together. However, before doing this, check that the number of electrons in each half-cell is the same – the number of electrons that is released from the anode is the same as the number of electrons taken in by the cathode – no more, no less. In this example, zinc releases two electrons and copper ions gain two electrons. The electrons are balanced.

Adding the equations together:

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

Since two electrons appear on each side of the equation, they can be cancelled out. The equation becomes:

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

Since the equations are added together, the $E°$ values are also added together:

$$(+0.76) + (+0.34) = +1.10\,V$$

Hence, the final reaction is written as:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq) \quad E° = +1.10\,V$$

The positive sign indicates that the reaction occurs spontaneously. In this reaction, energy is transformed from chemical potential energy to electrical energy.

Figure 13.2.1 shows the copper and zinc cells with the anode, cathode and direction of electron flow through the external circuit clearly labelled.

To summarise:

$$E°_{cell} = \underbrace{E°_{red} + E°_{ox}}_{\text{REDOX}}$$

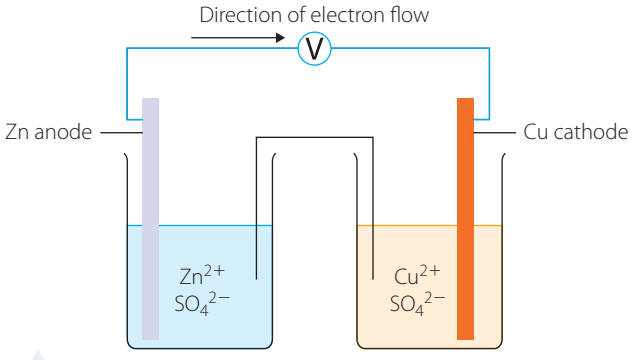


FIGURE 13.2.1 The galvanic cell between zinc and copper

WORKED EXAMPLE 13.2.1

Determine the standard cell potential, E°_{cell}, for a galvanic cell using aluminium and tin electrodes.

ANSWER

1 Identify the relevant equations from Table 13.1.1:

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E^\circ = -0.14\,V$$

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \quad E^\circ = -1.66\,V$$

2 Determine which metal is being oxidised (anode) and which metal is being reduced (cathode).
The standard electrode potential for Al, −1.66 V, is lower than that for Sn, −0.14 V. Therefore, the Al is being oxidised and is the anode while the tin is being reduced and is the cathode.

3 Use $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$ to determine the cell potential, remembering to reverse the sign of the Al cell potential because it is being oxidised.

$$E^\circ_{cell} = -0.14 + (+1.66) = +1.52\,V$$

$$E^\circ_{cell} = +1.52\,V$$

KEY FORMULA

When multiplying the equations, the E° values are not multiplied. The E° values give an indication of the difference in electrical potential energy between the two sides of the equation – this does not change when the quantities in the equation change.

This type of calculation requires the addition of two standard electrode potentials. Given that two electrons are transferred in the Sn half-equation and three electrons are transferred in the Al half-equation, it might be tempting to multiply the E° values to reflect that the same number of electrons are transferred. Remember that when multiplying the equations, E° values are not multiplied.

SECTION REVIEW 13.2

REMEMBERING

1 Define:
- **a** standard cell potential
- **b** positive cell potential
- **c** negative cell potential.

2 List the three steps required to determine the standard cell potential for a galvanic cell.

UNDERSTANDING

3 Mathematically, how can you tell that there is a spontaneous chemical reaction occurring in a galvanic cell?

4 Use Table 13.1.1 to determine the E° value for each of the following half-equations:
- **a** $Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$
- **b** $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$
- **c** $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$.

5 Explain why E° values must not be multiplied when determining the standard cell potential for a galvanic cell.

APPLYING

6 The standard cell potential for a galvanic cell that included a cadmium electrode was found to be +1.91 V. Use Table 13.1.1 to determine the other electrode. Which is the anode?

7 **a** Determine the standard cell potential using a chlorine gas/Pt electrode and an $Fe(NO_3)_2(aq)$/Pt electrode.
- **b** Determine the standard cell potential using a hydrogen gas/Pt electrode and a silver electrode.

13.3 The limitations associated with standard electrode potentials

In Sections 13.1 and 13.2 we showed that the table of standard electrode potentials (Table 13.1.1) was useful when making predictions about whether a redox reaction would occur or not and the voltage produced by redox reactions in a galvanic cell. However, there are some limitations to this method.

Kinetic stability

Consider the oxidation of magnesium by water:

$$Mg(s) + 2H_2O(l) \rightarrow Mg^{2+}(aq) + H_2(g) + 2OH^-(aq)$$

Writing the oxidation and reduction half-equations gives:

$$\text{Oxidation: } Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \quad E^\circ = -(-2.37) = +2.37\,V$$

$$\text{Reduction: } 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^\circ = -0.83\,V$$

$$\text{Using } E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}:$$

$$E^\circ_{cell} = -0.83 + (+2.37) = \mathbf{+1.54\,V}$$

A positive value for cell potential indicates that the reaction will occur. However, the reaction occurs so slowly that it is imperceptible. In *QScience Chemistry Units 1 & 2*, you learned that reactions that have a high activation energy occur very slowly. In this case, the cell potential indicates that a reaction will occur but, in practice, there will be no perceptible reaction because of the high activation energy – this means the reactants are **kinetically stable**. However, you can speed up the rate of this reaction by reacting the magnesium with steam.

kinetically stable where the cell potential indicates that a reaction will occur but, in practice, there will be no perceptible reaction because of the high activation energy

Non-standard conditions

The table of standard reduction potentials is only useful if reactions are conducted under standard conditions:

- solutions must contain 1 mol L^{-1} of ions of the species being tested
- solutions must be at 25°C
- gases must be at 100 kPa and 25°C.

If the solutions used are either very concentrated or very dilute, then the electrode potentials will not be the standard electrode potentials and the magnitude or sign of the cell potential may be different from that predicted under standard conditions.

Consider the reaction between manganese dioxide and hydrochloric acid:

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

Writing the oxidation and reduction half-equations gives:

$$\text{Oxidation: } 2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad E^\circ = -(+1.36)\,V$$

$$\text{Reduction: } MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l) \quad E^\circ = +1.22\,V$$

$$\text{Using } E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}:$$

$$E^\circ_{cell} = +1.22\,V + (-1.36) = \mathbf{-0.14\,V}$$

A negative sign for cell potential indicates that the reaction will *not* occur. However, if we use concentrated hydrochloric acid, the high concentration of chloride ions means that more electrons can

be transferred from these ions. This gives rise to a smaller negative value for the oxidation of chloride ions, resulting in a positive electrode potential. Under these conditions, the reaction *will* occur.

Other issues

If the oxidising and reducing species are very close to each other in the table, it can be difficult to predict whether a reaction will occur under standard conditions.

Consider the reaction between tin and lead(II) nitrate solution:

$$Sn(s) + Pb(NO_3)_2(aq) \rightarrow Sn(NO_3)_2(aq) + Pb(s)$$

$$\text{Oxidation: } Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \quad E^\circ = -(-0.14)\,V$$

$$\text{Reduction: } Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \quad E^\circ = -0.13\,V$$

$$E^\circ_{cell} = -0.13 + (+0.14) = \mathbf{+0.01\,V}$$

According to the cell potential, the reaction should occur but, because of the proximity of the half-equations in the table, the reaction will be very slow.

Some of the more reactive metals can react with oxygen in the air to form an impervious oxide layer. The most notable instance is aluminium. When it is exposed to oxygen and water, the following reaction occurs:

$$4Al(s) + 3O_2(aq) + 6H_2O(l) \rightarrow 4Al(OH)_3(s)$$

$$\text{Oxidation: } Al(s) \rightarrow Al^{3+}(s) + 3e^- \quad E^\circ = -(-1.66)\,V$$

$$\text{Reduction: } O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \quad E^\circ = +0.40\,V$$

$$E^\circ_{cell} = +0.40 + (+1.66) = \mathbf{+2.06\,V}$$

This is a relatively high positive value, and so the reaction should occur. However, aluminium is widely used in the construction industry and is one of the major components in the manufacture of aircraft. The reaction above would prove catastrophic to both of these industries! Fortunately, because aluminium is such a reactive metal, it immediately forms a thin coating of aluminium oxide, Al_2O_3, when exposed to air. This coating prevents any further reactions.

SECTION REVIEW 13.3

REMEMBERING

1 Define:

- **a** kinetic stability
- **b** non-standard conditions.

2 Apart from kinetic stability of reactants and non-standard conditions, what other situations can cause problems when using the table of standard electrode potentials to predict whether or not a redox reaction will occur?

UNDERSTANDING

3 The reaction between potassium dichromate solution, $K_2Cr_2O_7(aq)$ and hydrochloric acid solution, HCl(aq), has a cell potential of –0.13 V. Suggest conditions under which this reaction will have a positive cell potential and will occur.

APPLYING

4 Determine the cell potential for the reaction of hydrogen peroxide, H_2O_2, with itself, according to the equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Explain why, if stored in a brown bottle, hydrogen peroxide can remain stable for up to two years.

13.4 Mathematical representations

The uses of standard electrode potentials

Standard electrode potentials have a number of uses:

- comparing the relative strengths of oxidising and reducing agents
- predicting whether a reaction will occur spontaneously or not
- calculating the standard cell potential of a galvanic cell.

Comparing the relative strengths of oxidising and reducing agents

All standard electrode potentials are measured relative to the hydrogen electrode, which has an $E°$ value of 0.00 V. The half-equation occurring in the standard hydrogen electrode is represented by the equation:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

This reaction is reversible, the direction of the reaction depending on the half-cell it is attached to.

Consider the hydrogen half-cell connected to a zinc half-cell:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E° = 0.00\,V$$
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E° = -0.76\,V$$

The value of −0.76 V for the zinc half-equation indicates that the zinc has a greater tendency to produce electrons than hydrogen. The voltmeter measuring the standard cell potential shows that the zinc electrode is much more negative than the hydrogen electrode. The equilibrium lies more to the left in the zinc half-cell than in the hydrogen half-cell.

Therefore, the zinc has been oxidised and has produced electrons. These electrons build up on the zinc electrode, making it more negative than the hydrogen electrode. Therefore, the zinc is a stronger reducing agent (preferring to lose its electrons) than hydrogen. Hydrogen is a stronger oxidising agent (preferring to gain electrons) than zinc. If the hydrogen half-cell is connected to a copper half-cell:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E° = 0.00\,V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E° = +0.34\,V$$

In this case, the hydrogen half-cell is less positive (more negative) than the copper half-cell. Therefore, hydrogen has a greater tendency to produce electrons than copper. Hydrogen is a stronger reducing agent than copper.

The table of standard electrode potentials is produced in this way – a wide variety of substances are connected to the standard hydrogen electrode and the cell potential measured. The magnitude and sign of the voltage produced indicates the ability of each substance to produce electrons relative to hydrogen.

Therefore, substances with a high (more positive) $E°$ value than hydrogen are the stronger oxidising agents. Those with a low (less positive) $E°$ value than hydrogen are the stronger reducing agents.

Predicting whether a reaction will occur spontaneously

If two half-cells are connected and a current flows, the more negative electrode, as shown in Table 13.1.1, will be oxidised and the more positive electrode will be reduced.

If the zinc half-cell and the copper half-cell are connected:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E° = -0.76\,V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E° = +0.34\,V$$

The more positive value for the zinc half-cell indicates that the zinc is oxidised and the copper ions are reduced, giving an overall reaction represented by:

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

According to the standard electrode potentials given above, this reaction occurs electrochemically. The standard cell potential is given by:

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$$

$$E^\circ_{cell} = +0.34 + (+0.76) = \mathbf{+1.10\,V}$$

This reaction occurs and produces a positive E°_{cell} value. Therefore, if a piece of zinc were added to a test tube containing a copper(II) nitrate solution, the above reaction would occur.

If a piece of copper were added to a zinc sulfate solution, the reaction would occur according to the equation:

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

The standard cell potential would be:

$$E^\circ_{cell} = -0.76 + (-0.34) = \mathbf{-1.10\,V}$$

This reaction would produce a negative E°_{cell} value. Therefore, if a piece of copper were placed into a zinc(II) nitrate solution, there would be no reaction.

Therefore, a reaction with a *positive* E°_{cell} value occurs *spontaneously*.

WORKED EXAMPLE 13.4.1

Predict whether cadmium metal will displace manganese from a solution of manganese(II) nitrate solution according to the equation:

$$Cd(s) + Mn(NO_3)_2(aq) \rightarrow Cd(NO_3)_2(aq) + Mn(s)$$

ANSWER

1 Write the relevant half-equations from Table 13.1.1:

$$Cd^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E^\circ = -0.04\,V$$

$$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \quad E^\circ = -1.18\,V$$

2 From the equation in the question, decide which metal is being oxidised and which is being reduced:

$$\text{Oxidation: } Cd(s) \rightarrow Cd^{2+}(aq) + 2e^- \quad E^\circ = -(-0.04)\,V$$

$$\text{Reduction: } Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \quad E^\circ = -1.18\,V$$

3 Calculate E°_{cell} using $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$

$$E^\circ_{cell} = -1.18 + (+0.04) = \mathbf{-1.14\,V}$$

The negative E°_{cell} value indicates that this reaction will *not* occur spontaneously.
The reaction is not spontaneous

Calculating the standard cell potential of a galvanic cell

Any spontaneous redox reaction can be used to produce a galvanic cell. The half-cell with the oxidising agent in it will be the one with the more positive standard electrode potential. The half-cell with the reducing agent in it will be the one with the more negative standard electrode potential.

WORKED EXAMPLE 13.4.2

Calculate the cell potential for the galvanic cell represented by the equation:

$$Fe(s) + Sn(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Sn(s)$$

ANSWER

1 Write the relevant half-equations from Table 13.1.1:

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \quad E^\circ = -0.45\,V$$

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E^\circ = -0.14\,V$$

2 From the equation in the question, decide which metal is being oxidised and which is being reduced:

$$\text{Oxidation: } Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad E^\circ = -(-0.45)\,V$$

$$\text{Reduction: } Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \quad E^\circ = -0.14\,V$$

3 Calculate E°_{cell} using $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$

$$E^\circ_{cell} = -0.14 + (+0.45) = +\mathbf{0.31\,V}$$

$$E^\circ_{cell} = +0.31\,V$$

WORKED EXAMPLE 13.4.3

Calculate the cell potential for the galvanic cell represented by the equation:

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

ANSWER

1 Write the relevant half-equations from Table 13.1.1:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(s) \quad E^\circ = +0.77\,V$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+} + 7H_2O(l) \quad E^\circ = +1.23\,V$$

2 From the equation in the question decide which metal is being oxidised and which is being reduced:

$$\text{Oxidation: } Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \quad E^\circ = -(+0.77)\,V$$

$$\text{Reduction: } Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+} + 7H_2O(l) \quad E^\circ = +1.23\,V$$

3 Calculate E°_{cell} using $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$

$$E^\circ_{cell} = +1.23 + (-0.77) = +\mathbf{0.46\,V}$$

$$E^\circ_{cell} = +0.46\,V$$

TRY THESE YOURSELF

a Calculate the cell potential for the galvanic cell represented by the equation:

$$10Cl^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5Cl_2(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$$

b A half-cell consists of a piece of platinum dipping into a mixture of tin(II) nitrate and tin(IV) nitrate solutions. To what half-cell does it need to be connected to produce a galvanic cell with an EMF of 2.52 V?

SECTION REVIEW 13.4

UNDERSTANDING

1 Explain why an oxidising agent has a higher standard electrode potential than that of the hydrogen electrode.

2 List the following elements in order of decreasing reducing strength:

$$Fe, Co, Br_2, Ag, O_2, Cu, Cl_2, Hg.$$

APPLYING

3 **a** Predict whether a spontaneous reaction will occur between cobalt and acidified potassium permanganate solution, according to the equation:

$$5Co(s) + 2MnO_4^- + 16H^+(aq) \rightarrow 5Co^{2+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l).$$

b Will potassium iodide crystals decolourise bromine water?

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

CHAPTER REVIEW QUESTIONS

CATEGORY QUESTIONS

1 Use the table of standard electrode potentials to decide which of the following reactions will occur spontaneously:

a $Hg(l) + Zn(NO_3)_2(aq) \rightarrow Hg(NO_3)_2(aq) + Zn(s)$

b $3Pb(s) + 8HNO_3(aq) \rightarrow 3Pb(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

c $Au(s) + 4HNO_3(aq) \rightarrow Au(NO_3)_3(aq) + NO(g) + 2H_2O(l)$

d $5C_2O_4^{2-}(aq) + 16H^+(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(aq)$

EVIDENCE QUESTIONS

2 A scientist carried out a number of experiments in which strips of unknown metals were dipped into solutions of the unknown metal nitrates.

The standard electrode potentials of the unknown metals are given in the table below.

OXIDISED FORM	REDUCED FORM	E° (V)
X^{2+}	X	−2.11
Q^{2+}	Q	−1.14
T^{2+}	T	+0.12
R^{2+}	R	+1.17
M^{2+}	M	−2.19
G^{2+}	G	−1.62

Use the table of standard electrode potentials to predict whether each combination will react spontaneously.

Indicate your decision in each case with a ✓or a X.

Copy the table below in your workbook. For each ✓, write the balanced equation and calculate the cell potential.

	$X(NO_3)_2(aq)$	$Q(NO_3)_2(aq)$	$T(NO_3)_2(aq)$	$R(NO_3)_2(aq)$	$M(NO_3)_2(aq)$	$G(NO_3)_2(aq)$
X						
Q						
T						
R						
M						
G						

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END-OF-CHAPTER EXAM

End-of-chapter test

1 Which one of the following is *not* used as part of a standard hydrogen electrode?

A H^+ ions

B Pt

C OH^- ions

D hydrogen gas

2 Which one of the following is the strongest oxidising agent?

A Br_2

B Cu^{2+}

C Ag^+

D Cu

3 For the galvanic cell composed of the Sn^{2+}, Sn^{4+} and Co, Co^{2+} half-cells, which one of the following identifies the anode and gives the correct cell potential?

A Sn, +0.43 V

B Co, +0.13 V

C Sn, –0.43 V

D Co, +0.43 V

4 Which one of the following represents a non-spontaneous redox reaction?

A $Pb(s) + 2AgNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + 2Ag(s)$

B $Pt(s) + Cu(NO_3)_2(aq) \rightarrow Pt(NO_3)_2(aq) + Cu(s)$

C $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

D $6I^-(aq) + 2MnO_4^- + 4H_2O(l) \rightarrow 3I_2(aq) + 2MnO_2(aq) + 8OH^-(aq)$

5 If the cell potential of a galvanic cell has a negative sign, what can be said of the reaction it represents?

6 A galvanic cell is constructed using a strip of silver dipping into a silver nitrate solution and a strip of platinum dipping into a mixture of iron(II) nitrate and iron(III) nitrate solutions. Which strip is the cathode?

7 The galvanic cell represented by the equation:

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

has a cell potential of –0.14 V.

What changes could be made to the system to produce a positive cell voltage?

8 An experiment was designed to compare the relative electrode potentials of five unknown metals, T, Q, M, G and L. For each experiment, a galvanic cell was constructed using a pair of metals and the voltage measured. The experimental set-up is shown in Figure 13.5.1.

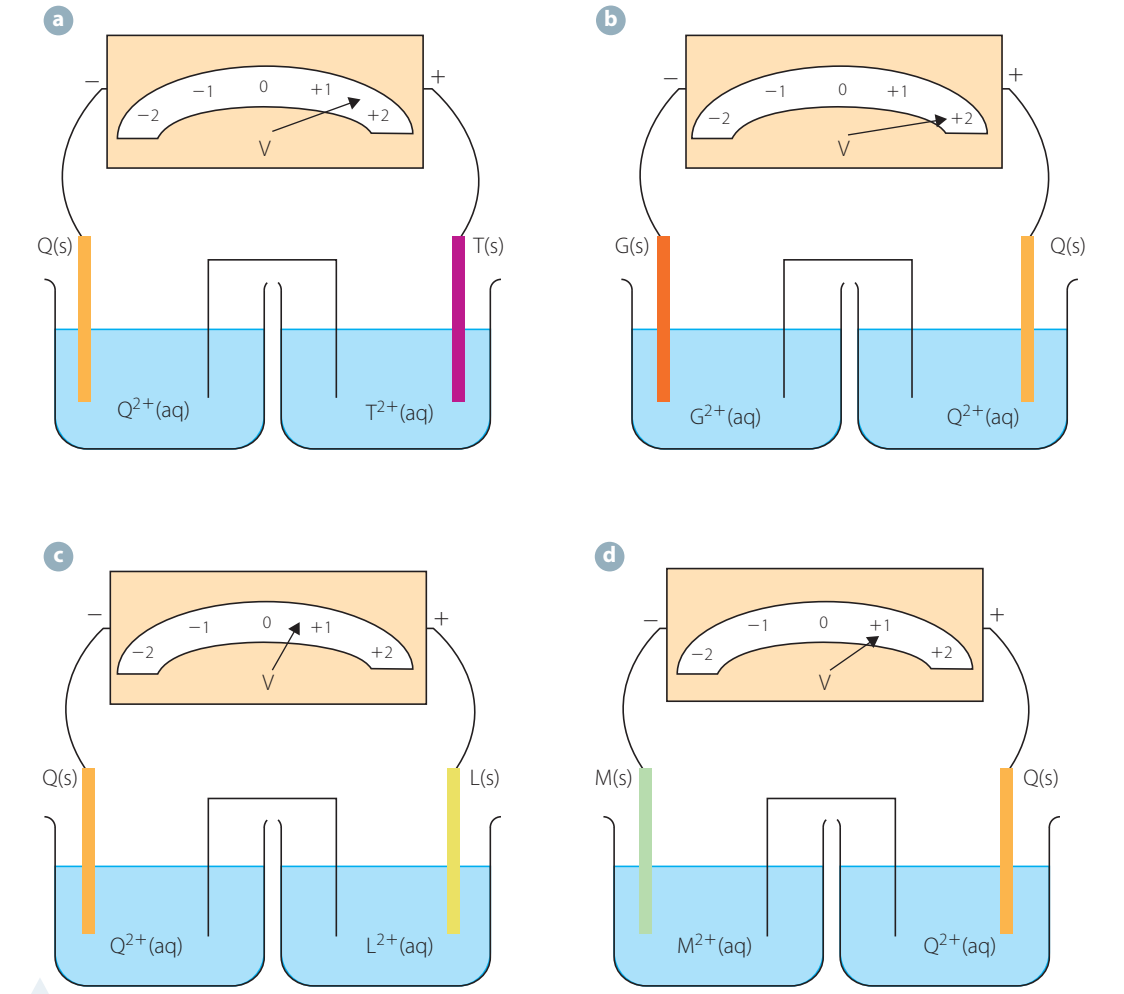

FIGURE 13.5.1 Set-up of an experiment to determine relative electrode potentials of five unknown metals.

Use this information to construct a table of electrode potentials, choosing an appropriate half-cell as the reference half-cell.

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14 ELECTROLYTIC CELLS

Introduction

During electrolysis, electrical energy is converted to chemical potential energy. Since electrical energy is used to produce a chemical reaction, it is not spontaneous. Electrolysis is used to force chemical reactions to occur. As discussed, batteries are galvanic cells, they convert chemical energy to electrical energy; but some batteries are rechargeable – electrical energy helps us to use them again.

Stimulus questions

How does a rechargeable battery 'recharge'?

When an electric current is passed through a sodium chloride solution, the products could be very dangerous. Is there a way that we could predict the products from this process?

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14.1 Electrolytic cells

Electrolysis is used in the mining industry when metals are extracted from their ores. The metals are the valuable commodities, not the ores. Hence, the industrial process of electrolysis is used to extract the metal.

Most metals are not found in their pure form. They are found in mineral compounds. Table 14.1.1 shows examples of common metals and the mineral compounds they are extracted from.

TABLE 14.1.1 Common metals and some of their minerals

METAL	NAME AND FORMULA OF MINERAL
Copper	Chalcopyrite, $CuFeS_2$; Malachite, $Cu_2(CO_3)(OH)_2$
Iron	Haematite, Fe_2O_3
Zinc	Sphalerite, (Zn,Fe)S
Silver	Argentite, Ag_2S
Aluminium	Generally bauxite, which is a mixture of gibbsite, $Al_2O_3.3H_2O$, and boehmite, $Al_2O_3.H_2O$
Lead	Galena, PbS

electrolysis
an electric current is passed through a substance to create a chemical change

Therefore, to extract the metal from the ore, it has to undergo several physical and chemical processes. These processes usually do not occur spontaneously; energy has to be put in to force them to occur. One of the chemical processes used is **electrolysis** where an electric current is used to create a chemical change. Electrolytic cells can be constructed in a single container – the two half-reactions are able to occur in the single container, since it is the anions and cations in the ionic compound or solution that are undergoing the reaction.

PRACTICAL ACTIVITY 14.1.1

Extracting copper with electrolysis

AIM

To extract copper from copper(II) carbonate using electrolysis.

EQUIPMENT

- 6 g copper(II) carbonate powder, $CuCO_3$
- Spatula
- Electronic balance
- 50 mL of 1 mol L^{-1} sulfuric acid, H_2SO_4
- 100 mL beaker
- Two graphite electrodes
- Small piece of Blu Tack
- Powerpack
- Two electrical wires with banana plugs
- Two alligator clips, one to be placed on each electrical wire
- Waste bottle for heavy metals

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WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.

RISK ASSESSMENT

PROCEDURE

Part A

1. Weigh out about 6 g of copper(II) carbonate into the 150 mL beaker.
2. Pour about 50 mL of 1 mol L^{-1} sulfuric acid into the beaker and stir it.
3. Record your observations.

Part B

4. Stand the two graphite electrodes in the beaker, securing them to the side with Blu Tack, as shown in Figure 14.1.1.
5. Attach the electrical wires to the electrodes and to the DC terminals of the powerpack.
6. Set powerpack to 6 V and turn it on.
7. Record your observations.
8. Dispose of the copper(II) sulfate by pouring it into the heavy metals waste bottle. Do not pour it down the drain.

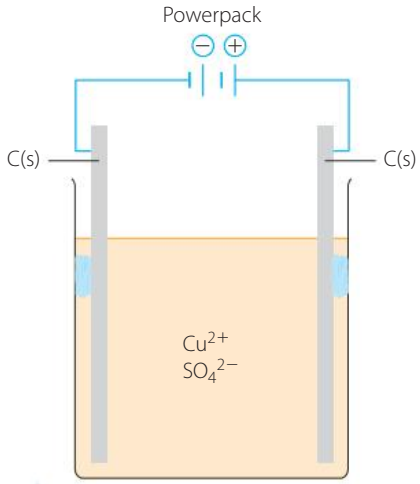


FIGURE 14.1.1 Set-up for the electrolysis of copper(II) sulfate solution

RESULTS

Record all observations for both parts of the experiment.

ANALYSIS OF RESULTS

1. How could you tell that a chemical reaction occurred when sulfuric acid was added to copper(II) carbonate?
2. Write a balanced equation for the reaction that occurred when sulfuric acid was added to copper(II) carbonate.
3. How could you tell that a chemical reaction occurred when the copper(II) solution was electrolysed?
4. Write a half-equation for the reduction of the copper(II) ions in solution.

DISCUSSION

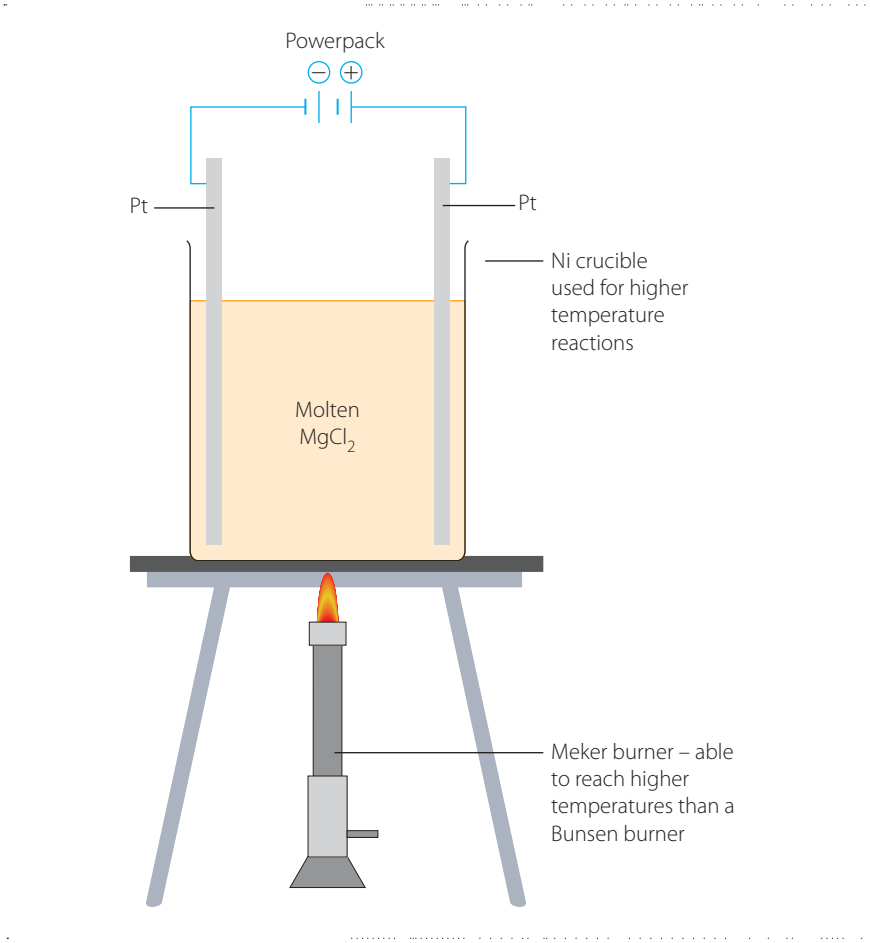
1. Discuss how you could tell when the reaction was complete.
2. How could you have increased the rate at which the electrolysis reaction occurred?
3. Why was the powerpack set to 6 V? Would this reaction have occurred at a lower voltage?

In Practical activity 14.1.1, you saw an electrolysis reaction where one of the products was copper metal. While it is a simple experiment to perform, there is a great deal of chemistry to understand. An aqueous solution of a copper salt was used, and this contains some complex chemistry because of the presence of water. So, rather than discuss aqueous solutions first, we will start the explanation of electrolysis using molten salts.

Electrolysis of molten salts

Molten salts are the liquid form of ionic compounds, such as magnesium chloride. Creating molten salts requires heating to temperatures above 700°C; for example, the melting point of magnesium chloride is 714°C. This is much higher than can be achieved in a school laboratory. However, the advantage of using molten salts is that no competing reactions occur. This is the method used industrially for extracting magnesium and sodium from their salts.

FIGURE 14.1.2
Set-up for electrolysis of molten magnesium chloride



Molten magnesium chloride contains Mg^{2+} and Cl^- ions, so these are the reactants for electrolysis. Electrolysis is an electrochemical reaction, so there must be an anode reaction and a cathode reaction. Remember: oxidation occurs at the anode and reduction occurs at the cathode.

$$\text{Anode:} \quad 2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

$$\text{Cathode:} \quad Mg^{2+}(l)\, 2e^- \rightarrow Mg(l)$$

We can use Table 13.1.1 (page 179) to find the $E°$ values for these half-equations.

$$\text{Anode:} \quad 2Cl^-(l) \rightarrow Cl_2(g) + 2e^- \quad E° = -1.36\,V$$

$$\text{Cathode:} \quad Mg^{2+}(l)\, 2e^- \rightarrow Mg(l) \quad E° = -2.37\,V$$

The electrons are balanced, and the equations and $E°$ values are added together to determine the overall equation and voltage for this electrolytic cell. Overall reaction:

$$Mg^{2+}(l) + 2Cl^-(l) \rightarrow Cl_2(g) + Mg(l) \quad E° = -3.73\,V$$

The negative sign for the voltage indicates that this is not a spontaneous reaction. This is the approximate voltage that must be applied to the system; that is, it must be provided by a battery or powerpack. Since the species present are not in standard conditions, this voltage is a guide only.

Electrolysis of aqueous solutions

Aqueous solutions contain ionic salts dissolved in water. An advantage of these electrolysis reactions over electrolysis of molten salts is that they can occur at room temperature.

Consider the electrolysis of concentrated copper(II) chloride solution (Figure 14.1.3).

Using inert carbon electrodes, the products of this experiment are chlorine gas, produced at the anode, and a thin layer of pure copper that sticks to the surface of the cathode. This is the basis for some extremely important industrial applications.

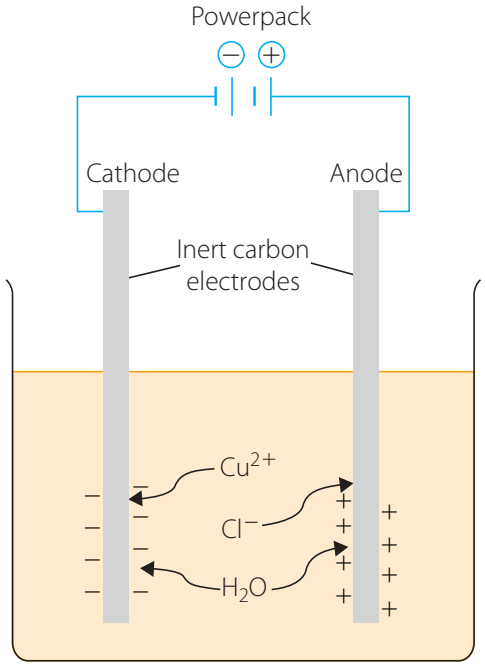


FIGURE 14.1.3 Set-up for the electrolysis of concentrated copper(II) chloride solution

Electroplating

Electroplating is an electrochemical process that enables a thin coating of a metal to be deposited on a metal object. The applications of this process include:

- Jewellery: gold and silver jewellery can be manufactured much more cheaply and made more durable by plating a hard metal object with a metal such as gold or silver.
- Car parts: metals such as chromium and nickel are plated onto car parts to provide low-friction surfaces that enhance a car's performance. These metals also protect the car parts and can make them look attractive.
- Cutlery: plating knives, forks and spoons with silver or gold can increase their durability and make them look more attractive.

The set-up for silver-plating a metal fork is shown below:

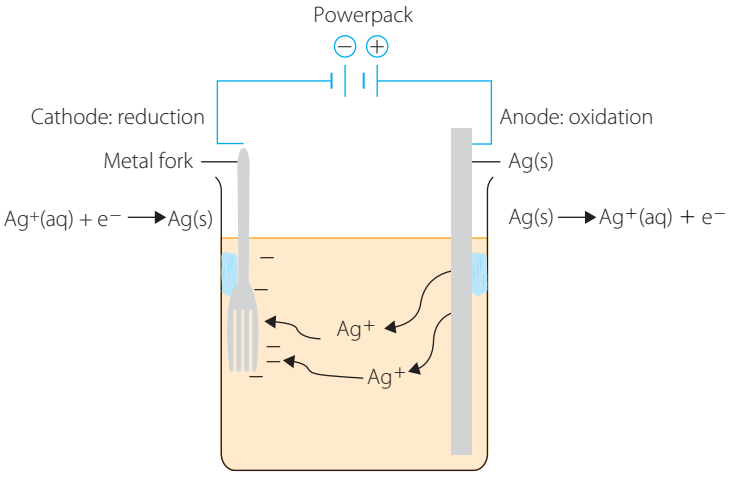


FIGURE 14.1.4 Set-up for silver-plating a metal fork

In this case, the anode is a piece of silver. During electrolysis the silver is oxidised to silver ions. These silver ions move into the silver nitrate electrolyte solution and migrate towards the metal fork cathode where they are reduced to silver metal. This forms a thin layer of silver on the fork.

Electrorefining copper

Electrorefining is used industrially to purify copper. This method of electrolysis is the final step in extracting copper from its ore to produce the pure copper necessary for electrical applications. The process starts with 'blister copper', which is about 98 per cent pure copper from the smelting process. The blister copper is at the anode. A sample of pure copper, about 99.9 per cent pure, is the cathode. The copper from the anode is oxidised and goes into solution. Pure copper is deposited on the cathode. The impurities either stay in solution or fall to the bottom of the electrolytic cell.

PRACTICAL ACTIVITY 14.1.2

Electroplating

Electroplating is an important industrial process. In this activity, you can model the process.

AIM

To silver-plate a piece of copper using electrolysis

MATERIALS

- 20 mL of a saturated potassium nitrate, KNO_3
- 30 mL of a 0.1 mol L^{-1} silver nitrate solution, $AgNO_3$
- Stirring rod
- Sandpaper
- Warm solution of detergent
- 100 mL beaker
- One graphite electrode
- One strip of copper
- Powerpack
- Two electrical leads with banana plugs
- Two alligator clips, one to be placed on each electrical wire
- Waste bottle for heavy metals

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Silver nitrate stains skin.	Rinse the piece of copper under water before touching it.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1 While stirring, add the saturated potassium nitrate to 30 mL of the silver nitrate solution until the precipitate that forms is dissolved.

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2 Clean the piece of copper using sandpaper, then wash in a warm solution of detergent and rinse thoroughly.
3 Attach the piece of copper to the negative terminal and the graphite electrode to the positive terminal of the powerpack.
4 Set the powerpack to 4 V and turn it on.
5 Record observations.
6 Dispose of the copper(II) sulfate by pouring it into the heavy metals waste bottle. Do not pour it down the drain.

RESULTS

Record all of your observations.

ANALYSIS

1 Identify the anode in this electrolytic cell.
2 Identify the cathode in this electrolytic cell.
3 Write the half-equation for the reaction occurring at the anode.
4 Write the half-equation for the reaction occurring at the cathode.

DISCUSSION

1 Write the overall equation for the electroplating reaction.
2 Justify why the metal to be electroplated onto the object is sometimes used as the anode instead of using an inert electrode such as graphite.
3 Explain why electroplating is used instead of using pure metal. For example, why would a jeweller use silver-plating instead of pure silver?
4 Relate your experimental method to the industrial use of electrolysis in electroplating.

SECTION REVIEW 14.1

REMEMBERING

1 Write the oxidation and reduction half-equations for the reactions occurring at the anode and cathode during the electrolysis of:
   a concentrated copper(II) bromide solution
   b molten copper(II) bromide.

UNDERSTANDING

2 Why are inert electrodes such as carbon and platinum used in electrolysis?

APPLYING

3 Draw a diagram of the apparatus used for electrorefining copper.

14.2 Predicting and explaining products

When carrying out the electrolysis of molten binary salts (those that contain the ions of just two elements) it is easy to predict the products – they are simply the elements produced by the ions in the salt. Molten sodium chloride would produce sodium metal and chlorine gas, molten aluminium oxide would produce aluminium metal and oxygen gas, and so on.

Predicting and explaining products from the electrolysis of aqueous solutions

Aqueous solutions contain ionic salts dissolved in water. Although electrolysis of aqueous solutions is easier to conduct in the laboratory, the chemistry is a little more complicated because as well as the ions in the electrolyte, water is also present and it could be electrolysed in place of the ions. There are competing reactions occurring and you need to be able to determine which is the main reaction occurring at each electrode.

You need to consider two factors when determining which chemical reaction occurs at the anode and cathode:

1. the nature of the electrolyte
2. the concentration of the electrolyte.

Nature of the electrolyte

The electrolyte is the solution that is used in the electrolytic cell. Different solutions have different ions, which have different $E°$ values for their half-equations. The water could also be oxidised at the anode and/or reduced at the cathode. We will use Table 13.1.1 (page 179) to assist with understanding the chemistry. To ensure that we are only investigating the effect of the nature of the electrolyte, the other factors must be kept constant. Therefore, the concentration of solution for all examples will be kept constant and the electrodes will be kept constant. Graphite electrodes will be used for each of these examples. Graphite electrodes are used in school experiments because they conduct electricity, they do not take part in the reaction (they are inert) and they are relatively cheap.

Consider a solution of copper(II) bromide, $CuBr_2$. The ions $Cu^{2+}(aq)$ and $Br^-(aq)$ are present, since it is a solution. The half-equations for these ions can be determined from Table 13.1.1.

$$\text{Oxidation:} \quad 2Br^-(aq) \rightarrow Br_2(l) + 2e^- \quad E° = -1.09\,V$$

$$\text{Reduction:} \quad Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E° = +0.34\,V$$

However, as stated earlier, water is also present. When water is electrolysed, it decomposes to form hydrogen gas and oxygen gas. The half-equations for the oxidation and reduction of water to form oxygen and hydrogen, respectively, can be determined from Table 13.1.1.

$$\text{Oxidation:} \quad 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E° = -1.23\,V$$

$$\text{Reduction:} \quad 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E° = -0.83\,V$$

Therefore, there are two possible oxidation reactions at the anode:

$$2Br^-(aq) \rightarrow Br_2(l) + 2e^- \quad E° = -1.09\,V$$

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

There are also two possible reduction reactions at the cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E° = +0.34\,V$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \; E° = -0.83\,V$$

For the electrolytic cell for the aqueous solution of copper(II) bromide where graphite electrodes are used, the half-equations are:

$$2Br^-(aq) \rightarrow Br_2(l) + 2e^- \; E° = -1.09\,V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \; E° = +0.34\,V$$

KEY FORMULA

The reaction that is more likely to occur is the one that requires the least input of energy; that is, the least negative voltage.

- At the anode, the preferred reaction is the oxidation of the bromide ions since its voltage is less negative than that of the oxidation of water.
- At the cathode, the preferred reaction is the reduction of copper since its voltage is less negative than that of the reduction of water.

The electrons are balanced, and then the equations and $E°$ values are added together to determine the overall reaction and cell voltage for this electrolytic cell. So the overall reaction is:

$$Cu^{2+}(aq) + 2Br^{-}(aq) \rightarrow Br_2(l) + Cu(s) \quad E° = -0.75\,V$$

Therefore, more than 0.75 V must be supplied for this reaction to occur.

Consider a solution of copper(II) chloride, $CuCl_2$. The ions $Cu^{2+}(aq)$ and $Cl^{-}(aq)$ are present since it is a solution. Water is also present. Therefore, the possible reactions for both the anode and cathode reactions are determined.

- Oxidation occurs at the anode:

$$2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-} \quad E° = -1.36\,V$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-} \quad E° = -1.23\,V$$

- Reduction occurs at the cathode:

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E° = +0.34\,V$$

$$2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq) \quad E° = -0.83\,V$$

The preferred reactions are those with the least negative voltage at each electrode. Water will be oxidised at the anode and copper will be reduced at the cathode.

$$\text{Anode:} \quad 2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-} \quad E° = -1.23\,V$$

$$\text{Cathode:} \quad Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E° = +0.34\,V$$

The electrons are balanced, and then the equations and $E°$ values are added together to determine the overall reaction and cell voltage for this electrolytic cell. So the overall reaction is:

$$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 2Cu(s) \quad E° = -0.89\,V$$

Polyatomic anions, such as sulfate (SO_4^{2-}), nitrate (NO_3^{-}) and phosphate (PO_4^{3-}), are much more stable than monatomic anions. Hence, much larger voltages are required for them to be oxidised. Thus, when polyatomic anions are present in solution, the water will always be oxidised preferentially to the polyatomic anions, since it has a less negative voltage.

So, the overall reaction for the electrolysis of a copper(II) sulfate solution, $CuSO_4$, would be the same as the equation above:

$$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 2Cu(s) \quad E° = -0.89\,V$$

Concentration of the electrolyte

In the electrolysis of aqueous solutions, there are competing reactions at both the anode and the cathode. The reaction at each electrode that has the lowest negative voltage – the reaction where the least voltage must be applied – is the favoured reaction. This is almost always true. However, where the $E°$ values for the competing reactions are very similar, we may need to consider the concentration of the solution.

Consider the previous example of copper(II) chloride, $CuCl_2$. At the cathode, there is a large difference between the $E°$ values for the reduction of copper(II) ions and the reduction of water. This indicates that the reduction of copper(II) ions is much more likely to occur than the reduction of water. Hence, concentration of the solution does not affect the preferred reaction for this electrode.

However, at the anode, there is only a very small difference between the $E°$ values for the oxidation of chloride and the oxidation of water. This indicates that there is little difference in the likelihood of each of these reactions occurring. Hence, the concentration of the solution does affect the preferred reaction for this electrode. In a more concentrated solution, there are more chloride ions in the same volume of solution, so it is more likely that the chloride ions will be oxidised. In a more dilute solution, where there are fewer chloride ions in the same volume of solution, it is less likely that the chloride ions will be oxidised. The water will be oxidised in this case.

So, in more dilute chloride solutions, the anode reaction will be:

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

while in more concentrated chloride solutions, the anode reaction will be:

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

This is the most common example of where the concentration of the solution can affect the preferred reaction occurring at one of the electrodes. The other, less common, example is where zinc solutions are used.

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

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E° = -0.83\,V$$

Again, the $E°$ values are very close together which indicates that each of the reactions is equally likely to occur. Generally, the reduction of zinc ions would be the preferred reaction since it has the less negative $E°$ value; that is, less voltage must be applied for this reaction to occur. However, for very dilute zinc solutions, there would be very few zinc ions present in the solution. In this case, water would be reduced.

SECTION REVIEW 14.2

REMEMBERING

1 Which factors do you need to consider when attempting to predict the products of the electrolysis of an aqueous solution?

UNDERSTANDING

2 Why is the electrolysis of an aqueous solution more complicated than the electrolysis of a molten substance?

3 When electrolysis of aqueous solutions of salts containing polyatomic ions such as nitrates, carbonates and sulfates is carried out, why is oxygen gas always produced at the anode?

APPLYING

4 A student set up an electrolysis experiment using a dilute solution of aqueous iron(II) iodide and inert electrodes.

- **a** Identify the anode reaction.
- **b** Identify the cathode reaction.
- **c** Outline the observations for each electrode.
- **d** Determine the voltage that would need to be applied to operate this electrolytic cell.

5 A student set up an electrolysis experiment using a dilute solution of aqueous calcium chloride and inert graphite electrodes.

- **a** Identify the anode reaction.
- **b** Identify the cathode reaction.
- **c** Outline the observations for each electrode.
- **d** How could you identify the products forming at each electrode?
- **e** Determine the voltage that would need to be applied to operate this electrolytic cell.

14.3 Describing an electrolytic cell

The reactions used in electrolysis are non-spontaneous, that is, they do not occur naturally. Molten magnesium chloride does not naturally decompose into magnesium and chlorine. Sodium chloride solution does not naturally decompose into sodium and chlorine. For these reactions to occur, there must be an external power source to provide the necessary energy.

This energy is provided by an electrical current in an electrolytic cell.
Electrolytic cells can be grouped into two main categories:

1. those used for the electrolysis of molten salts
2. those used for the electrolysis of aqueous solutions.

The electrolytic cell used for molten salts

The electrolysis of molten salts was introduced earlier in this chapter, but a more detailed description of the cell used may be useful. For example, consider the electrolysis of molten sodium chloride.

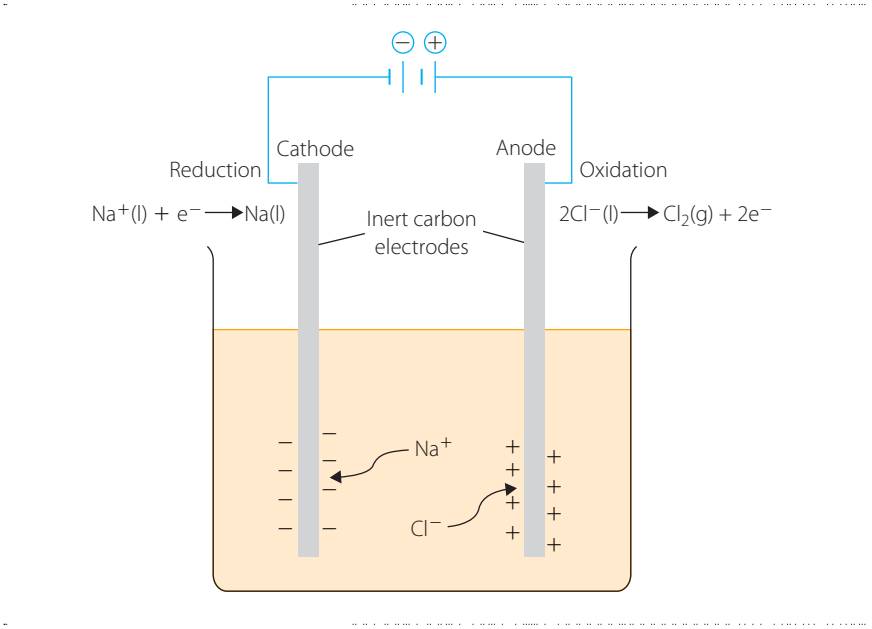


FIGURE 14.3.1
Set-up for the electrolysis of molten sodium chloride

Electrolysis of molten sodium chloride occurs as follows:

1. The sodium chloride is placed in a crucible.
2. Carbon electrodes are placed into the crucible and connected to a power supply.
3. The crucible is heated to the melting point of sodium chloride. The Na^+ ions and Cl^- ions separate and move around in the liquid state. This movement of ions enables electrical conduction to take place.
4. The electrode attached to the negative terminal of the power supply is the cathode. Electrons move from the power supply and enter the cathode, making it negatively charged.
5. The positively charged sodium ions are attracted to the negatively charged cathode and migrate towards it.
6. As the sodium ions encounter the cathode they accept an electron and undergo reduction:

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

7. The electrode attached to the positive terminal of the power supply is the anode.
8. The negatively charged chloride ions are attracted to the positively charged anode and migrate towards it.
9. As the chloride ions encounter the anode they release electrons and undergo oxidation:

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

10 So the overall reaction is:

$$2Na^+(l) + 2Cl^- \rightarrow 2Na(l) + Cl_2(g)$$

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = -2.71 + (-1.36) = -4.07\,V$$

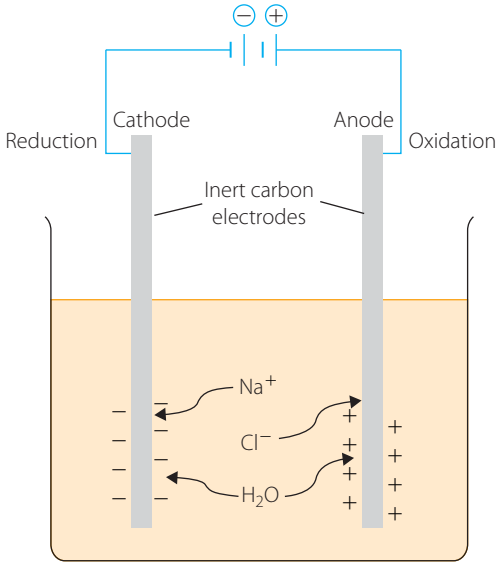
Therefore 4.07 V must be supplied to the cell by an external power source such as a battery or powerpack to enable this reaction to occur. Because of the non-standard conditions (the extreme temperature), the cell voltage of −4.07 V can only be regarded as approximate.

The electrolytic cell used for aqueous solutions

Because of the presence of water, the products from the electrolysis of aqueous solutions depend upon the nature and the concentration of the electrolyte.

Consider the electrolysis of a dilute sodium chloride solution:

FIGURE 14.3.2
Set-up for the electrolysis of a dilute sodium chloride solution



Electrolysis of a dilute sodium chloride solution occurs as follows.

1 The sodium chloride solution is placed in a beaker.

2 Carbon electrodes are placed into the beaker and connected to a power supply.

3 The Na^+ ions and Cl^- ions move around in the aqueous state. This movement of ions enables electrical conduction to take place.

4 The electrode attached to the negative terminal of the power supply is the cathode. Electrons move from the power supply and enter the cathode, making it negatively charged.

5 The positively charged sodium ions are attracted to the negatively charged cathode and migrate towards it.

6 Two possible reactions can occur at the cathode:

$$Na^+(aq) + e^- \rightarrow Na(s) \quad E^\circ = -2.71\,V$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^\circ = -0.83\,V$$

7 The preferred reaction is the one with the *least* negative voltage. Therefore, water will be reduced.

8 The electrode attached to the positive terminal of the power supply is the anode.

9 The negatively charged chloride ions are attracted to the positively charged anode and migrate towards it.

10 Two possible reactions can occur at the anode:

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

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E^\circ = -(+1.23) = -1.23\,V$$

11 The preferred reaction is the one with the *least* negative voltage. Therefore, water will be oxidised.

12 So, the overall reaction is:

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

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = -0.83 + (-1.23) = -2.06\,V$$

Therefore 2.06 V must be supplied to the cell by an external power source such as a battery or powerpack to enable this reaction to occur.

WORKED EXAMPLE 14.3.1

With reference to Table 13.1.1 (page 179), predict the products formed from the electrolysis of a concentrated sodium chloride solution. Write an equation for the overall reaction and determine the voltage required to enable this reaction to occur.

ANSWER

1 Identify the relevant electrode reactions:

$$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq) \quad E^\circ = -2.19\,V$$

$$\text{Cathode: } Na^+(aq) + e^- \rightarrow Na(s) \quad E^\circ = -2.71\,V$$

or

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^\circ = -0.83\,V$$

$$\text{Anode: } 2Cl^-(aq) \rightarrow Cl_2(g) + 2e \quad E^\circ = -(+1.36) = -1.36\,V$$

or

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E^\circ = -(+1.23) = -1.23\,V$$

2 Use the fact that the reaction with the least negative E° value is the preferred reaction to determine which will occur:

$$\text{Cathode: } 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^\circ = -0.83\,V$$

$$\text{Anode: } 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E^\circ = -(+1.23) = -1.23\,V$$

but, since the two E° values at the anode are so similar and Cl^- ions are in such high concentration, it is $Cl_2(g)$ that is produced.

$$\text{Anode: } 2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad E^\circ = -(+1.36) = -1.36\,V$$

3 Add the half-equations to give the overall equation:

$$2H_2O(l) + \cancel{2e^-} + 2Cl^-(aq) \rightarrow H_2(g) + 2OH^-(aq) + Cl_2(g) + \cancel{2e^-}$$

4 Use $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$ to determine the voltage required:

$$E^\circ_{cell} = -0.83\,V + (-1.36) = -2.19\,V$$

$$-2.19\,V$$

SECTION REVIEW 14.3

UNDERSTANDING

1. When electrolysing aqueous solutions, what principle determines the products formed at each electrode?
2. Explain why, when electrolysing concentrated and dilute chloride solutions, the concentrated chloride solution produces chlorine gas at the anode while the dilute chloride solution produces oxygen gas.

APPLYING

3. What minimum voltage must be applied to electrolyse a 1.0 M solution of zinc(II) nitrate solution?
4. With reference to Table 13.1.1, on page 179, predict the products formed from the electrolysis of a concentrated sodium nitrate solution. Write an equation for the overall reaction and determine the voltage required to enable this reaction to occur.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:

- **a** electrolysis
- **b** electroplating
- **c** electrorefining.

ELABORATION QUESTIONS

2 A student set up an electrolysis experiment to decompose a sample of molten zinc bromide using graphite electrodes.

- **a** Identify any risks associated with this practical activity and describe how you could minimise them.
- **b** Identify the anode reaction, cathode reaction and cell voltage for this electrolytic cell.

EVIDENCE QUESTIONS

3 With reference to Table 13.1.1, predict the products formed from the electrolysis of a concentrated copper(II) sulfate solution. Write an equation for the overall reaction and determine the voltage required to enable this reaction to occur.

4 Suggest a reason why, if a concentrated sodium chloride solution is electrolysed, chlorine gas is produced, but if the cell is allowed to run for an extended amount of time, the chlorine gas is slowly replaced by oxygen gas.

END-OF-CHAPTER EXAM

End-of-chapter test

1 In electrolysis, the anode and cathode are determined by:

A the electrode potentials of the ions in the electrolyte

B the connection of the electrodes to the external power supply

C the site of the oxidation and reduction

D the movement of ions in the electrolyte

2 The half-reaction that occurs at the anode during the electrolysis of a concentrated potassium bromide solution is:

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

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

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

D $K^+(aq) + e^- \rightarrow K(s)$

3 When electroplating a coating of zinc onto a piece of iron, what will the anode and the electrolyte be?

A Zinc and iron(II) nitrate

B Iron and zinc nitrate

C Zinc and zinc nitrate

D Iron and iron(II) nitrate

4 What is the minimum voltage required to enable the electrolysis of dilute zinc sulfate to occur?

A –2.75V

B –1.99V

C –3.22V

D –0.47V

5 If the cell potential of an electrolytic cell has a negative sign, what can be said of the reaction it represents?

6 An electrolytic cell is comprised of two carbon electrodes dipping into a dilute copper(II) bromide solution. What will be the product at the cathode?

7 An experiment was carried out according to Figure 14.4.1, on the next page, and under standard conditions.

a Use Table 13.1.1 (page 179) to suggest the identity of metal B and solution A.

b What substances will be produced at electrodes C and D?

c Identify all electrodes as anodes or cathodes and label each as the site where oxidation or reduction occurs.

d Support your answers with appropriate half-equations.

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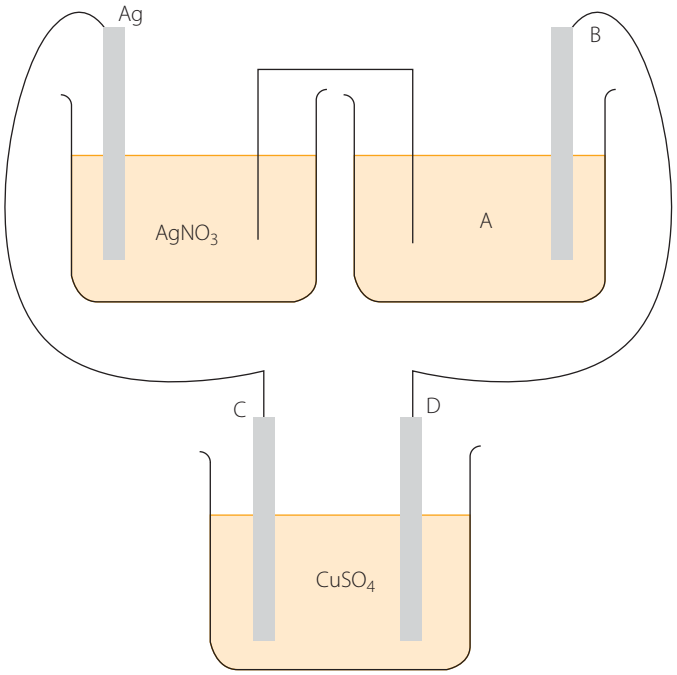

FIGURE 14.4.1 Experimental set-up

8 An experiment was carried out in which a 1 M sodium chloride solution was electrolysed. A few drops of universal indicator were placed into the solution. The set-up for this experiment is shown in Figure 14.4.2.

KEY FORMULA

In acidic solution, universal indicator turns red. In basic solution, universal indicator turns blue.

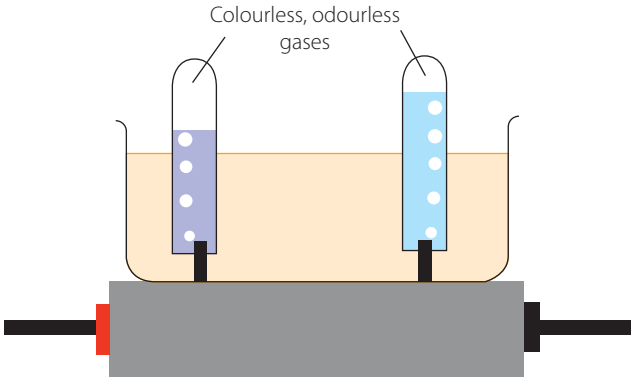

FIGURE 14.4.2 Experimental set-up

a What chemical tests could a student perform to identify the unknown gases?

b Using the information given, identify the anode and the cathode.

c Suggest a reason why the amounts of gases produced are not the same.

» UNIT FOUR

STRUCTURE, SYNTHESIS AND DESIGN

- Topic 1: Properties and structures of organic materials
- Topic 2: Chemical synthesis and design

Chemical synthesis and the design and production of new materials is one of chemistry's most important uses. As part of this, chemistry is also part of the debate around how we use the world's resources. In this unit, students focus on the principles and applications of chemical synthesis, particularly in organic chemistry, and consider where and how functional groups can be incorporated into already existing carbon compounds to generate new substances with properties that can be used in a range of contexts.

Current and future applications of chemistry include developing specialised techniques to create or synthesise new substances as pharmaceuticals, fuels, polymers and nanomaterials. Of particular importance is the potential contradiction between organic chemistry advances and the environmental impact accompanying these practices.

UNIT OBJECTIVES

By the end of this unit, students should be able to:

1. describe and explain the properties and structure of organic materials and chemical synthesis and design
2. apply understanding of the properties and structure of organic materials and chemical synthesis and design
3. analyse evidence about the properties and structure of organic materials and chemical synthesis and design
4. interpret evidence about the properties and structure of organic materials and chemical synthesis and design
5. investigate phenomena associated with the properties and structure of organic materials and chemical synthesis and design
6. evaluate processes, claims and conclusions about the properties and structure of organic materials and chemical synthesis and design
7. communicate understandings, findings, arguments and conclusions about the properties and structure of organic materials and chemical synthesis and design.

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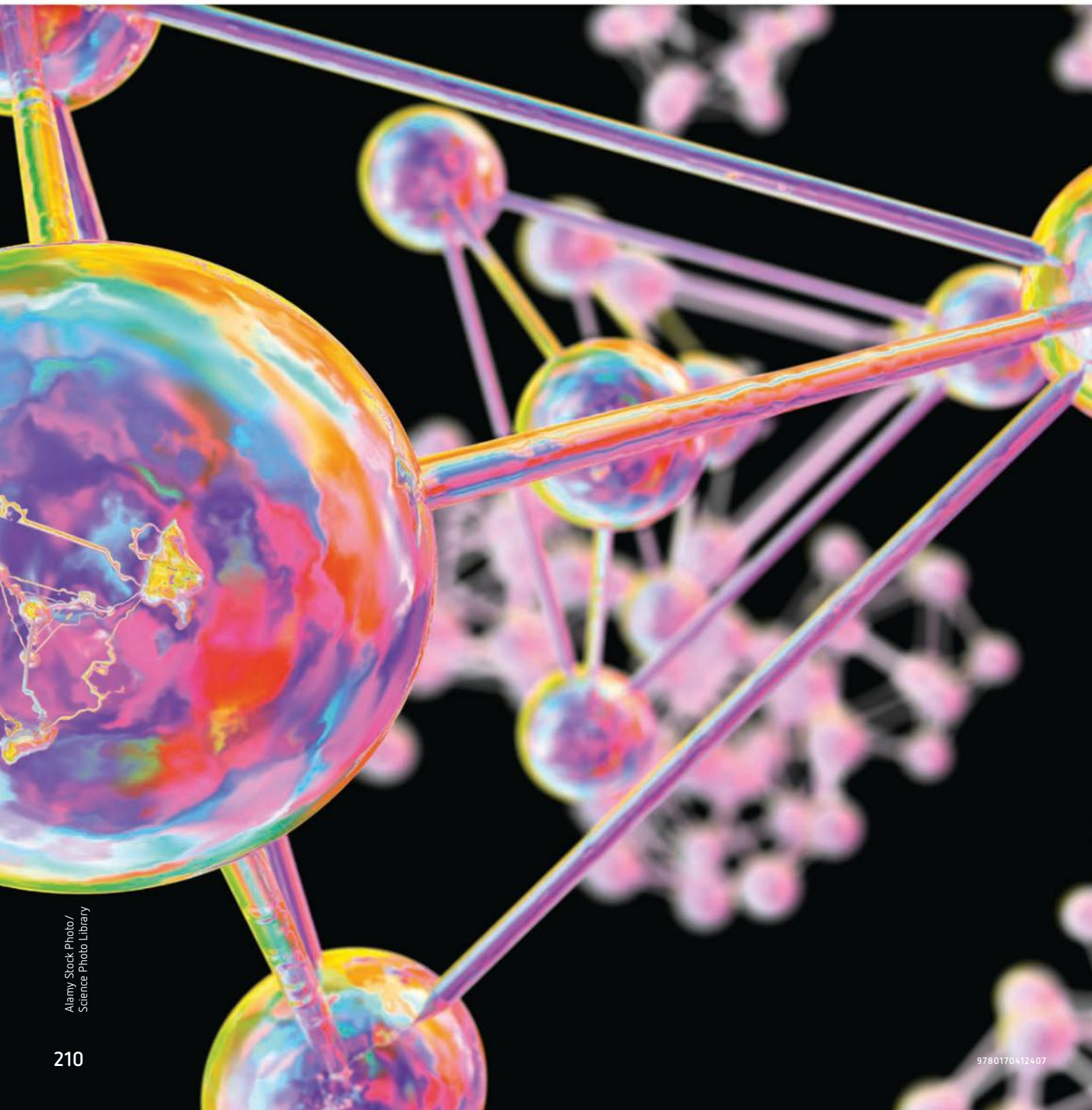
» UNIT FOUR

STRUCTURE, SYNTHESIS AND DESIGN



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Topic 1: Properties and structures of organic materials

Organic chemistry, the chemistry of carbon-based molecules, is critical to many applications of chemistry. In this topic, students study the nomenclature and terminology used to describe and distinguish organic molecules. We study the physical properties, patterns and trends that can be observed within and between the different classes of molecules and explain the reasons behind these observations. We also study the specific types of reaction that each class of organic molecule participates in and, therefore, learn how synthetic reaction pathways can be constructed from a series of reactions. We then study how these characteristics are observed and incorporated into biomolecules and consequently, how the behaviour of biomolecules can be understood and explained. Finally in this topic, we look at the use of machines that have been developed to analyse and determine the structure of complex biomolecules and understand how to interpret the information they provide.

SCIENCE AS A HUMAN ENDEAVOUR

Students should be given opportunities to investigate:

- functional groups and organic chemistry
- green polymer chemistry
- use of organochlorine compounds as insecticides.

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15 STRUCTURE OF ORGANIC COMPOUNDS

Introduction

Chemists in the 17th and 18th centuries knew that chemicals such as sugars, carbohydrates, fats, oils and proteins, which were obtained from living things, were different from the chemicals obtained from rocks. The term organic compound is used to describe substances obtained from living things, while the term inorganic compound describes any substance not obtained from living things.

Early chemists believed that only organic chemicals could be used to make other organic chemicals. Ideas changed quickly when the German chemist Friedrich Wöhler synthesised a typical organic compound, urea, from a typical inorganic compound, ammonium cyanate. As more organic compounds were made from inorganic sources, it became clear that compounds found in living things and those obtained from non-living sources such as rocks and minerals were part of the same chemical system. Therefore, we now differentiate organic and inorganic compounds on the basis that organic compounds are carbon-based.

Stimulus questions

How can we determine the structure of an organic compound from its name?

How can we make sense of the vast range of organic molecules by grouping and classifying them?

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15.1 Representing organic compounds

The reason that carbon can be the basis of so many compounds is its ability to **catenate** or form long chains and rings of atoms. These long sequences of atoms form what is known as a **carbon skeleton**.

Organic compounds are grouped into series of families, called **homologous series**. The members of a homologous series have the same functional group and similar chemical properties, but different length carbon chains, and so their physical properties can vary accordingly.

The length of the carbon skeleton is represented in the name of the molecule, as shown in Table 15.1.1, which shows the first 10 members of the alkane homologous series, consisting purely of carbon and hydrogen atoms. This name stem is used in all homologous series to identify the number of carbon atoms in the skeleton.

catenate
the ability of carbon atoms to bond with other carbon atoms to form chains and rings

carbon skeleton
the arrangement of carbon atoms that other atoms join to in an organic molecule

homologous series
a series of organic molecules with the same functional group but different length carbon chains

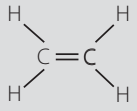
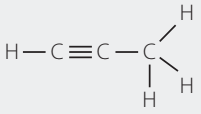
TABLE 15.1.1 Names of the first 10 alkanes

NUMBER OF CARBON ATOMS	NAME STEM	ALKANE
1	Meth-	Methane (CH_4)
2	Eth-	Ethane (C_2H_4)
3	Prop-	Propane (C_3H_8)
4	But-	Butane (C_4H_{10})
5	Pent-	Pentane (C_5H_{12})
6	Hex-	Hexane (C_6H_{14})
7	Hept-	Heptane (C_7H_{16})
8	Oct-	Octane (C_8H_{18})
9	Non-	Nonane (C_9H_{20})
10	Dec-	Decane ($C_{10}H_{22}$)

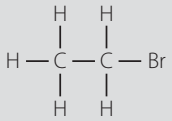
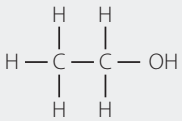
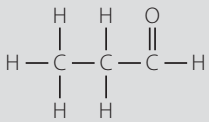
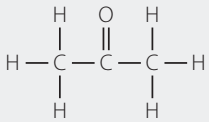
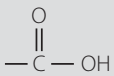
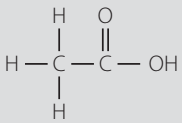
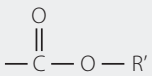
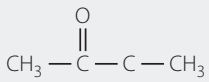
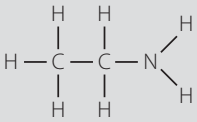
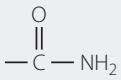
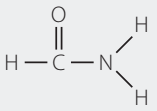
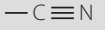
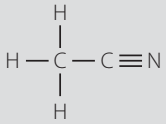
The other feature of organic compounds is **functional groups**, or particular groups of atoms, which may or may not include carbon, but which determine the key chemical properties of the compound. Table 15.1.2 shows some commonly occurring functional groups, their names and the homologous series of compounds that contain that group.

functional group
a group of atoms in a molecule that causes the molecule to chemically react in a distinctive way

TABLE 15.1.2 Functional groups

NAME	FUNCTIONAL GROUP	PREFIX OR SUFFIX	HOMOLOGOUS SERIES	EXAMPLE	NAME OF EXAMPLE
Alkene	—C=C—	-ene	Alkenes		Ethene
Alkyne	—C≡C—	-yne	Alkyne		Propyne

»

NAME	FUNCTIONAL GROUP	PREFIX OR SUFFIX	HOMOLOGOUS SERIES	EXAMPLE	NAME OF EXAMPLE
Haloalkane	Halogen –F, –Cl, –Br, –I	Fluoro-, chloro-, bromo-, iodo-	Haloalkanes		Bromoethane
Hydroxyl	–OH	-anol or hydroxyl-	Alcohols		Ethanol
Aldehyde		-anal	Aldehydes		Propanal
Ketone		-anone or oxo-	Ketones		Propanone
Carboxyl		-anoic acid	Carboxylic acids		Ethanoic acid
Ester		alkyl -oate	Esters		Methyl ethanoate
Amine	$-NH_2$	-anamine	Amines		Ethanamine
Amide		-anamide	Amides		Methanamide
Nitriles		-nitrile or cyano-	Nitriles/ cyanides		Ethane nitrile

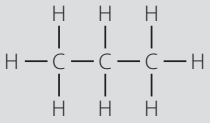
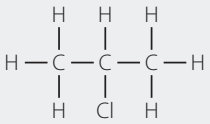
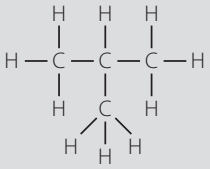
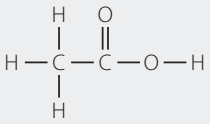
structural formula
a displayed arrangement of the atoms in a molecule, showing all bonds

semi-structural formula
a condensed version of the structural formula showing the sequence of atoms listed by carbon atom but not the bonds

Molecules are represented by a **structural formula**, which shows all of the bonds between the atoms within a molecule and indicates how the atoms are joined together.

Sometimes a condensed structural formula or **semi-structural formula** is used, for brevity. In a semi-structural formula, no bonds are shown. Each carbon atom in the chain is listed in order. Where multiple atoms (including branched chains) are bonded to a carbon atom in the middle of a chain, brackets are used. Table 15.1.3 shows the structural and semi-structural formulas of some different molecules.

TABLE 15.1.3 Structural and semi-structural formulas of some different molecules

NAME	STRUCTURAL FORMULA	SEMI-STRUCTURAL FORMULA
Propane		$CH_3CH_2CH_3$
2-chloro propane		$CH_3CHClCH_3$
Methyl propane		$CH_3CH(CH_3)CH_3$
Ethanoic acid		CH_3COOH

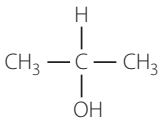
SECTION REVIEW 15.1

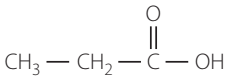
REMEMBERING

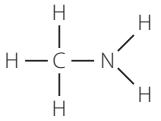
1 Describe what is meant by a functional group.

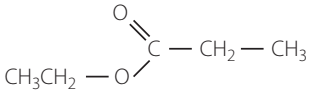
UNDERSTANDING

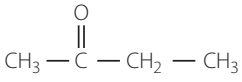
2 Identify the functional group in each of the following compounds.

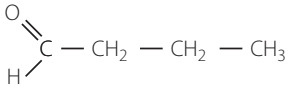
a 

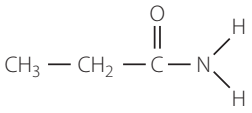
b 

c 

d 

e 

f 

g 

15.2 Naming organic compounds

Organic compounds are named systematically. This means that the structure of the molecule can be directly deduced from the name. The name therefore needs to describe the carbon skeleton from which the molecule is formed, together with the functional groups that are present and the specific location of these groups on the carbon skeleton.

prefix
a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the start of the name

suffix
a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the end of the name

stem
the part of the name of an organic molecule that denotes the length of the longest carbon chain

Organic molecules are named in three parts: **prefix** – **stem** – **suffix**. The **prefix** and **suffix** describe the functional groups in the molecule. Table 15.1.2 shows some of the prefixes and suffixes that can be used to indicate the functional group present. The **stem** describes the length of the carbon skeleton. Table 15.1.1 shows the first 10 stems that are used, according to the number of carbon atoms in the chain.

Therefore, in order to name an organic molecule, we need to take the following steps:

1 Establish the number of carbon atoms in the longest continuous chain in the molecule. The stem of the molecule is named accordingly, using the names shown in Table 15.1.1. Note that the way in which molecules can appear to be drawn can be misleading as shown in figure 15.2.1.

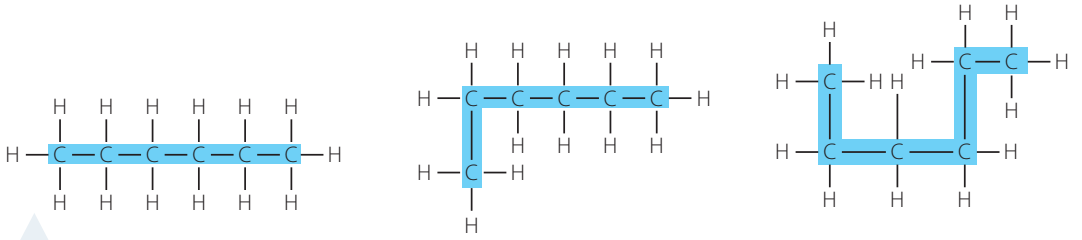


FIGURE 15.2.1 All of these molecules have 6 carbons in a continuous chain and are therefore different representations of the same molecule, hexane

2 Identify the functional groups in the molecule, and, using the prefix or suffix listed in Table 15.1.2, name and number them according to their position on the longest chain of carbon atoms. A dash is written between the number and the name of the molecule. Importantly as molecules can be represented in a number of different orientations, the convention is that the numbers associated with each functional group are as low as possible reading from right or left. For example, Figure 15.2.2 shows two molecules where this convention is important. The first molecule is named 2-chlorobutane, not 3-chlorobutane and the second molecule is 1-butanol, not 4-butanol

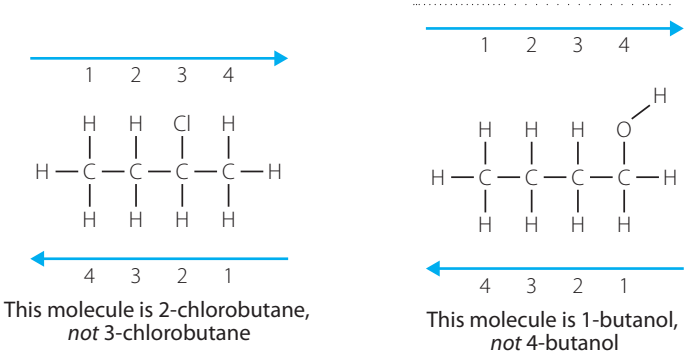
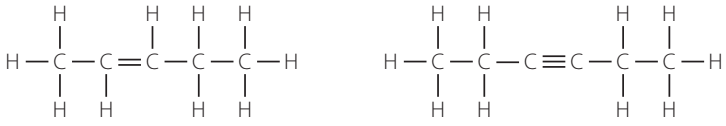


FIGURE 15.2.2 The molecules 2-chlorobutane and 1-butanol. In both of the molecules, the carbon atoms could either be numbered from left to right or from right to left. The convention is that the numbers are always as small as possible.

For functional groups indicated by a suffix rather than a prefix, the number can either be written before the stem, or between the stem and the suffix. Therefore, the molecule 1-butanol could also be written as butan-1-ol.

3 In the case of alkenes and alkynes, the position of the double or triple bond is indicated by listing the lower of the numbers of the two carbon atoms. Figure 15.2.3 shows two examples of this.



2-pentene, NOT 3-pentene

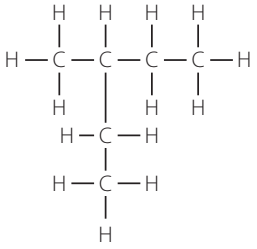
3-hexyne, NOT 4-hexyne

FIGURE 15.2.3 The numbering should always be as low as possible

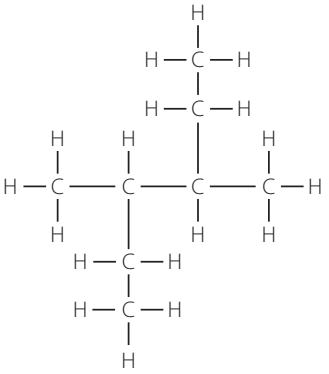
4 If the molecule has a branched carbon chain, then the sections that are not part of the longest chain are known as alkyl chains and are named according to Table 15.2.1. The alkyl chains are named and numbered according to their position on the longest chain in the same way as a functional group, as seen in figure 15.2.4.

TABLE 15.2.1 Names of the first 10 alkyl chains

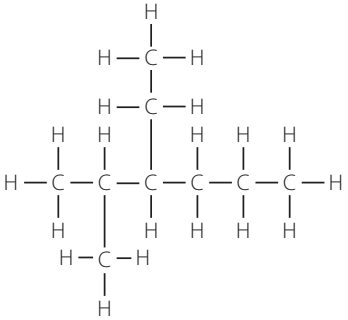
NUMBER OF CARBON ATOMS	NAME
1	Methyl
2	Ethyl
3	Propyl
4	Butyl
5	Pentyl
6	Hexyl
7	Heptyl
8	Octyl
9	Nonyl
10	Decyl



3-methylpentane



3,4-dimethylhexane



3-ethyl-2-methylhexane

FIGURE 15.2.4 Branched chain alkanes

5 If there is more than one of the same functional group or alkyl chain present in the molecule, then the prefixes di-, tri- or tetra- are used to denote this. The numbers of each of the groups are indicated first, separated by commas, as seen in figure 15.2.5.

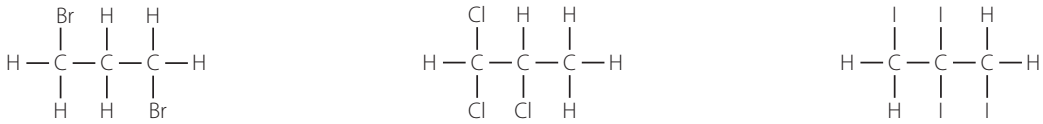


FIGURE 15.2.5 Molecules with more than one of the same functional group

6 If one of the functional groups is what is known as a terminal functional group, which can only exist at the end of a chain, such as a carboxyl or an aldehyde group, then the carbon atom to which this group is attached is always numbered as 1, as shown in Figure 15.2.6.

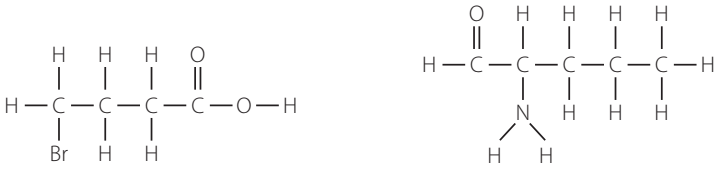
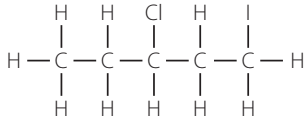


FIGURE 15.2.6 Examples of molecules with terminal functional groups

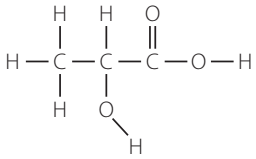
7 If there is more than one functional group in the molecule, then the functional groups are listed in alphabetical order, each with the number indicating its position on the longest chain. Figure 15.2.7 shows an example of this naming convention.

FIGURE 15.2.7
The molecule 3-chloro, 1-iodopentane.



If one of the functional groups can be represented by either a prefix or a suffix, then this is used when the other functional group does not have this option. Figure 15.2.8 shows the molecule 2-hydroxypropanoic acid (commonly known as lactic acid), where the hydroxyl group is indicated by the prefix and the carboxyl group by the suffix.

FIGURE 15.2.8
The molecule 2-hydroxypropanoic acid



8 The names of esters and amides consist of two words. Esters are formed from the reaction of an alcohol and a carboxylic acid, and amides are formed from an amine and a carboxylic acid. The linkages that are formed are shown in Figure 15.2.9.

FIGURE 15.2.9 An example of an ester and an amide

a The first part of the name is the alkyl group. This comes from the alcohol or amine from which the ester was formed.

b The second part of the name comes from the carboxylic acid. For esters, the end of the acid name is changed from -oic acid to -oate.

c For amides, the end of the acid name is changed from –oic acid to –anamide. In addition, the alkyl chain that originated from the amine is written as 'N-alkyl-' to emphasise that it is joined directly to the nitrogen atom.

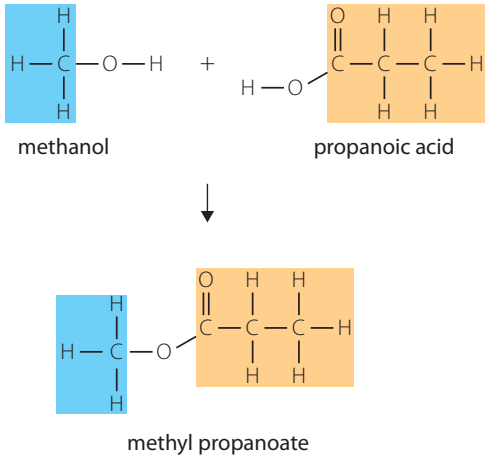


FIGURE 15.2.10 Formation of methyl propanoate, showing the origin of the name

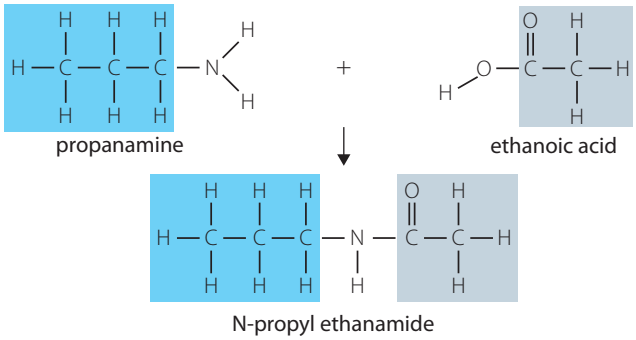


FIGURE 15.2.11 Formation of N-propyl ethanamide, showing the origin of the name

SECTION REVIEW 15.2

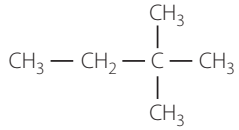
UNDERSTANDING

1 Draw a structural formula for:

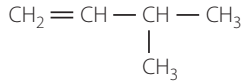
- **a** propane
- **b** 3-hexyne
- **c** 3,3-dimethyl-1-butene
- **d** 3-methyl-1-butanol
- **e** butanal
- **f** 3-methyl-2-pentanone
- **g** 2,3-dimethylbutanoic acid
- **h** butyl ethanoate
- **i** 2-methyl-3-octanamine
- **j** N-methylmethanamide.

2 Name the following compounds:

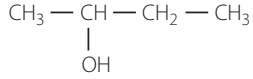
a



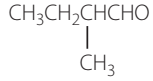
b



c

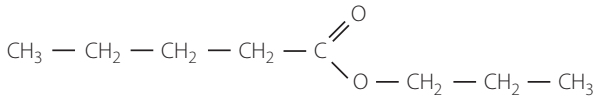


d



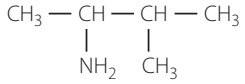
e $HOOCCH_2CH_2CH_2CH_3$

f

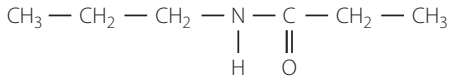


g $CH_3CH_2CH_2CH_2CH_2CH_2OH$

h



i

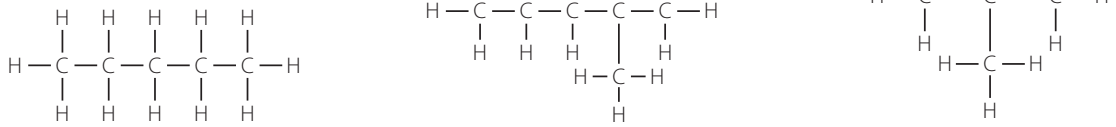


15.3 Structural isomers

molecular formula the number of atoms of each element present in a molecule

structural isomers two molecules with the same molecular formula but a different arrangement of the atoms

Isomers are molecules with the same **molecular formula** (that is, number of each atom) but different arrangements of atoms. **Structural isomers** are molecules where the number and types of bonds between the atoms, and therefore the arrangement of atoms, is different. For example, Figure 15.3.1 shows three structural isomers with the same molecular formula of C_5H_{12}.



pentane 2-methylbutane 2,2-dimethylpropane

FIGURE 15.3.1 Three structural isomers of C_5H_{12}.

The number of possible structural isomers increases with the size of the molecule and the number of different elements present. It is important to name each isomer identified, as there are often many different possible representations of the same molecule. By identifying the longest chain of carbon atoms

present and the position of each of the different functional groups, we can identify the name and make it clear whether or not two molecules are in fact the same compound. Figure 15.3.2 shows an example of this.

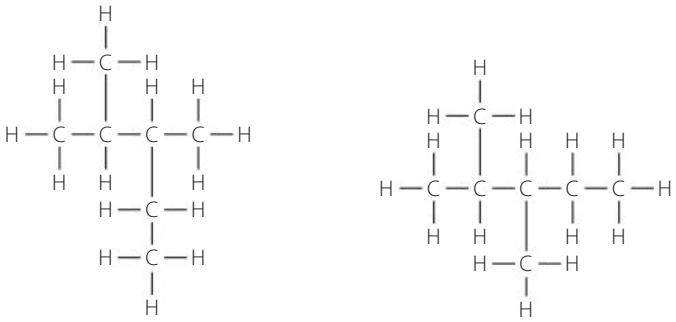


FIGURE 15.3.2 Two different representations of the same molecule – 2,3-dimethylpentane.

The majority of structural isomers have the same functional groups; however, it is worth noting that carboxylic acids and esters are usually structural isomers of one another.

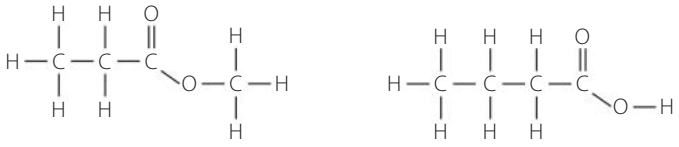


FIGURE 15.3.3 Structural isomers with different functional groups

Methyl propanoate and butanoic acid both have the same molecular formula of $C_4H_8O_2$ and are therefore structural isomers of one another, with different functional groups

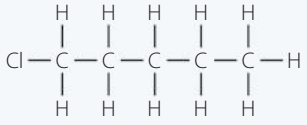
WORKED EXAMPLE 15.3.1

There are eight structural isomers with a molecular formula of $C_5H_{11}Cl$. Draw and name each one.

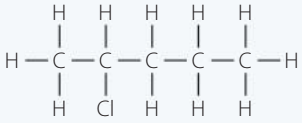
ANSWER

A good strategy is to start with the molecules with the longest continuous chain of carbon atoms and then gradually reduce the length of the chain until all the molecules have been identified

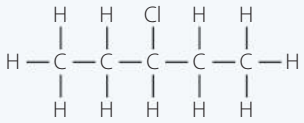
Molecules with a longest chain of 5 carbon atoms:



1-chloropentane

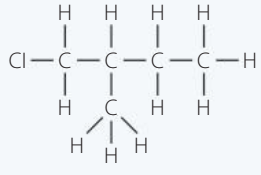


2-chloropentane

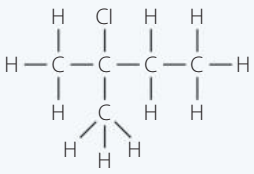


3-chloropentane

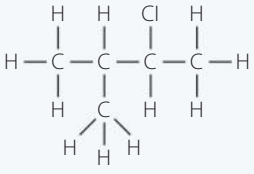
Molecules with a longest chain of 4 carbon atoms:



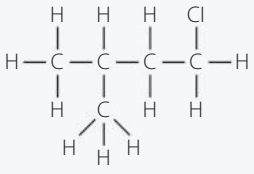
1-chloro, 2-methylbutane



2-chloro, 2-methylbutane

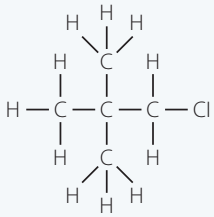


2-chloro, 3-methylbutane



1-chloro, 3-methylbutane

Molecules with a longest chain of 3 carbon atoms:



1-chloro, 2,2-dimethylpropane

SECTION REVIEW 15.3

1. Name and draw the structural formulas of two isomers of an alcohol with the molecular formula C_4H_9OH.
2. Draw the structural formula and name the straight-chain isomers of C_5H_{10}.
3. Draw the structural formulas for three esters of molecular formula $C_4H_8O_2$ and name them.

15.4 Stereoisomers

Alkenes are molecules that contain a double bond between two carbon atoms. They are named using the suffix '-ene' with an appropriate number to denote the position of the double bond. If we consider molecules with the formula C_4H_8, we can initially identify two structural isomers.

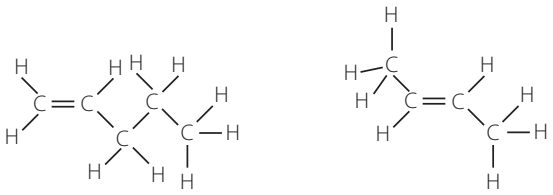


FIGURE 15.4.1 1-butene and 2-butene

Figure 15.4.1 clearly shows the difference in geometry when double bonds are present between carbon atoms. Carbon atoms not involved in double bonds have a tetrahedral geometry, with the four bonds equally spaced around the atom in three dimensions.

However, the shape of alkene molecules is significantly different to those without double bonds because the geometry around the double bond is planar with all the bond angles being 120°. Carbon atoms on either side of the double bond cannot rotate around the bond. The isomerism resulting from the presence of a double bond is **stereoisomerism** or **geometrical isomerism**. Geometrical isomerism is possible whenever each carbon on the double bond has at least one branch; that is, the double bond is not attached to the first carbon atom in a chain.

stereoisomers or **geometric isomers** two molecules with the same structural formula but different arrangement of atoms in space

2-butene is an example of a molecule that exhibits stereoisomerism. Figure 15.4.2 shows the two forms of this molecule.

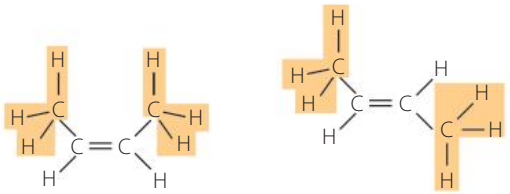


FIGURE 15.4.2 The cis and trans isomers of 2-butene

In the first structure in Figure 15.4.2, both the methyl groups are on the same side of the double bond, so this compound is named cis-2-butene. In the second structure, they are on opposite sides, so it is named trans-2-butene. These two structures represent distinct compounds with different melting points, boiling points and densities, as shown in Table 15.4.1.

TABLE 15.4.1 Different properties of cis- and trans-2-butene

COMPOUND	MELTING POINT (0°C)	BOILING POINT (0°C)	DENSITY (g mL^{-1})
cis-2-butene	2139	4	0.615
trans-2-butene	2105.6	1	0.598

It can be seen that the properties of stereoisomers are very similar, as could be predicted from their identical size and composition. However, the slightly differing shapes in the molecules results in slightly different physical properties.

MANDATORY PRACTICAL 15.4.1

Constructing models of organic molecules

AIM

To use a model kit to construct organic molecules, and to help determine the structures of isomers.

EQUIPMENT

- Molecular model kit

PROCEDURE

Part 1 Structural isomers

1. Use the molecular model kit to construct a model of hexane, C_6H_{14}.
2. There are three other isomers of pentane that have the same molecular formula. Reform the model that you have made to show each of the three other isomers.

3 Draw and name the structures of the four molecules you have constructed, using a table such as the one below.

ISOMER	NAME	STRUCTURE
1		
2		
3		
4		

ANALYSIS

Use the model kits to show why 2-methylpentane and 4-methylpentane are, in fact, the same molecule.

Part 2 Geometrical isomers

1 Use the model kit to construct an alkene with the molecular formula C_5H_{10}.

2 Four further isomers of this molecule are alkenes. Reform the model that you have already constructed to show each of these isomers.

3 Draw and name the structures of each isomer you have made in a table similar to the one below.

ISOMER	NAME	STRUCTURE
1		
2		
3		
4		
5		

ANALYSIS

Use the model kit to show why 2-pentene can show geometric isomerism, when 1-pentene cannot.

SECTION REVIEW 15.4

UNDERSTANDING

1 What is the difference between a geometric isomer and a structural isomer?

APPLYING

2 Draw and name the cis and trans isomers of 2-pentene.

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CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Explain why classes of organic compounds are based on functional groups.

2 Describe the difference between the aldehyde and ketone functional groups.

3 Describe the relationship between an amine and an amide.

CATEGORY QUESTIONS

4 Which of the following is an alkane, which is an alkene and which is an alkyne? Explain your choice.

a C_6H_{10}

b C_6H_{12}

c C_6H_{14}

d C_6H_{16}

5 Draw structural formulas of:

a 3-ethyl-3-methylhexane

b 2-methyl-2-pentene

c 2,3-dimethyl-3-pentanol

d 3-methyl-4-octanol

e 4-methylpentanal

f 3-hexanone

g ethanoic acid

h 2-methylpropanoic acid

i propyl methanoate

j dipropanamine

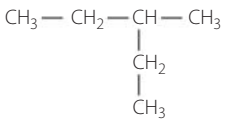
k propanamide.

6 Name the following compounds.

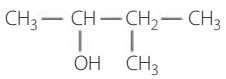
a C_5H_8

b C_4H_{10}

c

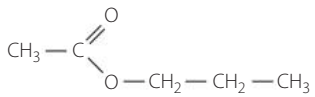


d



e $CH_3CH_2CH_2COCH_3$

f



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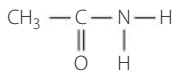
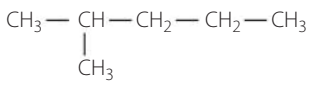
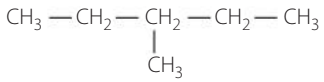


ELABORATION QUESTIONS

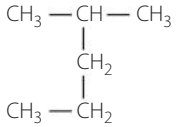
7 Which of the following pairs represent structural isomers?

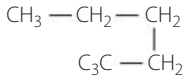
a





b





8 The following compounds have been named incorrectly. Draw their structural formulas and give the correct names.

a 3-ethylbutane

b 1-methyl-4-propylhexane

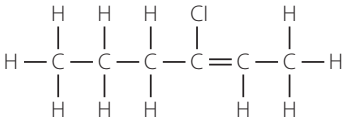
c 3-methyl-3-butene

d 2-ethyl-2-methyl-3-butyne

END-OF-CHAPTER EXAM

End-of-chapter test

1 The correct name for the molecule below is:



A 4-chloro-5-hexene

B 2-chloro-2-hexene

C 3-chloro-3-hexene

D 3-chloro-2-hexene

2 The molecule that is *not* an isomer of 2,2,4-trimethylpentane is

A 2,4-dimethylhexane

B 3-ethylhexane

C 2,4-dimethylpentane

3 For which one of the following molecular formulas is there only one possible structure?

A C_3H_7Cl

B $C_3H_7CH_2OH$

C $C_3H_7NH_2$

D H_2NCH_2COOH

4 Draw and name the eight molecules that are isomers of $C_5H_{11}Br$.

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16 PHYSICAL PROPERTIES AND TRENDS OF ORGANIC MOLECULES

Introduction

Understanding the physical properties of organic molecules is key to understanding their varied uses and applications in society. In addition, as new organic molecules are frequently being developed, it is important that the patterns and trends we see in the currently known molecules are extrapolated so we can accurately predict the properties of these new molecules.

Key to our ability to extrapolate this knowledge are two things: understanding how the physical properties of molecules vary within a homologous series, as the carbon chain length increases; and comprehending how molecules are affected by the presence of different functional groups.

Stimulus questions

How do the properties of molecules vary as their size increases?

How can we accurately predict the physical properties of newly developed substances?

How can we use our understanding of physical properties to help design new organic molecules?

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16.1 Intermolecular forces

intermolecular forces
forces that act between molecules; these forces largely determine the physical properties of molecules

dispersion forces
the weakest intermolecular forces that exist between all molecules

dipole–dipole interactions
intermolecular forces that exist between molecules that have a permanent dipole

hydrogen bonds
strong intermolecular forces that exist between molecules that possess O–H, N–H or F–H bonds

polarity
a bond is said to be polar when there is a significant difference in electronegativity between the atoms of a covalent bond, and therefore an unequal distribution of electron density across the bond

As for all covalent molecules, the physical properties of organic molecules depend on the nature and strength of the **intermolecular forces** that exist between them. These forces are **dispersion forces**, **dipole–dipole interactions** and **hydrogen bonds** and we discussed their origins in Chapter 13 of *QScience Chemistry Units 1 & 2*. The stronger the intermolecular force present, the higher the energy required to separate the molecules, which means the higher the melting and boiling points will be. In addition, molecules where hydrogen bonding is present are more likely to be soluble in water, because of the formation of hydrogen bonds between these functional groups and water molecules.

The type of intermolecular force present between the different classes of organic molecule depends on the **polarity** of the bonds within the molecules and therefore the nature of the atoms present. Table 16.1.1 provides a summary of the classes of compound and the forces occurring between them.

TABLE 16.1.1 The types of intermolecular forces in the different classes of organic compound

CLASS OF ORGANIC MOLECULE	TYPES OF BOND PRESENT	POLARITY	TYPE OF INTERMOLECULAR FORCE ACTING	STRONGEST TYPE OF INTERMOLECULAR FORCE ACTING BETWEEN MOLECULES
Alkane	C—C	Non-polar	Dispersion	Dispersion
	C—H	Non-polar	Dispersion	
Alkene	C═C	Non-polar	Dispersion	Dispersion
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Alkynes	C≡C	Non-polar	Dispersion	Dispersion
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Haloalkane	C—X	Polar	Dipole–dipole	Dipole–dipole
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Alcohol	O—H	Polar	Hydrogen	Hydrogen
	C—O	Polar	Dipole–dipole	
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Amine	N—H	Polar	Hydrogen	Hydrogen
	C—N	Polar	Dipole–dipole	
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Aldehyde	C═O	Polar	Dipole–dipole	Dipole–dipole
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	

»

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CLASS OF ORGANIC MOLECULE	TYPES OF BOND PRESENT	POLARITY	TYPE OF INTERMOLECULAR FORCE ACTING	STRONGEST TYPE OF INTERMOLECULAR FORCE ACTING BETWEEN MOLECULES
Ketone	C═O	Polar	Dipole–dipole	Dipole–dipole
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Carboxylic acid	O—H	Polar	Hydrogen	Hydrogen
	C═O	Polar	Dipole–dipole	
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Nitrile	C≡N	Polar	Dipole–dipole	Dipole–dipole
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Ester	C═O	Polar	Dipole–dipole	Dipole–dipole
	C—O	Polar	Dipole–dipole	
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	
Amide	N—H	Polar	Hydrogen	Hydrogen
	C═O	Polar	Dipole–dipole	
	C—N	Polar	Dipole–dipole	
	C—C	Non-polar	Dispersion	
	C—H	Non-polar	Dispersion	

The strength of the different intermolecular forces in descending order is:

Hydrogen bonding ⟶ Dipole-dipole force ⟶ Dispersion force

On the basis of the bonds present, we can expect organic molecules that have hydrogen bonds, such as alcohols, amines, carboxylic acids and amides, to have higher melting and boiling points than other classes. These molecules are also more likely to be water soluble. Molecules such as alkanes and alkenes, which are non-polar molecules with only dispersion forces present between them, have comparatively low melting and boiling points and are insoluble in water.

SECTION REVIEW 16.1

REMEMBERING

1 What are the three types of intermolecular force in order of increasing strength?

UNDERSTANDING

2 Explain why carboxylic acids, amines and alcohols show hydrogen bonding between molecules, whereas other classes of organic molecules do not.

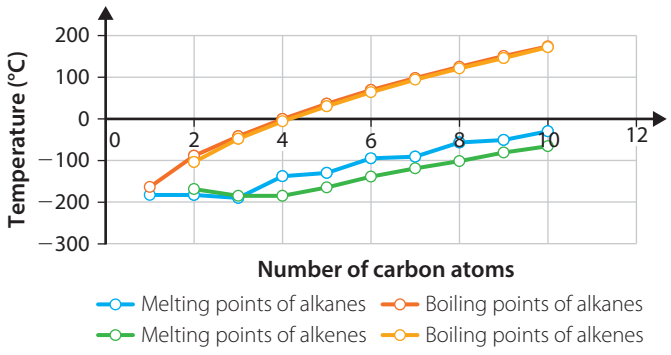
16.2 Trends in melting and boiling points

We can clearly see evidence of the intermolecular bonding occurring between organic molecules when we examine the trends in melting and boiling points within and between different homologous series. Table 16.2.1 and Figure 16.2.1 show the melting and boiling point data for the first 10 alkanes and alkenes.

TABLE 16.2.1 The melting and boiling points of the first 10 alkanes and alkenes

NUMBER OF CARBON ATOMS	ALKANES		ALKENES	
	MELTING POINT (°C)	BOILING POINT (°C)	MELTING POINT (°C)	BOILING POINT (°C)
1	–183	–164		
2	–183	–89	–169	–104
3	–190	–42	–185	–48
4	–138	–0.5	–185	–6
5	–130	36	–165	30
6	–95	69	–139	64
7	–91	98	–119	94
8	–57	125	–101.7	121
9	–51	151	–81	146
10	–30	174	–66	172

FIGURE 16.2.1 The melting and boiling points of the first 10 alkanes and alkenes



The effect of molecular size and shape

As the size of both alkane and alkene molecules increases, the trend in melting and boiling points is clear to see: the larger the molecule, the greater the melting and boiling points. This means the larger the molecule, the greater the temperatures at which the intermolecular forces – dispersion forces, as these molecules are all non-polar – are overcome sufficiently to allow a change in state.

The larger the molecules, the greater the area of surface overlap between them, where the dispersion forces can act. This means the larger the molecules, the higher the energy required to separate them from one another, which again means higher melting and boiling points. The melting and boiling point values for alkanes and alkenes are similar – both increase with molecular size. The presence of the non-polar C=C bond has very little effect, as it does not significantly affect the area available for dispersion forces to act between molecules.

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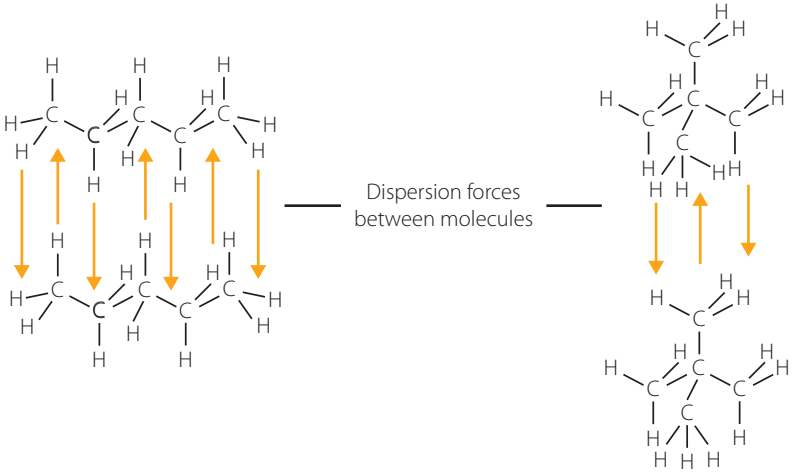
It is interesting also to compare the boiling points of straight-chain and branched-chain alkanes. Figure 16.2.2 compares pentane and 2,2-dimethylpropane, two molecules of identical molecular mass. Their different shapes result in different boiling points – the boiling point of pentane is higher, because of the greater level of dispersion force acting between the molecules.



Pentane
boiling point = 36°C

2,2-dimethylpropane
boiling point = 10°C

FIGURE 16.2.2 The boiling points of pentane and 2,2-dimethylpropane

The effect of functional groups

Table 16.2.3 and Figure 16.2.3 show the boiling points for molecules in four different homologous series, so we can discern the effect of the different functional groups.

TABLE 16.2.3 Boiling point trends in different homologous series

NUMBER OF CARBON ATOMS	BOILING POINTS			
	ALKANES (°C)	ALKENES (°C)	ALCOHOLS (°C)	CARBOXYLIC ACIDS (°C)
1	–164		65	100
2	–89	–104	78	118
3	–42	–48	97	141
4	–0.5	–6	118	163
5	36	30	138	187
6	69	64	157	205
7	98	94	178	222
8	125	121	195	240
9	151	146	214	256
10	174	172	229	270

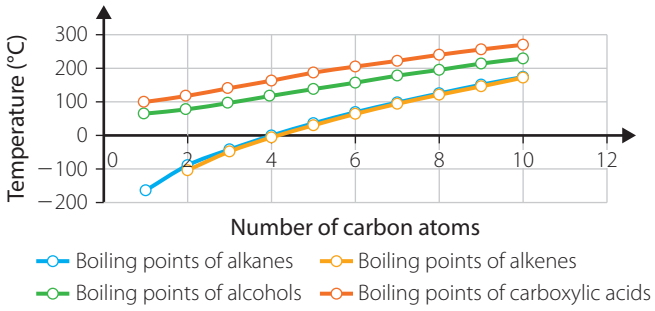


FIGURE 16.2.3 Boiling point trends in different homologous series

Figure 16.2.3 shows again that increased molecular size results in a higher boiling point and this is evident for all of the homologous series shown. However, this graph also shows clearly that the boiling points of alcohols and carboxylic acids are significantly higher than their equivalent alkane and alkene. This is due to hydrogen bonding between molecules, caused by the highly polar O—H bonds they possess, in addition to dispersion forces.

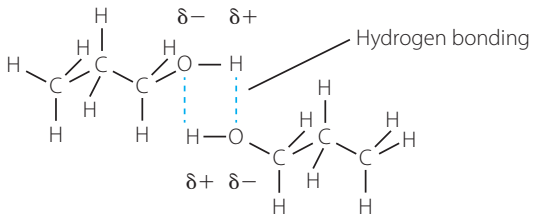


FIGURE 16.2.4 Hydrogen bonding between propanol molecules; there is an unequal distribution of electron density along this bond, represented in the figure by the symbols δ+ and δ−.

We can also observe that the larger the molecule, the smaller the difference in boiling point between the non-polar molecules and their polar counterparts. As the molecular size of the alcohols or carboxylic acids increases, it is the number of non-polar carbon and hydrogen atoms that increases. The number of polar hydroxyl or carboxyl groups and therefore hydrogen bonding does not increase, and hence the relative effect of the hydrogen bonding is not as great in larger molecules.

SECTION REVIEW 16.2

UNDERSTANDING

1. Explain why boiling point increases with molecular size in all homologous series.
2. Explain why straight chain molecules generally have a higher boiling point that their branched chain isomers.
3. Explain why the boiling points of alcohols are greater than that of their equivalent alkanes, and the boiling points of carboxylic acids are greater than that of their equivalent alcohols.

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16.3 Trends in solubility

The water solubility of organic molecules varies considerably. In order to be water soluble, a molecule needs to be able to form intermolecular bonds with water molecules. Water molecules are highly polar and therefore will bond with other polar molecules. The molecules most likely to dissolve in water are alcohols, as they can form hydrogen bonds, or carboxylic acids, which can ionise.

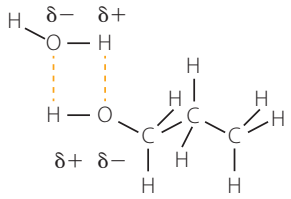


FIGURE 16.3.1 Alcohols form hydrogen bonds with water

Alkanes and alkenes are non-polar molecules and are therefore insoluble in water. Table 16.3.1 shows the solubilities of molecules in different homologous series that have polar bonds, and can therefore form attractive intermolecular interactions with water molecules.

TABLE 16.3.1 Solubilities of different homologous series (g/100 mL). Miscible implies that the substance mixes completely with water and, as such, has no solubility limit.

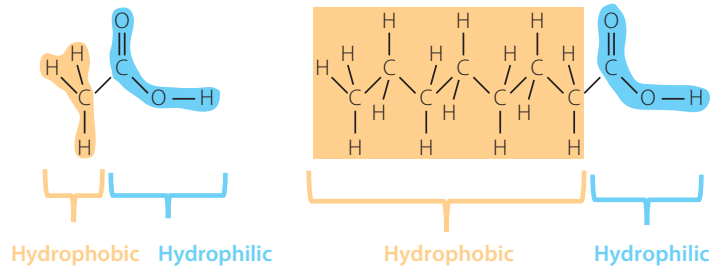
NUMBER OF CARBON ATOMS	ALCOHOLS	ALDEHYDES	CHLOROALKANES	KETONES	CARBOXYLIC ACIDS
1	Miscible	Miscible	0.53		Miscible
2	Miscible	Miscible	0.48	Miscible	Miscible
3	Miscible	20	0.33	Miscible	Miscible
4	7.3	7.6	0.05	29	Miscible
5	2.2	1.4	0.02	5	5
6	0.59	Insoluble	Insoluble	1.4	1.1
7	0.1	Insoluble	Insoluble	0.4	0.24

The solubility of all of these molecules decreases as the number of carbon atoms increases. The polar section of these molecules that interacts attractively with water is described as **hydrophilic**. The non-polar hydrocarbon section of these molecules is described as **hydrophobic**. As the carbon chain length increases, the molecule becomes proportionately more hydrophobic and less hydrophilic, hence its solubility decreases. If the hydrophobic section of the molecule becomes sufficiently large, then the molecule is insoluble in water, despite the presence of the hydrophilic section. This is shown in Figure 16.3.2, which compares the structures of two carboxylic acid molecules.

hydrophilic
a molecule that bonds attractively with water

hydrophobic
a molecule that does not bond attractively with water

The solubility of the chloroalkanes is lower than that of the other homologous series. Although they are polar molecules, chloroalkanes do not form hydrogen bonding interactions with water as they do not possess an oxygen atom. Consequently, they are not as strongly attracted to water molecules – they are less hydrophilic than other classes of compound.



Ethanoic acid – miscible with water Octanoic acid – insoluble in water

FIGURE 16.3.2 The hydrophobic and hydrophilic sections of two carboxylic acid molecules

The solubility of the other classes of compound shows a similar pattern in decreasing order: carboxylic acids → ketones → alcohols → aldehydes. These compounds all form hydrogen bonding interactions with water and their solubility varies because of the differing polarities of their C—O and O—H bonds, which therefore affects the strength of their attraction to water.

SECTION REVIEW 16.3

UNDERSTANDING

1 Explain why solubility decreases with molecular size in all homologous series.
2 Rank the following molecules in decreasing order of solubility in water and explain your reasoning: 1-propanol; propane; 1-chloropropane; propanoic acid.

16.4 Properties of functional groups

Properties of amines

electronegativity the tendency of an atom to attract electrons from outside a covalent bond

Nitrogen is the fourth most **electronegative** element after fluorine and oxygen, so the —NH_2 functional group is very polar. Primary and secondary amines can form hydrogen bonds due to the presence of N—H bonds within the molecule. Because nitrogen is less electronegative than oxygen, the hydrogen bonds formed by amines are weaker than those formed by alcohols. So the boiling points of amines are lower than those of similar-sized alcohols. The hydrogen bonding means the smaller amines are soluble in water. Tertiary amines cannot form hydrogen bonds because there is no N—H bond in the molecule. Consequently, their boiling points are lower than those of primary and secondary amines and they are generally insoluble in water. Amines also have an ammonia-like smell.

Properties of esters

The presence of the C═O and C—O bonds makes esters polar. However, esters tend to be liquid at room temperature and their boiling points are much lower than carboxylic acids of similar mass. This is because their main intermolecular forces are dipole–dipole forces, which are weaker than the hydrogen bonding in carboxylic acids and alcohols.

Most esters are not very soluble in water because of the lack of hydrogen bonding and the presence of hydrophobic alkyl groups. However, they are soluble in organic solvents. Many esters are also used as solvents in industry. For example, ethyl ethanoate is a common solvent in nail polish remover.

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Properties of amides

Amides have both N—H and C═O polar bonds. This means they form hydrogen bonds between the H of one molecule and the O of another, as well as with water. Therefore, most amides are solids at room temperature and their melting points are high considering the size of the molecule.

Small amides are soluble in water, but their solubility decreases as the amides get larger or more alkyl groups are attached to the nitrogen.

SECTION REVIEW 16.4

UNDERSTANDING

1 Compare and contrast the physical properties of amines, esters and amides, by considering and explaining the relative strength of the intermolecular forces that exist.

CHAPTER REVIEW QUESTIONS

REMEMBERING

1. Explain why:
   - **a** alcohols are soluble in water.
   - **b** solubility decreases as the alkane chain of the alcohol gets longer.
2. Explain why smaller carboxylic acids are soluble in water but those with longer chains are not.
3. Explain why esters have little solubility in water, yet the two chemical groups from which they are formed are quite soluble.
4. Explain why amines and amides have higher melting and boiling points and are soluble in water.

UNDERSTANDING

5. Explain why the physical properties of alkanes, alkenes and alkynes are similar but their chemical properties are different.
6. Why are smaller aldehydes and ketones soluble in water but larger molecules are not?
7. Carboxylic acids have higher boiling points than alcohols of corresponding mass. Explain in terms of bonding why this is so.

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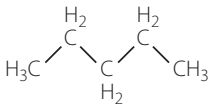
END-OF-CHAPTER EXAM

End-of-chapter test

1 Four organic molecules are shown below:



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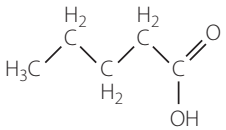

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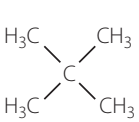

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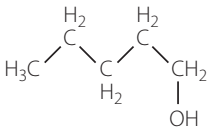


Z

Which of the options below is the correct sequence of molecules in descending order of boiling point?

A Z>X>W>Y

B X>Z>W>Y

C Y>W>Z>X

D Y>X>W>Z

2 Which of the phenomena listed below is the strongest intermolecular force present between molecules of chlorobutane?

A Hydrogen bonding

B Dispersion forces

C Dipole–dipole forces

D Ion-dipole forces

3 Which of the phenomena listed below is the strongest intermolecular force present between molecules of 2-pentanamine?

A Hydrogen bonding

B Dispersion forces

C Dipole–dipole forces

D Ion-dipole forces

4 Soaps consist of molecules that can form positive interactions with both non-polar oils that are insoluble in water and with water itself. This means they can all be washed away. Explain why carboxylic acid molecules can be used in soaps.

17 ORGANIC REACTIONS AND REACTION PATHWAYS

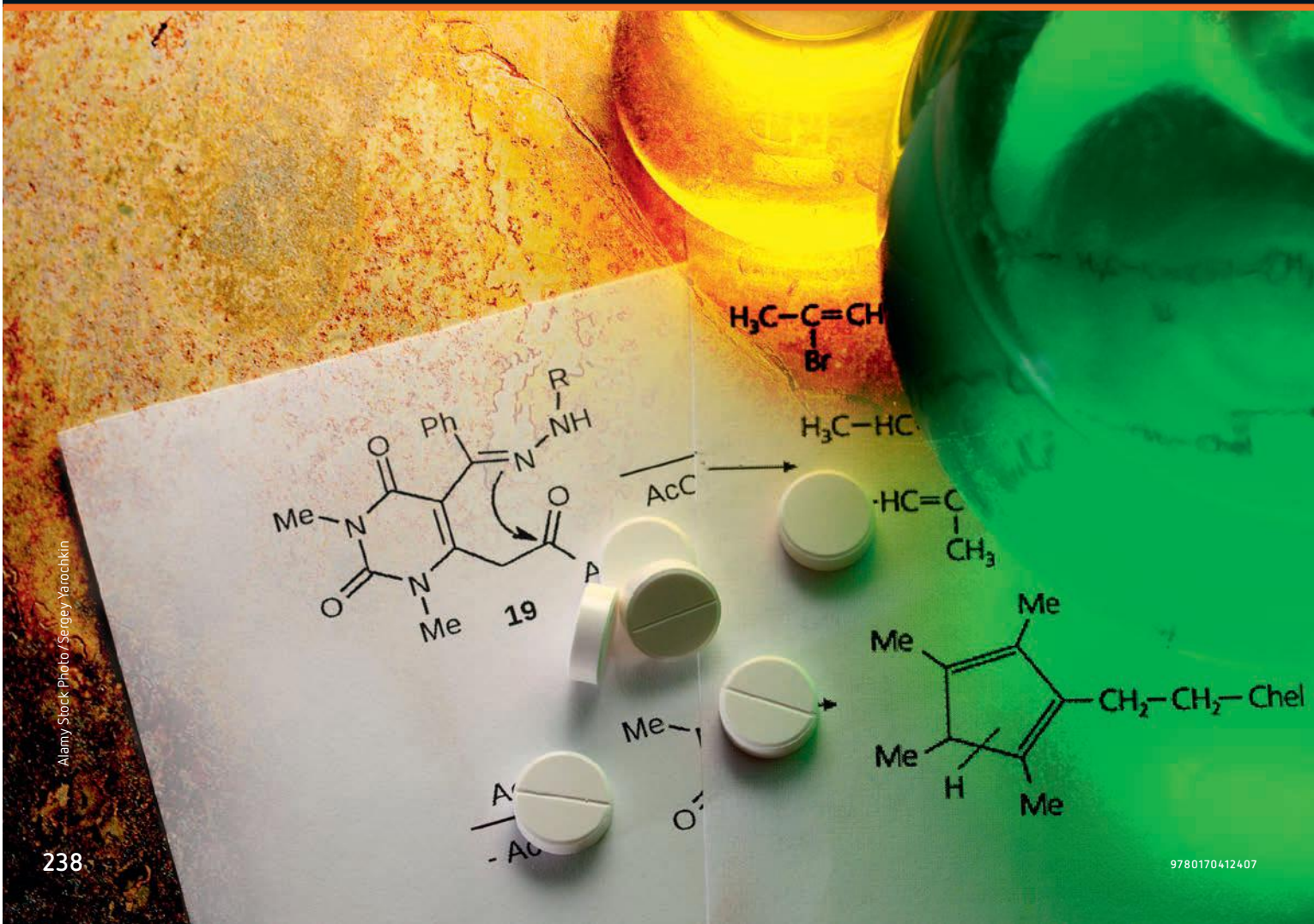
Introduction

Organic molecules take part in a wide range of chemical reactions, depending on the functional groups that they contain. These reactions are critical when synthesising larger molecules and, hence, are the basis for the entire organic chemical manufacturing industry.

Stimulus questions

Why do different organic chemicals react in different ways?

How can we predict the products of an organic reaction?



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17.1 Reactions of alkanes

Alkanes contain unreactive C—C and C—H bonds; therefore, they do not react with most substances. They can only perform two important reactions: combustion and substitution.

Combustion

Combustion is the most significant reaction that alkanes undergo, and their ability to combust is the reason why we primarily use them as fuels. When ignited in a plentiful supply of oxygen, alkanes react readily to produce water, carbon dioxide and a large quantity of heat. Balanced equations for the combustion of methane and octane are shown below.

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

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

These reactions represent **complete combustion**, where the alkanes have been fully oxidised to form carbon dioxide and water. We can see that for this reaction to occur, the ratio of oxygen to methane should be 2:1. For the larger hydrocarbon octane, the ratio is significantly larger, at 25:2.

complete combustion burning of an organic compound in sufficient oxygen to produce carbon dioxide and water

If there is insufficient oxygen to fully oxidise the methane, then **incomplete combustion** occurs and either carbon monoxide or carbon are formed as shown below.

incomplete combustion burning of an organic compound in limited oxygen to produce carbon monoxide or carbon and water

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g)$$

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

Carbon monoxide is a toxic gas, which can be produced when methane or other hydrocarbons are combusted in poorly ventilated conditions. When larger hydrocarbon molecules, such as octane, present in petrol, are burned in air, it is impossible to achieve complete combustion, as the percentage of oxygen in air is relatively low, around 20 per cent. Therefore, car exhausts always contain carbon monoxide, which is why drivers should never run a car engine in an enclosed space.

The presence of carbon particles in the second reaction above has significance for Bunsen burners, as this reaction causes a glowing orange 'safety' flame to occur when the methane is burned in a limited supply of oxygen – a lower-temperature, visible flame which occurs when the air hole is closed. The blue 'roaring' flame of a Bunsen burner occurs when the air hole is open. It has a much higher temperature because there is complete combustion, as the open air hole ensures a plentiful supply of oxygen.

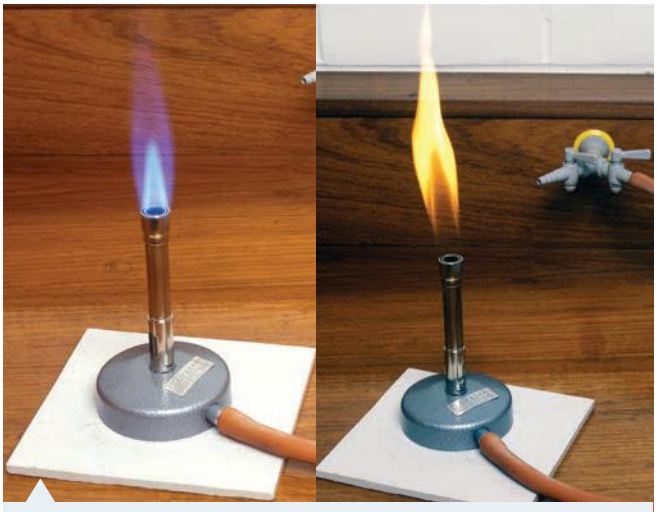

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FIGURE 17.1.1 The blue and orange flames of a Bunsen burner.

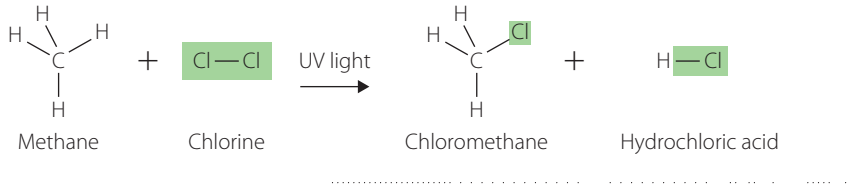
Free radical substitution

Substitution reactions involve replacing one atom in a molecule with another. In the case of alkanes, **free radical substitution** reactions take place with other molecules such as chlorine or bromine. These reactions require a significant amount of energy, in the form of ultraviolet (UV) light.

free radical substitution UV-light-initiated reaction, where a hydrogen atom is replaced with a halogen atom

The equation below shows an example of such a reaction between methane and chlorine, where you can see in the methane that one hydrogen atom has been replaced by one chlorine atom, producing chloromethane.

FIGURE 17.1.2
Free radical substitution reaction



intermediate species
species formed during a reaction pathway as precursors to the desired product

The UV light provides the energy for the chlorine molecule to break up into highly reactive **intermediate species**, called free radicals. The methane molecule is relatively unreactive and so it requires a highly activated substance, such as a free radical, to initiate the reaction. The reaction is highly exothermic and often results in a violent explosion.

It is possible for any of the hydrogen atoms on the methane molecule to be substituted and also, more than one of the hydrogen atoms from a single methane molecule can be substituted. As such, a range of products will be formed from this reaction in an uncontrolled manner, meaning that it has little practical use.

SECTION REVIEW 17.1

REMEMBERING

1 Explain what is meant by a:
   - **a** free radical substitution reaction
   - **b** combustion reaction.

2 How are the reaction products different in complete and incomplete combustion reactions?

UNDERSTANDING

3 Write an equation to show the complete combustion of pentane.

4 Write an equation to show the incomplete combustion of pentane, forming carbon as a product.

5 Write an equation to show the free radical substitution reaction of pentane with chlorine, and draw the structures of four possible products.

APPLYING

6 Write an equation for the complete combustion of octane and explain why octane is more likely to burn with a sooty flame than pentane.

ANALYSING

7 Suggest why the free radical substitution reaction of alkanes is not widely used in synthesising useful chemical products.

17.2 Reactions of alkenes

unsaturated compound
a chemical compound that contains carbon-carbon double bonds or triple bonds, such as those found in alkenes or alkynes, respectively

saturated compound
a chemical compound that resists addition reactions; less reactive than unsaturated compounds

The alkene family contains hydrocarbons in which one pair of carbon atoms is joined by a double bond and all the other carbon atoms are joined by single bonds. Compounds that contain multiple bonds between carbon atoms are called **unsaturated compounds**. Alkenes are therefore unsaturated hydrocarbons.

Alkenes are hydrocarbons and therefore take part in combustion and free radical substitution reactions in the same way as alkanes. However, the presence of the double bond makes alkenes far more reactive than alkanes. Alkenes can participate in addition reactions, where the double bond is lost, to form a **saturated** molecule.

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Addition reactions

Addition reactions involve adding more atoms to a compound by breaking the double bond and forming a saturated molecule. Addition reactions to alkenes can occur with a variety of different molecules.

addition reaction
unsaturated molecules combining with another molecule to become saturated

hydrogenation
an addition reaction where hydrogen is the molecule added

reduction
a hydrogenation reaction of either alkenes or amines

Addition reaction with hydrogen

An alkene is converted to an alkane with the aid of a catalyst, usually a finely divided metal such as platinum, palladium or rhodium, at a temperature of 150°C. This reaction is also described as **hydrogenation** or **reduction**.

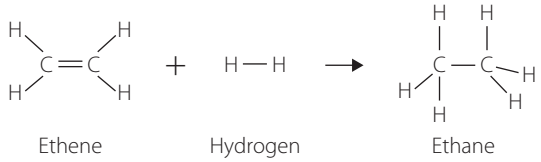


FIGURE 17.2.1
Addition reaction of ethene with hydrogen

Addition reaction with a halogen

When a halogen such as chlorine or bromine reacts with an alkene, halogen atoms add across the double bond to form a di-substituted haloalkane.

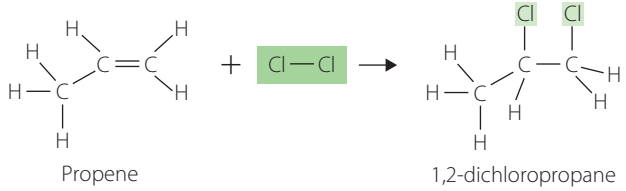


FIGURE 17.2.2
Addition reaction of propene with chlorine

This reaction is commonly used to test for the presence of unsaturated molecules. If brown bromine water is added to an alkene, it will lose its colour because of the addition reaction that takes place.

Addition reaction with water (hydration)

In this reaction, water, in the presence of a phosphoric acid catalyst at 350°C, will take part in an addition reaction with an alkene. An H and OH are added across the double bond to produce an alcohol. For example, ethene is converted to ethanol, as seen in Figure 17.2.3.

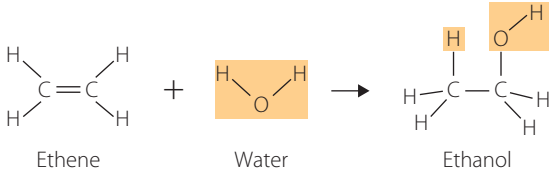
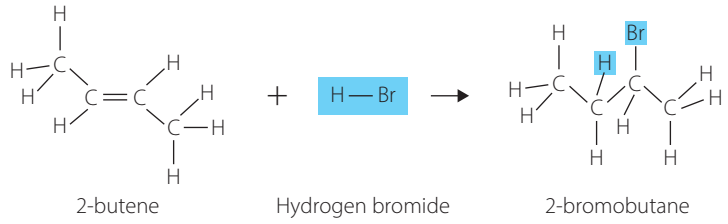


FIGURE 17.2.3
Addition reaction of ethene with water

Addition reactions with halogen halides

Halogen halides are the hydrides of Group 17 elements, in other words HF, HCl, HBr or HI. These compounds also take part in addition reactions with alkenes to form a haloalkane, as seen in Figure 17.2.4.

FIGURE 17.2.4
Addition reaction of 2-butene with hydrogen bromide

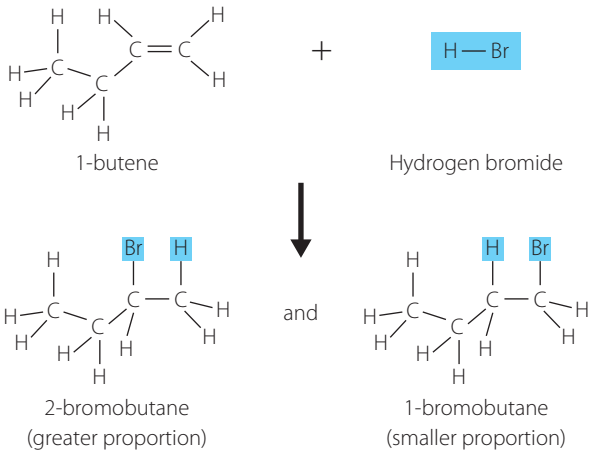


Markovnikov's rule – addition to unsymmetrical alkenes

In the reaction in Figure 17.2.4, adding hydrogen bromide to 2-butene can only lead to one product, 2-bromobutane. However, if we used 1-butene instead, two products would be possible, as shown in Figure 17.2.5. These products could then be separated from each other, usually by **fractional distillation** as they have marginally different boiling points.

fractional distillation
separation of a mixture of organic compounds according to their different boiling points

FIGURE 17.2.5
Addition of HBr to 1-butene



KEY LAW

Markovnikov's Law states that in an addition reaction of hydrogen halides or water to unsymmetrical alkenes, the hydrogen atom is added preferentially to the carbon atom from the C=C bond that is already bonded to the greater number of hydrogen atoms.

While a mixture of both 2-bromobutane and 1-bromobutane are produced in this reaction, in fact, there would be a greater proportion of 2-bromobutane produced. This is explained by Markovnikov's rule of addition to unsymmetrical alkenes. In 1-butene, carbon atom 1 has two hydrogen atoms whereas carbon atom 2 has one. Therefore, the hydrogen from the HBr is more likely to be added to carbon atom 1, leading to a greater proportion of 2-bromobutane in the mixture. However, some 1-bromobutane will also be formed.

Polymerisation

In the presence of a suitable catalyst and reaction conditions, ethene molecules will react with themselves to form long chains. This type of reaction is called **addition polymerisation**, and is discussed in more detail in Chapter 22.

addition polymerisation
formation of polymer chains by the addition reaction of unsaturated monomers

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SECTION REVIEW 17.2

REMEMBERING

1 Define:
   a addition reaction
   b addition polymerisation reaction.
2 Explain why alkenes can undergo addition reactions, yet alkanes cannot.

UNDERSTANDING

3 Write equations to show the reactions of the following chemicals. Where necessary, indicate the required reaction conditions:
   a propene with liquid bromine (Br_2)
   b 2-methyl propene with water
   c 1-butene with hydrogen (H_2)
   d 2-butene with HBr

APPLYING

4 Which of the reactions in Question 3 is likely to produce more than one product? For each of these reactions, list the possible products and indicate which is likely to be the preferred product.

17.3 Reaction of alkynes

planar
a molecule, or portion of a molecule such as a ring, where all of the atoms lie in the same plane

Alkynes are a family of hydrocarbons containing at least one triple bond between a pair of carbon atoms (C≡C). The alkynes, like the alkenes, are unsaturated hydrocarbons. The simplest member, ethyne, C_2H_2, is a linear molecule, as shown in Figure 17.3.1. The triple bond causes the overall molecular shape to become more planar, as with alkenes.

H—C≡C—H

FIGURE 17.3.1 Ethyne

The reactions of alkynes are similar to those of alkenes, and they can take part primarily in combustion and addition reactions, with the same reagents that are used for alkenes.

Combustion reactions

Like alkanes and alkenes, alkynes undergo combustion in a plentiful supply of oxygen to produce carbon dioxide and water. For example:

$$C_3H_4(g) + 4O_2(g) \rightarrow 3CO_2(g) + 2H_2O(g)$$

This highly exothermic reaction is key to the use of ethyne, (also known as acetylene) in oxyacetylene torches.

SantiPhotoSS / Shutterstock.com

FIGURE 17.3.2 Oxyacetylene torches are widely used for cutting and welding steel.

Addition reactions

Alkynes undergo addition reactions, but they are less reactive than alkenes. The addition reaction usually takes place in two steps. In the first step, addition of a reagent results in the triple bond being converted to a double bond, then in a second addition step, the double bond is broken, resulting in a saturated compound.

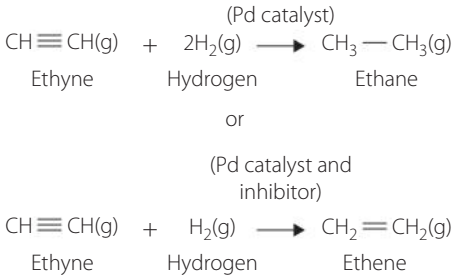


FIGURE 17.3.3 Addition of hydrogen to alkynes

Hydrogenation

The reaction of alkynes with hydrogen gas is known as hydrogenation. Under pressure, hydrogen adds to an alkyne in the presence of a metal catalyst, such as finely divided nickel, palladium or platinum, to form a corresponding alkene or alkane. This is shown in Figure 17.3.3.

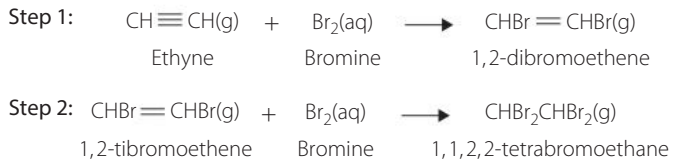
If we add an inhibitor, its presence prevents ethene from being hydrogenated to the saturated alkane.

Halogenation

Alkynes can react with a halogen (**halogenation**). For example, when bromine or chlorine are added across the triple bond, a substituted haloalkene is formed. A second step then produces a haloalkane. This is shown in Figure 17.3.4.

halogenation
addition reaction involving a halogen molecule

FIGURE 17.3.4
Addition of bromine to alkynes



PRACTICAL ACTIVITY 17.3.1

Comparing reactivities of alkanes and alkenes (teacher demonstration)

The reactivities of alkanes and alkenes are different. Alkanes react quite slowly by a process of substitution, while alkenes react rapidly, usually by the process of addition.

AIM

To compare the reactivities of alkanes and alkenes

EQUIPMENT

- 3 mL samples of alkanes and alkenes: hexane, cyclohexane and cyclohexene
- 4 mL of 0.01 mol L^{-1} potassium permanganate ($KMnO_4$) solution
- 5 mL of bromine (Br_2) water
- 2 mL of 2 mol L^{-1} sulfuric (H_2SO_4) acid
- Distilled water
- Four test tubes and test-tube rack
- Four graduated droppers
- 5 mL measuring cylinder

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WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Cyclohexane and cyclohexene are toxic.	Avoid contact with skin; wear gloves and a laboratory coat. Avoid inhaling vapours; use in a fume hood. Wash your hands at the end of the experiment. This activity is a teacher demonstration only.
Bromine water is poisonous and corrosive.	Avoid contact with skin; wear gloves and a laboratory coat. Avoid inhaling vapours; use in a fume hood. Wash your hands at the end of the experiment.
Sulfuric acid is corrosive.	Wear gloves and personal protective equipment to avoid contact with skin. Wash your hands at the end of the experiment.
Hexane, cyclohexane and cyclohexene are highly flammable.	Ensure no flame sources are present near either of these chemicals.

RISK ASSESSMENT

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

Part A Oxidation reactions with acidified $KMnO_4$ solution

1. Label three test tubes, one for each hydrocarbon.
2. Place 1 mL of each hydrocarbon into the corresponding test tube.
3. In a clean test tube, mix 4 mL of $KMnO_4$ solution and 2 mL of H_2SO_4.
4. Add 1 mL of the $KMnO_4/H_2SO_4$ solution to each of the test tubes containing the hydrocarbons.
5. Shake gently and observe for 5 minutes.
6. Dispose of the solutions in a chemical waste jar. Do not pour down the sink.
7. Rinse the test tubes and droppers with distilled water.

Part B Addition and substitution reactions with bromine

8. Place 1 mL of each hydrocarbon into the corresponding test tube.
9. Add 1 mL of Br_2 to each test tube.
10. Shake gently and observe for 5 minutes.
11. If a change is noted, add another 1 mL of Br_2 to that test tube and observe.
12. Dispose of the solutions in a chemical waste jar. Do not pour them down the sink.

RESULTS

Record the results in a table similar to the one below.

REAGENT		HEXANE	CYCLOHEXANE	CYCLOHEXENE
Acidified $KMnO_4$ solution	After addition			
	After 5 min			
Br_2	After addition			
	After 5 min			

ANALYSIS

1. Which of the hydrocarbons were readily oxidised by the acidified $KMnO_4$ solution?
2. Which reacted with the bromine solution?
3. Write the equation for any reaction that occurred with bromine.

CONCLUSION

State in your own words the difference between the reactivities of alkanes and alkenes.

17.3.1 Reaction

17.3.2 Explanation

SECTION REVIEW 17.3

REMEMBERING

1 Explain what is meant by an alkyne.

2 Explain why alkenes and alkynes are regarded as unsaturated hydrocarbons.

UNDERSTANDING

3 Write balanced equations to show the reactions of:

- **a** propyne with liquid bromine (Br_2)
- **b** ethyne with water
- **c** 1-butyne with hydrogen (H_2) to form butane
- **d** 2-butyne with HBr.

ANALYSING

4 Ethyne is also known as acetylene and is used as the fuel for high-temperature torches that cut and weld metals. What properties does ethyne possess that lead to it being used in these torches?

17.4 Reactions of haloalkanes

Whereas alkanes, alkenes and alkynes are non-polar molecules, the introduction of a halogen (F, Cl, Br or I) atom to a molecule means a polar carbon–halogen bond is formed, which significantly changes the way in which the molecule reacts.

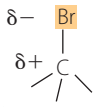

FIGURE 17.4.1 The polar carbon–bromine bond

Nucleophilic substitution

As the halogen atom is more electronegative than the carbon atom, there is an unequal distribution of electron density along this bond, so that the halogen atom is described as slightly negatively charged and the carbon atom, slightly positively charged. This is represented in Figure 17.4.1 by the symbols δ+ and δ–. Other species, which are known as 'nucleophiles' and which are either negatively charged or possess a lone pair of electrons, are attracted to the slightly positively charged carbon atom and can form bonds with it in preference to the halogen atom. Hence, this is a substitution reaction, although with a different mechanism to free radical substitution, which was described for alkanes and alkenes. This substitution reaction is known as **nucleophilic substitution**, because the halogen atom is substituted for the nucleophile to form a molecule with a different functional group.

nucleophilic substitution reaction of haloalkanes where the halogen atom is replaced by an electron-rich species called a nucleophile

The reactions below show examples of different nucleophiles commonly used in reactions with haloalkanes.

Reaction with sodium hydroxide

Aqueous sodium hydroxide or potassium hydroxide can be reacted with haloalkanes to produce alcohols. The nucleophile is the hydroxide ion OH^-, and the halide ion is produced as a by-product.

Reaction with ammonia

Ammonia solution can be reacted with haloalkanes to produce amines. The nucleophile is the ammonia molecule, NH_3. Note that the by-product is the halogen halide, as one of the hydrogen atoms from the ammonia molecule combines with the substituted halide ion.

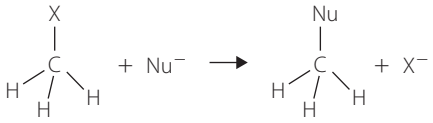

FIGURE 17.4.2 Nucleophilic substitution: X represents a halogen; Nu represents a nucleophile.

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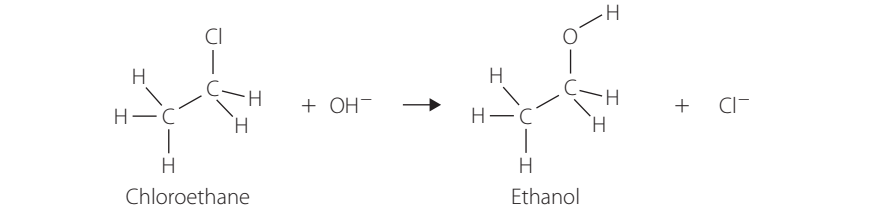


FIGURE 17.4.3 Reaction of chloroethane with hydroxide to form ethanol

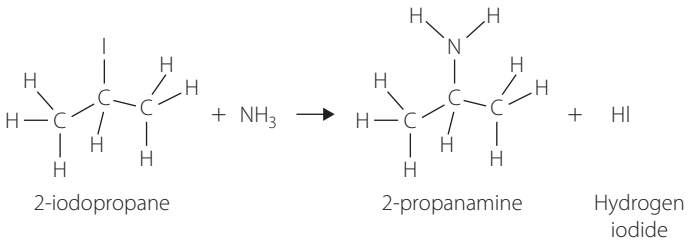


FIGURE 17.4.4 Reaction of 2-iodopropane with ammonia to form 2-propanamine

Reaction with cyanide

Potassium (or sodium) cyanide solution can be reacted with haloalkanes to produce nitriles. The nucleophile is the cyanide ion CN^-. The by-product is the substituted halide ion. This is a significant reaction in the synthetic production of new molecules, as it involves the formation of a new C—C bond, and hence the increase in size of the molecule.

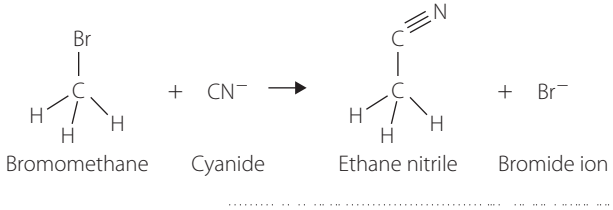


FIGURE 17.4.5 Reaction of bromomethane with potassium cyanide to form ethane nitrile

A common subsequent reaction to the formation of nitriles is the hydrogenation (or reduction) reaction to form amines, by reaction with hydrogen gas and with a metal catalyst such as nickel or palladium. Alternatively, the same reaction can be achieved by reaction with a metal hydride such as lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$). An example of this is shown in Figure 17.4.6.

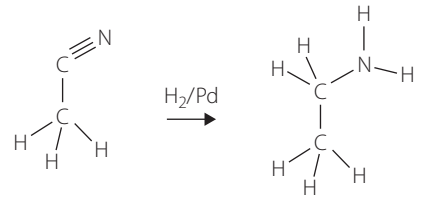


FIGURE 17.4.6 Reaction of ethane nitrile with hydrogen to form ethanamine

Elimination reactions

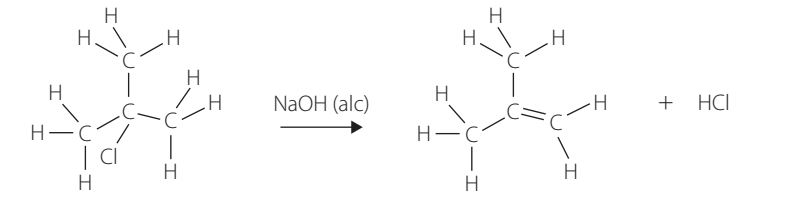
Haloalkanes can also take part in **elimination reactions**, resulting in the loss of a hydrogen halide molecule and the formation of C=C double bond to produce an alkene. The reagent used for this reaction is sodium hydroxide dissolved in ethanol, rather than the aqueous solution that is required for substitution.

We have now seen that there are two possible reactions for haloalkanes with the reagent sodium hydroxide, and there are several factors that determine whether substitution or elimination will occur:

- Primary haloalkanes tend to undergo substitution, whereas tertiary haloalkanes tend to undergo elimination. Secondary haloalkanes can undergo both reactions.

elimination reaction
reaction where a molecule is lost from a larger molecule, producing an unsaturated product

FIGURE 17.4.7
Elimination reaction of 2-chloro-2-methylpropane to form the alkene 2-methylpropene



- High concentrations of hydroxide solution favour elimination, whereas low concentrations favour substitution.
- A high proportion of water to ethanol in the solvent favours substitution. A greater proportion of ethanol favours elimination.
- A higher temperature favours elimination, a lower temperature favours substitution.

SECTION REVIEW 17.4

REMEMBERING

1. Explain what is meant by nucleophilic substitution reactions.
2. Explain what is meant by elimination reactions.
3. Explain what is meant by a polar covalent bond.
4. Explain how the reaction conditions can be used to determine whether substitution or elimination reactions occur.

UNDERSTANDING

5. Write balanced equations to show the reactions of:
   - **a** 1-bromopropane with aqueous sodium hydroxide
   - **b** 2-chlorobutane with ammonia
   - **c** iodoethane with potassium cyanide
   - **d** 2-iodo-2-methyl propane with ethanolic sodium hydroxide.

APPLYING

6. The reaction of hot, concentrated aqueous sodium hydroxide with 2-bromopropane can lead to a mixture of products. Explain what the products are and how the conditions could be manipulated to produce each of these products in greater amounts.

17.5 Reactions of alcohols

Ethanol or ethyl alcohol is the most commonly known member of the alcohol family. It is also one of the most widely used compounds of carbon. Ethanol is used:

- in beverages such as wine, beer and spirits
- as an additive to petrol or alternative fuel for motor vehicles
- as a solvent in many products, including medicines, antiseptics and household cleaners
- as a reactant and solvent for product manufacturing, including in plastics, adhesives, pharmaceuticals and perfumes.

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Ethanol is only one member of the family of organic compounds called alcohols. The alcohol class has the hydroxyl functional group —OH and alcohols are represented by the general formula ROH.

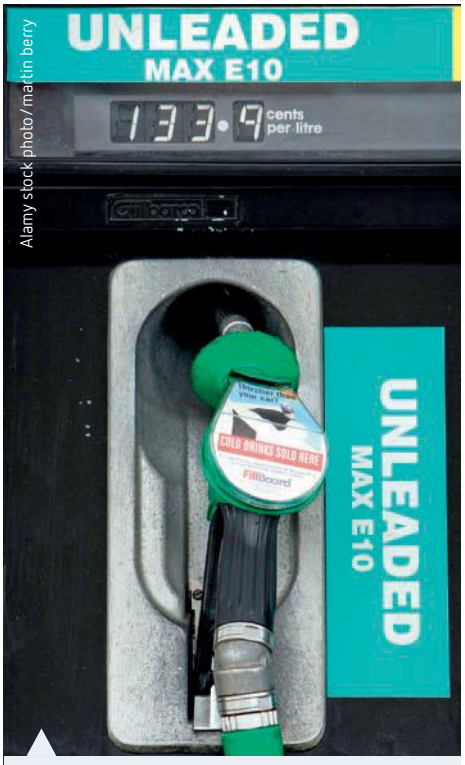


FIGURE 17.5.1 Ethanol is an additive in petrol

Types of alcohols

Alcohols can be classified according to the number of carbon atoms attached to the carbon bearing the —OH group:

- A **primary alcohol** is one in which one carbon atom is bonded to the carbon atoms attached to the hydroxyl group.
- A **secondary alcohol** is one in which two carbon atoms are bonded to the carbon attached to the hydroxyl group.
- A **tertiary alcohol** is one in which three carbon atoms are bonded to the carbon attached to the hydroxyl group.

Figure 17.5.2 shows primary, secondary and tertiary alcohols with the molecular formula C_4H_9OH.

primary alcohol
an alcohol where the —COH group is joined to one other carbon atom

secondary alcohol
an alcohol where the —COH group is joined to two other carbon atoms

tertiary alcohol
an alcohol where the —COH group is joined to three other carbon atoms

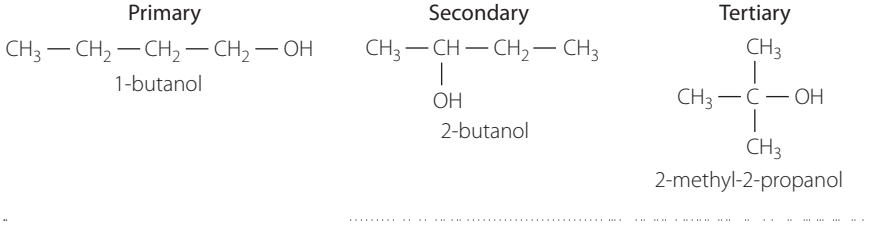


FIGURE 17.5.2 Primary, secondary and tertiary alcohols

The three different groups of alcohols have different physical properties and chemical reactivity. This is because the strength of the hydrogen bonding in alcohols depends on the extent to which the —OH group is available for bonding. When the —OH group is on the end of the carbon chain, as in primary alcohols, it is more available for bonding than when it is surrounded by alkyl groups in tertiary alcohols. This means that the boiling points decrease from primary to secondary to tertiary alcohols.

This also applies to their chemical reactivity. The most vigorous reaction with sodium occurs with a primary alcohol while the least vigorous is with the tertiary alcohol. Similarly, primary alcohols are more readily oxidised by a strong oxidising agent such as potassium permanganate than secondary alcohols, whereas tertiary alcohols are not oxidised.

Combustion reactions of alcohols

As for alkanes, alkenes and alkynes, alcohols undergo combustion, and can be used as fuels. They burn readily in air to produce carbon dioxide and water. For example:

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

Dehydration (elimination) reactions of alcohols

dehydration
an elimination reaction where a molecule of water is lost from an alcohol to form an alkene

Alcohols also undergo **dehydration** by losing water to form alkenes when heated with concentrated sulfuric or phosphoric acid catalysts. This is an example of elimination, where one larger molecule is converted into two smaller molecules. For example:

$$\underset{\text{2-butanol}}{CH_3CH_2CHOHCH_3(l)} \rightarrow \underset{\text{1-butene}}{CH_3CH_2CH{=}CH_2(g)} + H_2O(g)$$

Oxidation reactions of alcohols

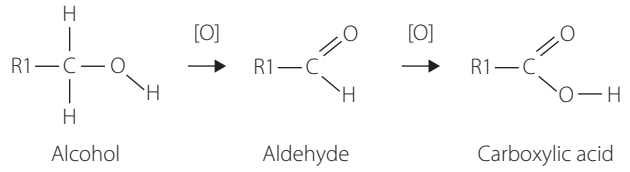
oxidation
a reaction where an oxidising agent is used to convert primary alcohols to aldehydes, and carboxylic acids and secondary alcohols to ketones

Alcohols readily undergo **oxidation** with strong oxidising agents such as acidified permanganate or dichromate solutions. The products of the reaction depend on the structure of the alcohol.

Oxidation of primary alcohols

Primary alcohols are oxidised to form aldehydes, which are in turn oxidised to form carboxylic acids. These general reactions are shown below. The [O] above the arrow in the equation represents the oxidising agent that is reacting with the alcohol. Commonly, either acidified potassium dichromate(VI) or acidified potassium manganate(VII) are used for this purpose.

FIGURE 17.5.3 Oxidation of primary alcohols (R1 indicates the alkyl section of the molecule)



Acidified potassium dichromate(VI)

$$\underset{\text{orange}}{Cr_2O_7^{2-}} + 14H^+ + 6e^- \longrightarrow \underset{\text{green}}{2Cr^{3+}} + 14H_2O$$

Acidified potassium manganate(VII)

$$\underset{\text{purple}}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow \underset{\text{pale pink}}{Mn^{2+}} + 4H_2O$$

FIGURE 17.5.4 Half-equations for the reduction of acidified potassium dichromate (vi) and acidified potassium manganate (vii)

Potassium dichromate(VI) ($K_2Cr_2O_7$) is a distinctive orange colour that turns to green Cr^{3+} when it is reduced by the alcohol. Potassium manganate(VII) ($KMnO_4$) is a purple colour that turns a very pale pink when it is reduced to Mn^{2+} ions.

The half-equations for the reduction of both of these alternative reagents can be seen in Figure 17.5.4. In both cases, acid is required as the source of the H^+ ions, and sulfuric acid should be used, as the sulfate ion that is also present will not be oxidised by the reagent.

The following example shows the oxidation of ethanol to the aldehyde ethanal, then the further oxidation of ethanal to ethanoic acid using acidified potassium dichromate as the oxidising agent. (The oxidation and reduction half-reactions can be derived from the overall reactions given.)

$$\underset{\text{Ethanol}}{3CH_3CH_2OH(aq)} + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow \underset{\text{Ethanal}}{3CH_3CHO(aq)} + 2Cr^{3+}(aq) + 7H_2O(l)$$

$$\underset{\text{Ethanol}}{3CH_3CHO(aq)} + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow \underset{\text{Ethanoic acid}}{3CH_3COOH(aq)} + 2Cr^{3+}(aq) + 7H_2O(l)$$

Aldehydes are easily oxidised to form carboxylic acids, so the final product will not contain any aldehyde; it will contain only the carboxylic acid. A sample of an aldehyde can be obtained if an excess of the alcohol is used and the aldehyde is distilled off as soon as it forms, before it can be oxidised.

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The overall equation for the oxidation of ethanol to ethanoic acid can be obtained by adding the two previous equations together:

$$\underset{\text{Ethanol}}{3CH_3CH_2OH(aq)} + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow \underset{\text{Ethanoic acid}}{3CH_3COOH(aq)} + 4Cr^{3+}(aq) + 11H_2O(l)$$

Oxidation of secondary alcohols

Secondary alcohols are oxidised to form ketones, which cannot be further oxidised. So the final product in the oxidation of a secondary alcohol is a ketone. Again, either acidified potassium manganate(VII) or potassium dichromate(VI) are the oxidising agents that are used. The general equation for the oxidation of a secondary alcohol is shown in Figure 17.5.5.

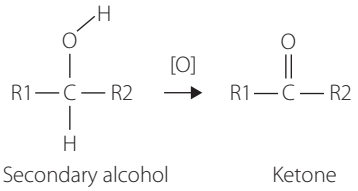


FIGURE 17.5.5 Oxidation of secondary alcohols

The half and overall equations for the oxidation of 2-propanol with acidified potassium manganate(VII) are:

$$\text{Oxidation: } 5CH_3CHOHCH_3(aq) \rightarrow 5CH_3COCH_3(aq) + 10H^+(aq) + 10e^-$$

$$\text{Reduction: } 2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

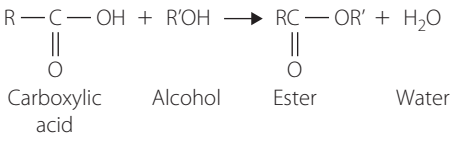
$$\text{Overall: } \underset{\text{2-propanol}}{5CH_3CHOHCH_3(aq)} + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow \underset{\text{Propanone}}{5CH_3COCH_3(aq)} + 2Mn^{2+}(aq) + 8H_2O(l)$$

Oxidation of tertiary alcohols

Tertiary alcohols are not oxidised in the same way as primary and secondary alcohols, as it takes a large amount of energy to break a C—C bond. Consequently, there is no change to the colour of either acidified potassium dichromate(VI) or acidified potassium manganate(VII) if we attempt this reaction with a tertiary alcohol.

Esterification (condensation) reactions of alcohols

Alcohols react with carboxylic acids to form esters. The general equation for this reaction is shown below. These reactions will be discussed later in this chapter.



Reaction of alcohols with sodium

Alcohols react with sodium to form an alkoxide anion (RO^-) and hydrogen gas. This is a similar reaction to the one between sodium and water but is less vigorous.

$$2ROH + 2Na \rightarrow 2RO^-Na^+ + H_2$$

For example:

$$\underset{\text{Ethanol}}{2CH_3CH_2OH(l)} + \underset{\text{Sodium}}{2Na(s)} \rightarrow \underset{\text{Sodium ethoxide}}{2CH_3CH_2O^-Na^+(aq)} + \underset{\text{Hydrogen}}{H_2(g)}$$

In this reaction, the alcohol acts as an acid. The alkoxide produced is a strong base and is the conjugate of the weak acid, which is the alcohol. The alkoxide readily reacts with water to form the original alcohol and produce OH^- ions. For example:

$$CH_3CH_2O^-(aq) + H_2O(l) \rightarrow CH_3CH_2OH(aq) + OH^-(aq)$$

PRACTICAL ACTIVITY 17.5.1

Distinguishing between primary, secondary and tertiary alcohols (teacher demonstration)

You will investigate the reactions of primary, secondary and tertiary alcohols with an oxidising agent and with sodium to identify a way of distinguishing between the three groups.

AIM

To examine and compare the reactions of primary, secondary and tertiary alcohols

EQUIPMENT

- 10 mL each of ethanol, 1-butanol, 2-butanol, 2-methyl-2-propanol
- 5 mL of 0.1 mol L^{-1} sodium dichromate ($Na_2Cr_2O_7$) solution
- 5 mL of 0.01 mol L^{-1} potassium permanganate ($KMnO_4$) solution
- 5 mL of 6 mol L^{-1} H_2SO_4
- Four very small pieces of Na
- Hot plate or water bath
- Thermometer
- 250 mL beaker
- 10 large test tubes
- 10 mL measuring cylinder
- Metal tongs
- Dropper
- Tweezers

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Sodium dichromate is toxic.	Avoid contact with skin; wear gloves and a laboratory coat. Avoid inhaling vapours; use in a fume hood. Wash your hands at the end of the experiment. This practical activity is a teacher demonstration only.
Sodium metal oxidises rapidly in air and is highly reactive with water. Contact will burn the skin.	Wear gloves and a laboratory coat. Do not allow the substance to come into contact with water. Handle only with tweezers and use a very small amount.
Sulfuric acid is corrosive.	Wear gloves and personal protective equipment and avoid contact with the skin. Wash your hands at the end of the experiment.
Alcohols are highly flammable.	Ensure no flame sources are present in the location of these chemicals.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

PART A: REACTIONS WITH OXIDISING AGENTS

Reaction with permanganate (MnO_4^-)

1. Pour 2 mL of each of the alcohols into four separate, labelled test tubes.
2. In a separate test tube mix 4 mL of potassium permanganate solution with 1 mL of sulfuric acid.

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3 Using the dropper place 4–5 drops of the permanganate mixture into each of the test tubes containing the alcohols.
4 Record your observations, including smell.
5 Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour them down the sink.
6 Rinse out your test tubes ready for the reaction with $Cr_2O_7^{2-}$.

Reaction with dichromate ($Cr_2O_7^{2-}$)

1 Prepare a water bath at a temperature of 80ºC.
2 Pour approximately 2 mL of each of the alcohols into four separate, labelled test tubes.
3 In a separate test tube mix 4 mL of sodium dichromate solution with 2 mL of sulfuric acid.
4 Place 1 mL of this solution into each of the test tubes containing the alcohols, shaking gently to mix.
5 Place the test tubes in the water bath for 5 minutes. Shake gently occasionally.
6 Record any changes, including smell.
7 Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour them down the sink.

PART B: REACTION WITH SODIUM METAL

1 Pour 2 mL of each of the alcohols into separate, dry, labelled test tubes.
2 Obtain four very small pieces of sodium from your teacher. Place one piece in each test tube.
3 Carefully observe the rates at which the reactions occur. Record your observations.
4 Dispose of the solutions in a chemical waste jar as directed by your teacher. Do not pour them down the sink.

RESULTS

Draw up a table to record your observations.

ANALYSIS

1 Rank the alcohols in order of reactivity.
2 Generalise this to a statement about the relative reactivities of primary, secondary and tertiary alcohols.
3 Write the names and formulas of the products formed where reactions took place.
4 Write separate balanced equations for the oxidation of ethanol by MnO_4^- to ethanal and ethanoic acid.
5 Write a general equation for the reaction of alcohols with sodium.

CONCLUSION

In your own words, state the difference between the reactivities of the different classes of alcohols.

EXTENSION

Use your understanding of the reactions of ethanol to use these tests to distinguish between alcoholic and non-alcoholic wine.

SECTION REVIEW 17.5

REMEMBERING

1 Explain, with examples, what is meant by the terms primary, secondary and tertiary alcohols.
2 Identify the commonly used oxidising agents in reactions with alcohols are.
3 Draw the following functional groups:
   a hydroxyl
   b aldehyde
   c ketone
   d carboxyl.

UNDERSTANDING

4 Write balanced equations to show the reactions of:

- **a** 1-propanol with acidified potassium dichromate(VI)
- **b** 2-butanol with acidified potassium manganate(VII)
- **c** 2-methyl-2-pentanol with acidified potassium dichromate(VI)
- **d** propanal with acidified potassium manganate(VII)
- **e** methanol with sodium.

APPLYING

5 Explain why sugars containing aldehyde functional groups are known as 'reducing sugars', but those containing ketone groups are not.

6 Suggest why wine can develop an acidic, 'vinegary' taste if left uncorked more than three days.

17.6 Reactions of carboxylic acids and esters

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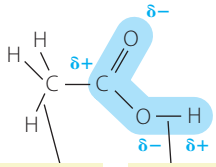
FIGURE 17.6.1 Ants inject formic acid when they sting.

Carboxylic acids can be found throughout nature. A few of the more common acids are formic (methanoic) acid, which is a chemical defence for some ants that they inject when they bite. Ethanoic acid is found in vinegar, propanoic acid is found in cheese, butanoic acid is in spoiled butter, citric acid is found in citrus fruits and lactic acid is found in milk and other dairy products. Many of these carboxylic acids have strong, unpleasant odours. Synthetic compounds manufactured from carboxylic acids include soap, some plastics, pharmaceuticals and herbicides.

monoprotic an acid that dissociates to produce one hydrogen ion per molecule

The carboxylic acid group is **monoprotic**. This is because the only hydrogen atom that can react with a base is the one in the —COOH group, as shown in Figure 17.6.2. Carboxylic acids undergo the usual reactions of acids.



This bond is virtually non-polar and so this H cannot be drawn away and leave its electron behind.

This bond is highly polar. Since the electrons spend more time near the O atom, H can be drawn away by a base and leave its electron behind.

Smith et al. 2010 Chemistry in use. Book 2

FIGURE 17.6.2 Why ethanoic acid can only act as a monoprotic acid

Reaction with reactive metals

Carboxylic acids react with reactive metals to produce a salt and hydrogen gas.

For example:

$$Mg(s) + 2CH_3COOH(aq) \rightarrow Mg^{2+}(aq) + 2CH_3COO^-(aq) + H_2(g)$$

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Reaction with base (neutralisation)

Carboxylic acids react with a base to produce a salt and water in a neutralisation reaction.

For example:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq) + H_2O(l)$$

They will also react with carbonates, another form of base, to produce a salt plus carbon dioxide and water. This reaction is commonly used to test for the presence of an acid, by adding carbonate and observing the evolution of bubbles of carbon dioxide. For example:

$$2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2Na^+(aq) + 2CH_3COO^-(aq) + CO_2(g) + H_2O(l)$$

Esterification

Esterification is the reaction of a carboxylic acid with an alcohol to produce an ester. Esters are an important group of organic compounds found in a wide range of biological systems. They have pleasant, fruity odours and are responsible for the flavours and fragrances of many fruit and flowers. Solid animal fats, and animal and vegetable oils are natural esters.

esterification
the condensation reaction where an ester is formed from an alcohol and a carboxylic acid

Alamy stock photo/Lucie Lang

FIGURE 17.6.3 Beeswax is a natural ester

The ester ethyl butanoate is found in pineapples, peaches and apricots. The ester group formed is also an **ester link** because it links the two molecules that react, an alcohol and a carboxylic acid, to produce it.

The esterification reaction between an alcohol and a carboxylic acid is moderately slow at room temperature. To speed up the reaction, the mixture is heated in the presence of an acid catalyst, usually concentrated sulfuric acid. The general reaction can be written as shown in Figure 17.6.5.

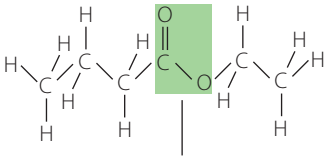


FIGURE 17.6.4 Ethyl butanoate

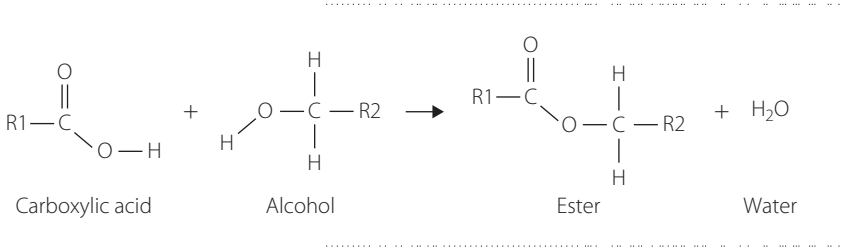


FIGURE 17.6.5 The formation of an ester

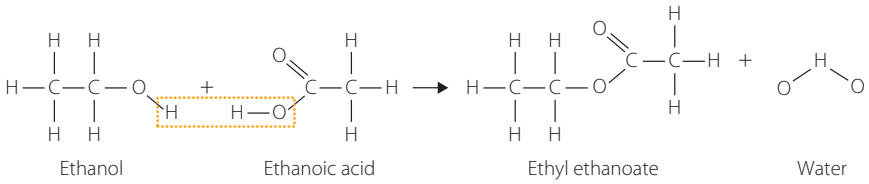
ester link
the —COOC— group that links two alkyl chains in an ester molecule

Notice that this reaction produces a water molecule. A reaction in which the functional groups of two molecules join and a small molecule is released is called a **condensation reaction**.

Figure 17.6.6 shows the condensation reaction between ethanoic acid and ethanol to produce ethyl ethanoate and water.

condensation reaction
a reaction where two molecules combine to form a larger molecule and produce water as a by-product

FIGURE 17.6.6
Reaction between ethanoic acid and ethanol

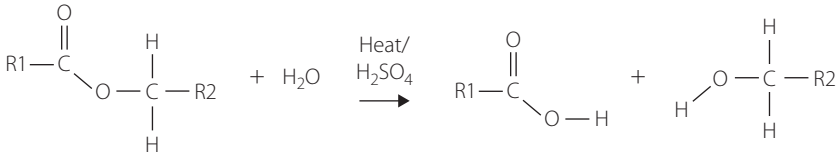


Hydrolysis of esters

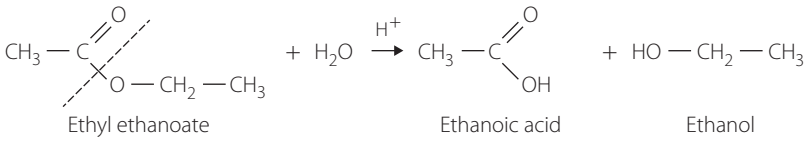
The reaction for forming esters is reversible and so, under certain conditions, esters can react with water to produce the original acid and alcohol from which they were made. This reaction with water is called **hydrolysis**. Hydrolysis can occur under both acid and alkaline conditions. Under acid conditions (in the presence of heat and sulfuric acid), the reaction is as shown in Figure 17.6.7.

hydrolysis
a reaction where a larger molecule is split into two smaller molecules by reacting with water in the presence of an acid or base catalyst

FIGURE 17.6.7
The acid hydrolysis of an ester

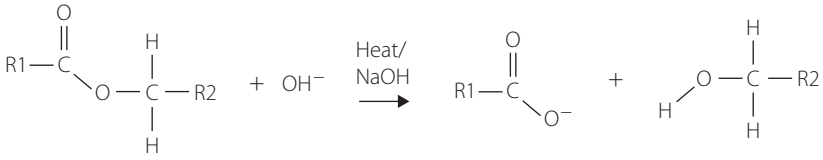


For example:

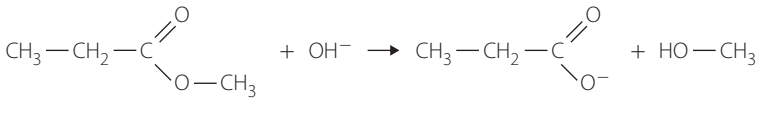


Under alkaline conditions (in the presence of heat and sodium hydroxide), the reaction is as shown in Figure 17.6.8.

FIGURE 17.6.8
The alkaline hydrolysis of an ester



For example:



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PRACTICAL ACTIVITY 17.6.1

Preparation of some esters

Aspirin (acetylsalicylic acid), oil of wintergreen (methyl salicylate) and ethyl ethanoate (used in nail polish remover) are all esters. Esters can be synthesised in the laboratory. The low rate of reaction between these compounds means we need to apply heat. The commonly used method is a technique called refluxing, in which the mixture is boiled and the vapours produced are condensed and collected.

AIM

To prepare some different esters

EQUIPMENT

- 5 g salicylic acid
- 10 mL each of methanol, ethanol, 1-butanol, 1-octanol, 3-methyl-1-butanol, 3-methyl-1-pentanol
- 10 mL each of glacial acetic acid (ethanoic acid), pentanoic acid, butanoic acid, propanoic acid, concentrated sulfuric acid (18 mol L^{-1})
- Hot plate
- Six test tubes
- Two 500 mL beakers
- 10 mL graduated cylinder
- Dropper
- Thermometer
- Distilled water
- Ice in an ice bath

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Concentrated sulfuric acid and acetic acid are corrosive. Concentrated (18 M) sulfuric acid will char flesh if spilled on it.	Wear gloves and personal protective equipment and avoid contact with the skin. Wash your hands at the end of the experiment.
Alcohols are highly flammable.	Ensure no flame sources are present in the location of these chemicals.

RISK ASSESSMENT

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

You may choose your own combinations of alcohol and carboxylic acid to produce the esters. Different combinations will produce different esters.

1. Half fill the 500 mL beaker with water. Place this on the hotplate and heat to approximately 60°C. This is your water bath.
2. Number six test tubes. To each of the test tubes add 1 mL of an alcohol and 1 mL of a carboxylic acid from those provided. If using solid salicylic acid, add approximately 1 g.
3. Add 3–5 drops of concentrated sulfuric acid to each test tube.
4. Heat the test tubes in the water bath for 15 minutes.
5. Remove the test tubes from the water bath and cool them in an ice bath.
6. Add 5 mL of distilled water to each test tube. The ester is less dense than water so it will form a layer on top of the water.
7. Carefully smell the ester and note the odour.
8. Dispose of the chemicals according to your teacher's instructions.

RESULTS

Record your observations, and copy and complete the following results table.

TEST TUBE	ALCOHOL	CARBOXYLIC ACID	ODOUR	ESTER (NAME AND FORMULA)
1				
2				
3				
4				
5				
6				

ANALYSIS

1 Compare your results with those of others in your class and construct a table listing all the esters produced and their odours.

2 **a** Write a general equation for the esterification reaction.

b Write balanced equations to represent two of the esters you produced.

3 Compare the relative solubility of alcohols, carboxylic acids and esters and then suggest why water was added in step 6.

SECTION REVIEW 17.6

REMEMBERING

1 Explain why carboxylic acids are described as monoprotic.

2 Explain what is meant by a condensation reaction.

3 Draw the ester group.

UNDERSTANDING

4 Write balanced equations with named products to show the reactions of:

a methanoic acid with sodium

b 1-butanol with ethanoic acid

c 2-butanol with propanoic acid

d propyl ethanoate in the presence of heat and concentrated sulfuric acid

e methyl butanoate in the presence of heat and aqueous concentrated sodium hydroxide.

APPLYING

5 Methyl butanoate and butyl methanoate are two esters that are isomers of one another. Draw the two structures and explain the key differences in their synthesis.

17.7 Reactions of amines and amides

Amines have a wide range of uses as catalysts and solvents and in the manufacture of dyes, medicines and polymers, so they are an extremely important family of organic compounds. Amines are also found widely in nature as amino acids, which are the building blocks of proteins.

An amide is formed when an amine reacts with a carboxylic acid. Polyamides are an important group of synthetic plastics.

Urea, an important compound in industry and living systems, is a carbamide with the formula H_2NCONH_2. It has two NH_2 groups attached to a carbonyl (C═O) group. Urea was the first organic compound to be synthesised from inorganic starting materials, thus showing organic compounds were part of a chemical system and could be produced outside living things.

The amine functional group is —NH_2. Amines are compounds in which one or more atoms of hydrogen in ammonia (NH_3) are replaced by a carbon-containing group such as an alkyl group. Alkyl amines are represented by the general formula RNH_2.

As with alcohols and haloalkanes, amines may be classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the nitrogen. A primary amine has one alkyl group, a secondary amine has two alkyl groups attached to the nitrogen, and a tertiary amine has three alkyl groups attached to the nitrogen. Figure 17.7.1 shows examples of these.

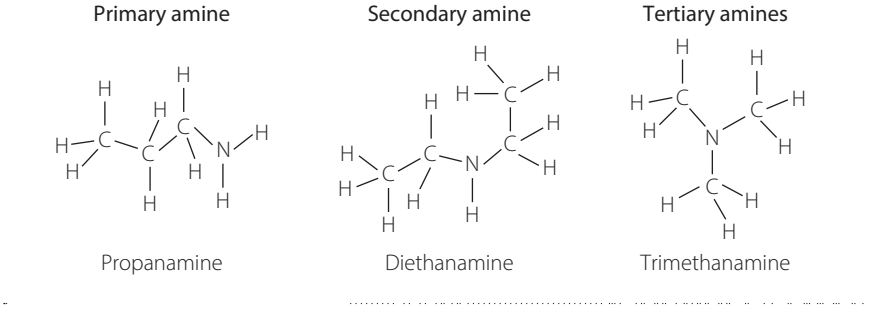


FIGURE 17.7.1
Primary, secondary and tertiary amines

Reaction with inorganic acids

Amines are weak bases, similar to ammonia from which they are formed. Therefore, they will undergo a neutralisation reaction with acids to form a salt and water. This can be represented generally as:

$$RNH_2(aq) + H^+(aq) \rightarrow RNH_3^+(aq)$$

For example:

$$CH_3NH_2(aq) + HCl(aq) \rightarrow CH_3NH_3^+Cl^-(aq)$$

Methanamine — Methylammonium chloride

Condensation reaction with organic acids

Amines react with carboxylic acids in a similar way to the reaction with an inorganic acid. However, under certain conditions amines and carboxylic acids undergo a condensation reaction (eliminating water) to form amides.

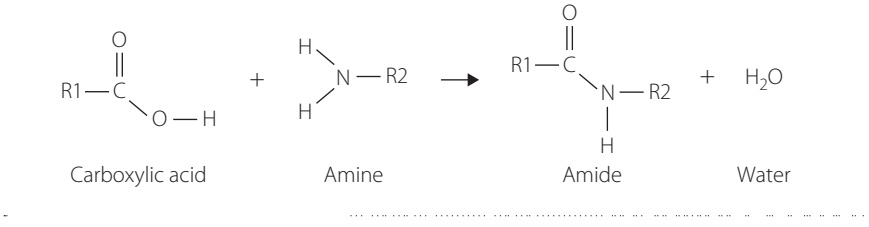
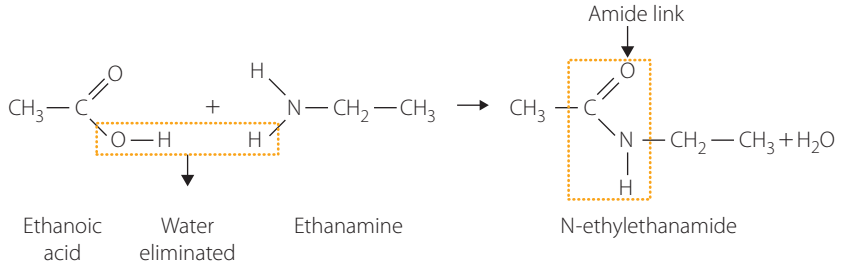


FIGURE 17.7.2
Formation of an amide

For example, the reaction to show how N-ethylethanamide is formed is shown below.



SECTION REVIEW 17.7

REMEMBERING

1 Explain the difference between amine and amide molecules.

UNDERSTANDING

2 Write balanced equations with named products to show the reactions of:

- **a** ethanamine with nitric acid
- **b** 2-butanamine with ethanoic acid.

3 Write an equation to represent the hydrolysis of N-propylmethanamide.

APPLYING

4 Would you expect an amide to be basic? Explain your answer.

17.8 Organic reaction types

Table 17.8.1 provides a summary of organic reaction types.

TABLE 17.8.1 Organic reaction types

REACTION	DESCRIPTION	CLASSES OF COMPOUNDS	REAGENTS AND CONDITIONS	EXAMPLE
Combustion	Burning in oxygen to produce carbon dioxide and water	All organic compounds	Oxygen and high temperature or flame to initiate	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
Substitution (free radical)	Replacement of a hydrogen atom with a halogen atom	All organic compounds	UV light	$C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl$
Substitution (nucleophilic)	Replacement of an electronegative atom (e.g. a halogen) with a nucleophile (e.g. hydroxide ion)	Haloalkanes	Aqueous solution of sodium or potassium hydroxide	$CH_3Cl + NaOH \rightarrow CH_3OH + NaCl$
Addition	Unsaturated molecules combine with other molecules	Alkenes and alkynes	H_2/Pd or halogens or halogen halides	$CH_2{=}CH_2 \rightarrow CH_3CH_3$
Elimination	Larger molecule forming two smaller ones	Haloalkanes	NaOH in ethanol solution	$CH_3CH_2Cl \rightarrow CH_2{=}CH_2 + HCl$
Oxidation	Primary alcohols forming aldehydes and carboxylic acids; secondary alcohols forming ketones	Primary and secondary alcohols	Either acidified $KMnO_4$ or acidified K_2CrO_7	$CH_3CHOHCH_3 \rightarrow CH_3COCH_3$
Reduction	Addition of hydrogen to nitriles to form amines or to alkenes to form alkanes	Nitriles or alkenes	H_2/Pd	$CH_3CN \rightarrow CH_3CH_2NH_2$
Condensation	Reaction of acid and alcohol to form ester or acid and amine to form amide, with the loss of a water molecule	Carboxylic acid and either alcohol or amine	Concentrated H_2SO_4 catalyst or reflux with NaOH	$CH_3COOH + CH_3NH_2 \rightarrow CH_3CONH_2 + H_2O$

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Each class of organic compounds is considered to have its own characteristic molecular structural features that lead to its physical properties and chemical reactions. These properties and reactions can be used to distinguish between and identify different classes of organic compounds. The classes considered in this section are alkanes, alkenes, alcohols, carboxylic acids, esters, amines and amides.

In devising a set of tests to distinguish between different classes of compounds, a test for the most easily identified is usually the starting point. Some tests that can be performed to determine the class of compound of an unidentified sample are listed in Table 17.8.2.

TABLE 17.8.2 Tests for determining class of organic compound

CLASS OF COMPOUND	TEST AND RESULT
Amines	Test with litmus paper or universal indicator. If the solution is basic, then it is an amine.
Carboxylic acid	Add drops of sodium carbonate solution to the sample. If bubbles of colourless gas form (CO_2), then the solution is a carboxylic acid.
Alcohol	Add granules of calcium chloride to remove any water present, and then add a small piece of sodium. If bubbles of colourless gas form (H_2), then the sample is an alcohol. (Carboxylic acids also react the same way but they will already have been identified.)
Amide	Add NaOH and gently heat the solution. If ammonia is produced, then the solution is an amine, and the pH will become less basic.
Alkene or alkyne	Add drops of bromine or bromine water to the organic solvent. If the solution loses colour, then a multiple bond is present as it is decolourised by alkenes.
Alkane or ester	If the above tests are negative, then the compound is an alkane or ester. Add a solution of bromine in hexachloroethane and expose it to UV light. If the colour fades, then the compound is an alkane.
Ester	There is no simple test for esters. If the compound has a pleasant smell, then it is probably an ester. Spectroscopy is needed to confirm the presence of this class of compounds.

SECTION REVIEW 17.8

ANALYSING

1 A certain gaseous hydrocarbon is bubbled through bromine. The bromine is not decolorised. What can you conclude about the unknown hydrocarbon?

2 Explain how you would distinguish between two clear liquids, knowing one is propanol and the other is propanoic acid.

3 Carboxylic acids can be produced by the oxidation of primary alcohols. What alcohol would you need to oxidise to produce butanoic acid?

4 Carboxylic acids have higher boiling points than alcohols of corresponding mass. Explain in terms of bonding why this is so.

APPLYING

5 You have samples of six organic compounds labelled A to F. You know that all of them have a very similar molecular mass, and they are butanoic acid, butane, butanamine, 1-butene, 1-butanol and butane. However, you do not know which compound is which. Describe a series of tests that you could perform to determine the identity of compounds A–F as efficiently as possible.

6 **a** What would you observe when sodium carbonate powder is added to a solution of propanoic acid?

b Write a balanced equation for the reaction.

17.9 Reaction pathways

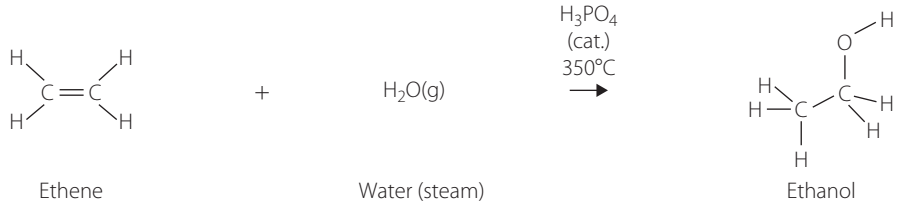
One of the most significant aspects of organic chemistry is its use in the synthesis and manufacture of other chemicals. Hydrocarbons such as alkanes and alkenes can be obtained as raw materials from crude oil. Using the reactions listed in this chapter as well as many others, hydrocarbons can be used to produce a vast range of other molecules with uses in any field. The specific issues to consider when synthesising and manufacturing chemicals are covered in Chapter 20; however, it is also important to consider how the reactions we have discussed can be combined in order to produce complex molecules from some simpler origins.

Formation of esters from alkenes

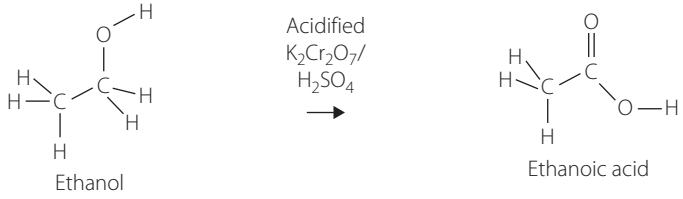
As well as being widespread in nature, esters are commonly used in industry. Esters can easily be synthesised and they are produced synthetically for use as artificial flavouring and colourings. Several billion kilograms of polyesters are produced annually to make a wide variety of products, including fabrics and bottles. They can be manufactured from alkenes using the reactions discussed in this chapter. For example, consider the production of ethyl ethanoate, used in glues and nail polish removers, from ethene.

FIGURE 17.9.1
Formation of an ester from an alkene

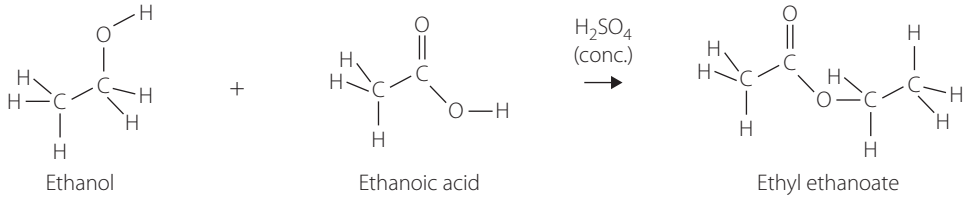
1 Addition of H_2O to ethene to form ethanol



2 Oxidation of ethanol to form ethanoic acid (retain 50% of the ethanol produced in stage 1 for use in stage 3)



3 Condensation of ethanol (from stage 1) and ethanoic acid to form ethyl ethanoate



Formation of amides from alcohols

Like the production of esters, the synthesis of amides is a similarly useful process. Here we consider the production of N-propyl ethanamide from ethanol.

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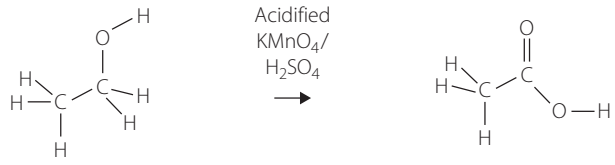
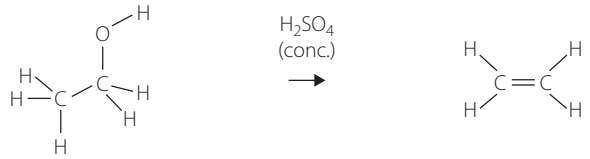
1 Oxidation of ethanol to form ethanoic acid (retain 50% of the ethanol for stage 2)



Ethanol — Ethanoic acid

2 Dehydration of ethanol to form ethene

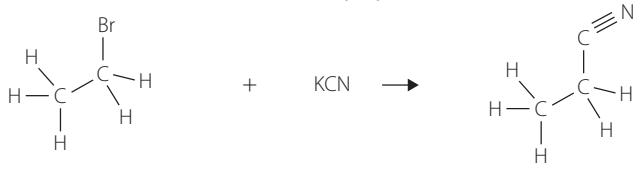


Ethanol — Ethene

3 Addition of HBr to ethene to form bromoethane

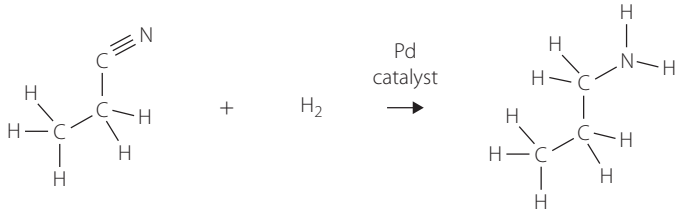
Ethene — Hydrogen bromide — Bromoethane

4 Substitution of bromoethane to form propane nitrile



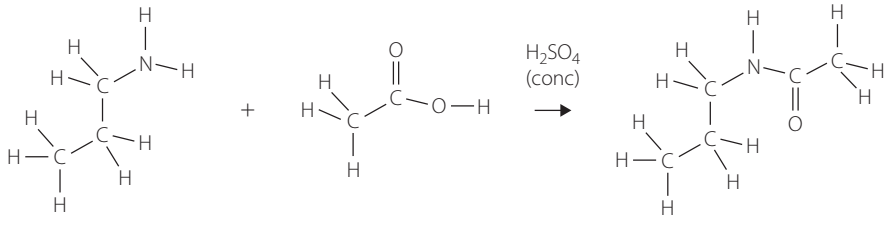
Bromoethane — Potassium cyanide — Propane nitrile

5 Reduction of propane nitrile to form propanamine



Propane nitrile — Potassium cyanide — Propanamine

6 Condensation of propanamine and ethanoic acid (from stage 1) to form N-propyl ethanamide



Propanamine — Ethanoic acid — N-propyl ethanamide

FIGURE 17.9.2 Formation of an amide from an alcohol

APPLYING

1 Describe a reaction pathway for the formation of the ester 2-butyl methanoate, using 2-butanol and chloromethane as the raw materials.

2 Describe a reaction pathway for the formation of the amide N-propyl butanamide, from chloropropane.

SECTION REVIEW 17.9

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Describe the three classes of alcohol and give an example of each class.

CATEGORY QUESTIONS

2 Explain the difference between saturated and unsaturated compounds.

3 Distinguish between substitution and addition reactions.

4 Describe the relationship between esterification and hydrolysis.

ELABORATION QUESTIONS

5 Write balanced equations for the:
- **a** combustion of pentyne
- **b** reaction of ethane with chlorine gas (under UV light)
- **c** reaction of 2-butene with water
- **d** reaction of ethyne with bromine.

6 Write equations for the following reactions, naming the products.
- **a** Dehydration of 3-pentanol
- **b** Hydration of 1-propene
- **c** Combustion of 2-butanol
- **d** Reaction of sodium with 1-hexanol

7 Identify the final product (if any) from oxidising:
- **a** 2-butanol
- **b** methanol
- **c** 2-methyl-2-hexanol.

8 Write balanced equations for the oxidation of:
- **a** 1-propanol to propanal by acidified permanganate solution
- **b** 2-pentanol by acidified dichromate solution.

9 What would you observe when sodium carbonate powder is added to a solution of propanoic acid? Write a balanced equation for the reaction.

10 Write equations for the reaction of:
- **a** butanoic acid and sodium hydroxide
- **b** methanoic acid and sodium metal.

11 Write equations for the reaction between the following compounds and name the esters produced.
- **a** 1-propanol and ethanoic acid
- **b** 1-pentanol and butanoic acid

12 Write equations for the reactions of:
- **a** propanamide with hydrochloric acid
- **b** methanoic acid with ammonium carbonate
- **c** methanoic acid with butanamine.

13 Write a balanced equation for the acid hydrolysis of pentyl propanoate.

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EVIDENCE QUESTIONS

14 A certain gaseous hydrocarbon is bubbled through bromine. The bromine is not decolorised. What can you conclude about the unknown hydrocarbon?

15 Explain how you would distinguish between two clear liquids, knowing one is propanol and the other is propanoic acid.

16 Carboxylic acids can be produced by the oxidation of primary alcohols. What alcohol would you need to oxidise to produce butanoic acid?

17 You are given two clear solutions – one is an amine and one is an amide. How would you identify which is the amine and which is the amide?

END-OF-CHAPTER EXAM

End-of-chapter test

1 Consider the following reactions:

$$CH_3CH{=}CHCH_3 + H_2O \rightarrow X$$
$$X + CH_3COOH \rightarrow Y$$

The structure of Y would be:

A $CH_3CH_2CH(CH_3)COOCH_3$.

B $CH_3COOCH(CH_3)CH_2CH_3$.

C $CH_3CH_2CH_2COOCH_3$.

D $CH_3OOCH_2CH_2CH_2CH_3$.

2 Which of the following statements about 1-butene is *not* correct?

A It undergoes an addition reaction with hydrogen to form butane.

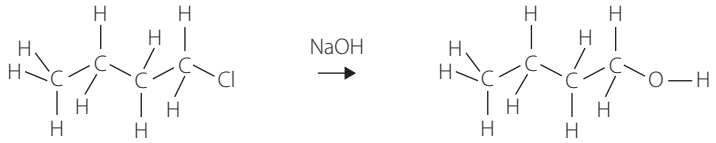
B It forms a single product when reacted with HBr.

C One 1-butene molecule will react with excess oxygen to produce four molecules of carbon dioxide and four molecules of water.

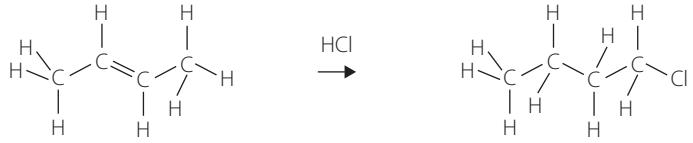
D It will undergo substitution reactions with chlorine in the presence of UV light.

3 Which of the following organic reactions does not result in the product shown on the right-hand side of the arrow?

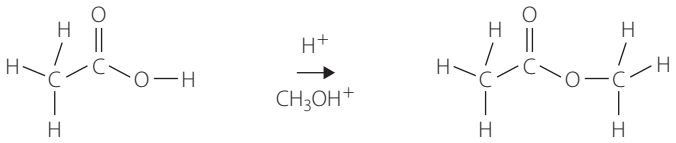
A



B



C



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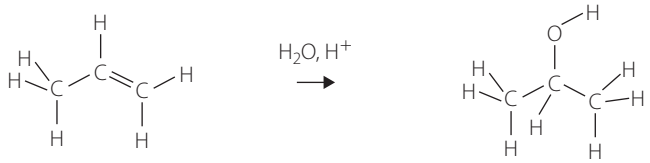

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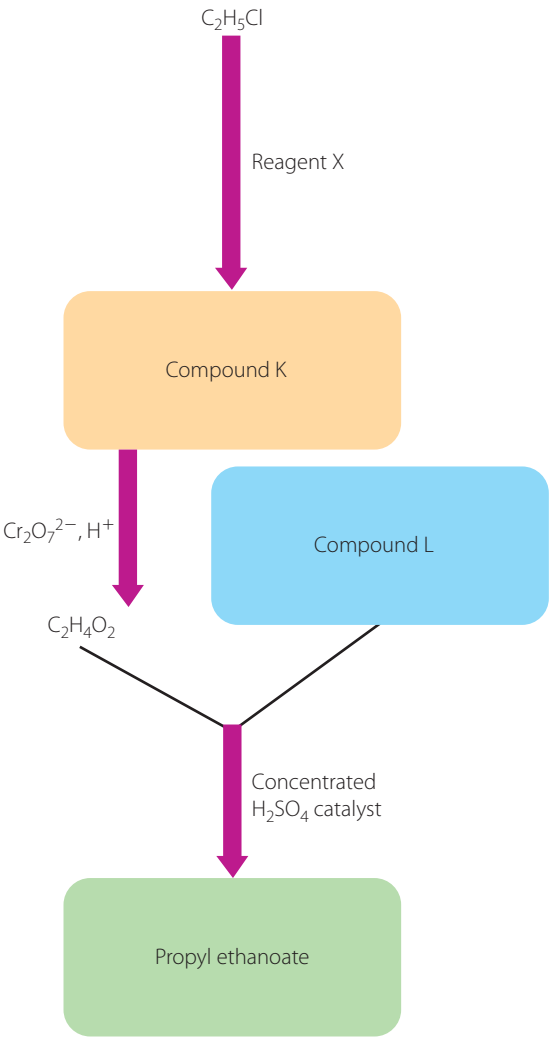
4 The ester propyl ethanoate has a characteristic odour and has been isolated from many fruits, including pineapple. A sample of this ester is to be prepared in the laboratory in order to develop a synthetic pineapple flavouring. A partially completed reaction pathway for this preparation is shown below:



In the appropriate box:

a write a structural formula for propyl ethanoate

b write structural formulas for compounds K and L

c write the formula of reagent X.

18 ORGANIC MATERIALS: STRUCTURE AND FUNCTION

Introduction

Apart from the inorganic molecules of water and oxygen, we depend more on organic molecules in every aspect of our lives than inorganic ones. The food we eat, the clothes we wear, the plastics we rely on in everyday products and the fuels that power transport vehicles are all mainly composed of organic compounds. The medicines we use to fight microbes and even the microbes themselves are largely made up of organic compounds.

Although inorganic water is the most abundant chemical in the body, most of the other chemicals are carbon-based organic chemicals. All living things are massive chemical machines composed largely of organic compounds interacting in a watery soup. The membranes of our cells, DNA and the enzymes that catalyse the chemical reactions within cells are all organic compounds. Muscles, fat and skin are all based on organic compounds and our bones are formed from a framework of organic compounds in which minerals become embedded.

The majority of these useful organic materials are polymers, and in this chapter, you will consider the structures of proteins, carbohydrates, lipids and synthetic polymers, and relate the structures to the properties that these substances have.

Stimulus questions

How do the structures and properties of synthetic polymers compare to those from the natural world?

How can large polymer molecules with an infinite range of possible conformations form the precise and consistent structures we observe in nature?

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18.1 Polymers

Polymers are giant molecules, often called macromolecules, which form when many thousands of smaller molecules, called **monomers**, are joined by covalent bonds. The process of linking monomers together is called **polymerisation**. If the polymer consists of more than one different monomer, it is known as a **copolymer**.

polymer
a large molecule made from many thousands of repeating units

monomer
an individual unit of a polymer

polymerisation
the process by which monomers link together to form a polymer

copolymer
a polymer made from more than one type of monomer

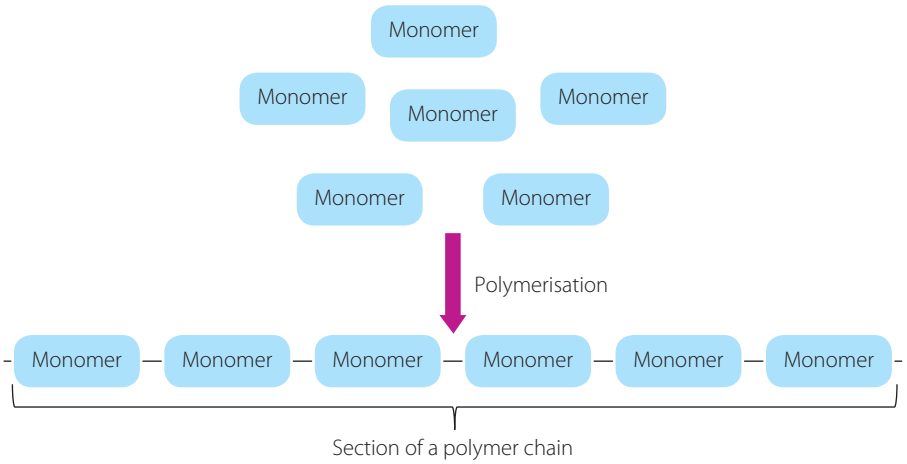

FIGURE 18.1.1 Polymers are formed from monomers.

The two most common polymerisation reactions are:

1. addition polymerisation, which involves an **addition reaction**
2. condensation polymerisation, which involves a **condensation reaction**.

addition reaction
where unsaturated molecules combine with another molecule to become saturated

condensation reaction
where two molecules combine to form a larger molecule and produce water as a by-product

Polymers may be natural or synthetic. Natural polymers such as silk, wool and hair (made of proteins), starch (made of carbohydrate) and DNA are manufactured by living organisms. Synthetic polymers, commonly referred to as plastics, are manufactured in laboratories or on larger scales in factories.

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FIGURE 18.1.2 Plastic drink bottles – made from a synthetic polymer

The structure of polymers

Like all chemicals, the properties of specific polymers depend on their structure. Depending on the type of polymer, the complexity of a structure can vary significantly and, hence, so can its properties. The structure of polymers can be understood by considering three different aspects: the primary, secondary and tertiary structures.

Primary structure

primary structure
the sequence of monomers in a copolymer chain

The **primary structure** of a copolymer is the sequence in which the monomers are joined in the chain. In polymers such as proteins and DNA, the sequence of the monomers is critical to the function of the protein molecule.

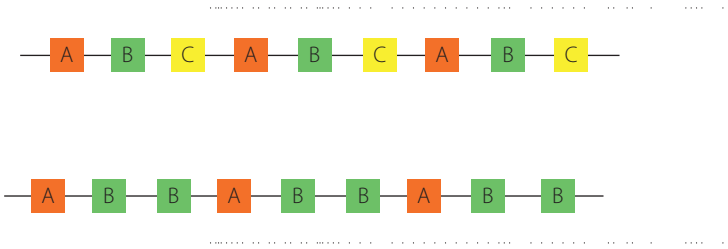

FIGURE 18.1.3 Two sections of co-polymer chains with different primary structures

Secondary structure

secondary structure
minor features of the shape of a polymer chain, caused by intermolecular interactions between side chains

The **secondary structure** is the way in which intermolecular interactions between monomers in the same chain affect the shape of the chain. Hence a long chain, rather than being straight, has secondary structures such as loops or twists in it.

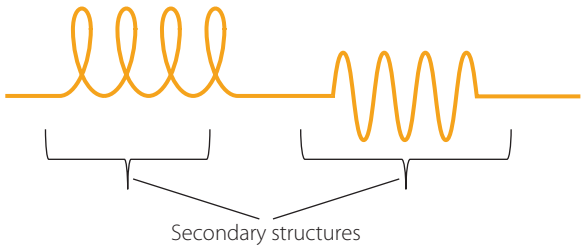

FIGURE 18.1.4 Secondary structures within a polymer chain

Tertiary structure

tertiary structure
the overall shape of a single polymer chain

The **tertiary structure** is the overall shape of a polymer chain, which results from the intermolecular forces that exist between the monomers. Polymer molecules tend to have distinctive and complex, yet consistent, shapes.

quaternary structure
the shape of two or more polymer chains aggregated together, held by intermolecular interactions

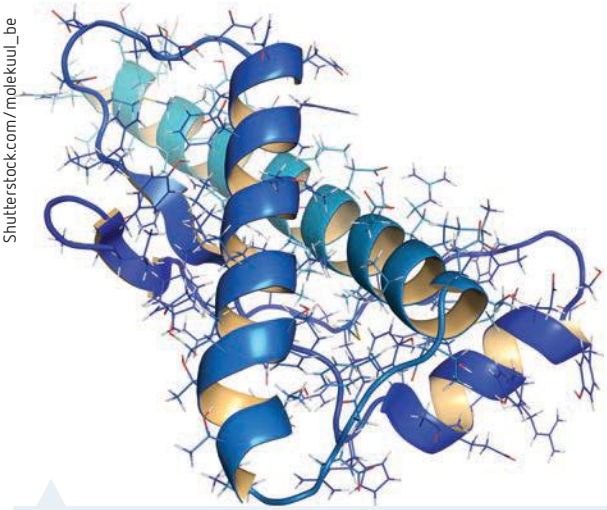

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FIGURE 18.1.5 Tertiary structure of a polymer, the overall shape of one complete chain

Quaternary structure

The **quaternary structures** of a polymer occur when several tertiary structures aggregate together, again held by intermolecular forces. They form complex structures that have biological significance. A good example of this is the structure of haemoglobin, a protein with a quaternary structure, which transports oxygen in red blood cells. Another example is the distinctive 'double helix' structure of DNA, which enables it to be replicated efficiently when cells divide. Both of these are shown in Figure 18.1.6.

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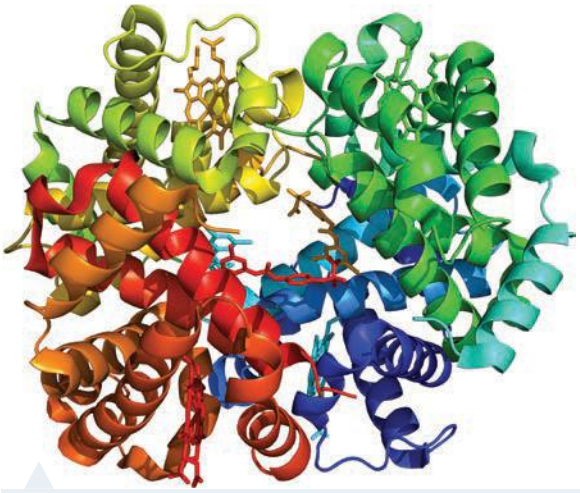

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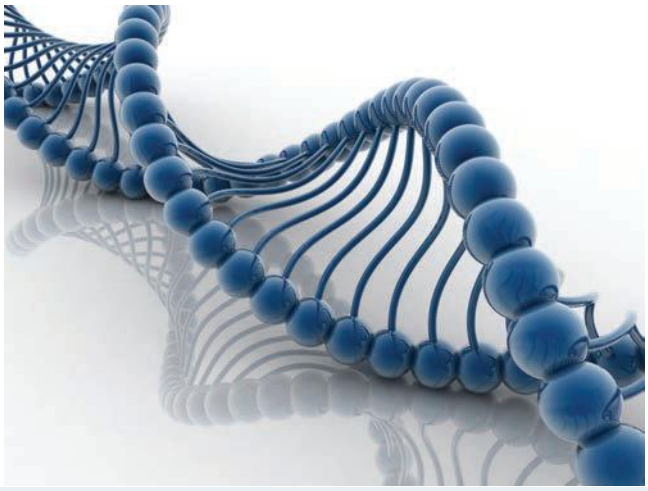

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FIGURE 18.1.6 The quaternary structures of haemoglobin and DNA – tertiary structures aggregated together; held by intermolecular interactions.

Properties of polymers

Polymers are long, complicated molecules held together by covalent bonds. They tend to be insoluble in water, despite the presence of polar functional groups in the chains. The following properties can vary according to the identity of the monomer units and the nature of the covalent bond holding them together.

Biodegradability

In general, natural polymers are more likely to be **biodegradable** than synthetic polymers. For example, proteins, carbohydrates and lipids can all be broken down by the action of enzymes, produced by living organisms such as naturally occurring bacteria. These polymers are all condensation polymers, and the condensation reaction is more easily reversible than the addition reaction.

Addition polymers such as polyethene, polypropene and polystyrene will not degrade naturally and so are a significant environmental problem throughout the world. Developments to improve the biodegradability of polymers include developing synthetic condensation polymers such as polyamides, polyesters and polysaccharides, which naturally occurring enzymes find much easier to digest.

biodegradable
a substance that will decay naturally as a result of enzymes produced by bacteria

Tensile strength

Many polymers are manufactured specifically to obtain high **tensile strength**. This includes synthetic polymers such as nylon, and natural polymers such as the 'silk' that spiders produce to form their webs. Again, this is achieved by synthesising polymers with appropriately strong structures, usually with a 'cross-linking' covalent bond, that hold the polymer chains rigidly in place.

Other polymers that do not have **cross-links** between the polymer chains have considerably less tensile strength. One example of this is polyethene.

Smith et al. 2010 Chemistry in use. Book 2

FIGURE 18.1.7 Cross-linking joins chains to each other

tensile strength
the resistance of a substance to being pulled or stretched

cross-links
covalent bonds that exist between polymer chains, holding them together firmly

density
the mass per unit volume

branching
where a polymer chain is not a single straight-chain, but has 'offshoots'

side groups
the different functional groups that can exist in a polymer chain, but which are not part of the main chain

Density

The **density** of polymers varies according to their structure, and in particular how tightly packed together the polymer chains are. Two factors that can affect this are the **branching** of the chains and the **side groups** that can be attached to the chains. Polymer chains with extensive branching and large side groups cannot fit together as tightly, and consequently their overall structure is less dense.

PRACTICAL ACTIVITY 18.1.1

Identifying plastics by their density

Plastics are synthetic materials with a wide range of properties. One property that can be used to help identify plastics is density. For this activity, you are to design an experiment to identify unknown samples and to separate and identify the pieces in the mixture.

WHAT IS YOUR AIM?

Write an aim for your practical activity.

WHAT WILL YOU NEED?

The information in Tables 18.1.1 and 18.1.2 will help you.

TABLE 18.1.1 Densities of common plastics

PLASTIC	DENSITY ($g\ mL^{-1}$)
HDPE	0.95–0.97
LDPE	0.917–0.940
PETE	1.38–1.39
PP	0.90–0.91
PS (in solid form)	1.04–1.05
PS (in foam form)	Variable, but always less than 1
PVC (rigid)	1.30–1.58
PVC (flexible)	1.16–1.35

TABLE 18.1.2 Densities of nine solutions

LIQUID	DENSITY ($g\ mL^{-1}$)
Methanol	0.79
52% ethanol/water mixture	0.911
38% ethanol/water mixture	0.9408
24% ethanol/water mixture	0.9549
Water	1.00
10% solution of NaCl	1.08
Saturated solution of $MgCl_2$	1.34
40% $CaCl_2$ solution	1.398
Saturated solution of $ZnCl_2$	2.01

WHAT ARE THE RISKS?

Construct a table similar to the one that follows. Identify specific risks involved in the practical activity and ways that you will manage the risks to avoid injuries or damage to yourself and others. Check the relevant MSDS.

»

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WHAT ARE THE RISKS IN DOING THIS PRACTICAL ACTIVITY?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Methanol and ethanol are highly flammable.	Ensure no flame sources are present near either of these chemicals.
Zinc chloride is a hazardous material that can cause skin and eye irritation.	Wear gloves and lab coat when handling this material. Do not dispose of zinc chloride down the sink; collect as a waste as per your teacher's instructions.

HOW WILL YOU CARRY OUT THE ACTIVITY?

1 Consider how you will verify the densities of known samples before testing unknown samples.

2 Take care that no air bubbles adhere to the samples, and shake the tube to check that samples are actually floating.

WHAT RESULTS WILL YOU COLLECT?

Would a data table be the best way to record your results?

HOW WILL YOU ANALYSE YOUR RESULTS?

Identify the unknown samples, giving reasons for your decisions.

WHAT HAVE YOU FOUND?

1 Decide which polymer would be best used for each of the following and why.
   - **a** As a replacement for the lead sinkers used in fishing
   - **b** To make a toy boat

2 Were any plastics difficult to distinguish? What other properties could be used to separate these plastics?

SECTION REVIEW 18.1

REMEMBERING

1 Explain the following terms.
   - **a** Polymer
   - **b** Monomer
   - **c** Addition polymerisation
   - **d** Condensation polymerisation
   - **e** Copolymer
   - **f** Primary structure
   - **g** Secondary structure
   - **h** Tertiary structure
   - **i** Quaternary structure
   - **j** Biodegradable
   - **k** Tensile strength
   - **l** Cross-links
   - **m** Density
   - **n** Branching
   - **o** Side groups

UNDERSTANDING

2 Explain how the following properties of polymers are affected by the structure:
   - **a** tensile strength
   - **b** density.

REFLECTING

3 Why are synthetic polymers much less likely to biodegrade than natural polymers?

18.2 Proteins

protein
an organic compound made from long chains of amino acids; food group essential for life

Proteins are an essential part of every living cell. They are the major structural component of hair, skin and muscle and so are tough, insoluble in water and have a stringy appearance. Proteins are essential to the chemical processes that take place in our bodies, including transporting oxygen (haemoglobin), nutrients and minerals through the bloodstream. Many hormones, such as insulin, are proteins and most enzymes (biological catalysts) and antibodies are proteins.

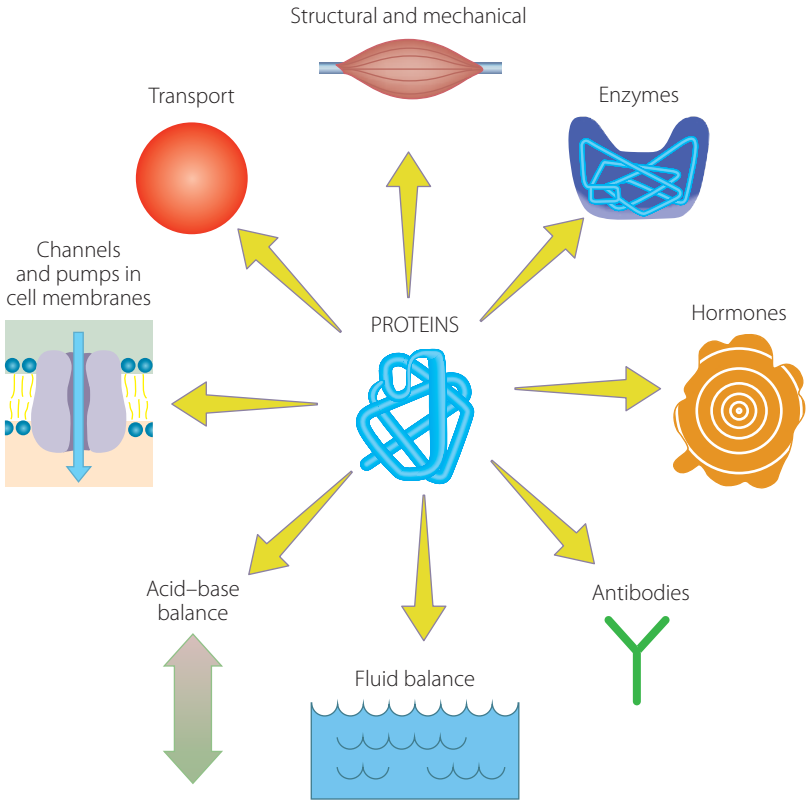


FIGURE 18.2.1 Protein functions

polyamide
a polymer held together by amide bonds – formed between the amino group of one monomer and a carboxyl group of the next monomer

SCIENCE AS A HUMAN ENDEAVOUR

PROTEINS

The word 'protein' derives from the Greek *protos*, meaning 'first'. Proteins were given this name when they were discovered in the 19th century because they were believed to be the chemical essence of life. We now know that life depends on the interaction of thousands of chemicals. Proteins are only one group of these. Nevertheless, proteins make up about half of the body's non-water mass.

polypeptide
a polyamide chain which constitutes a protein

amino acid
an organic compound containing a carboxyl and an amino group

Proteins are large polymers (**polyamides** or **polypeptides**) formed when many smaller monomer molecules link together in a condensation polymerisation reaction. The monomer building blocks of proteins are **amino acids**. Although there are only 20 different amino acids found in proteins, there are hundreds of thousands of different proteins.

All protein molecules are long, chain-like molecules with different side groups strung out along a repeating backbone of mainly carbon atoms. The long protein chains are normally folded into complex and highly specific shapes, allowing them to perform very specialised functions within living organisms.

The most important features of a protein that enable it to perform its specific biological function include the:

- nature and sequence of amino acids that make up the polymer chain and give the primary structure
- way the polymer chain is arranged within segments to give it its secondary structure
- way the secondary structure is arranged to give the whole molecule its tertiary, and sometimes quaternary, structure.

The primary structure of proteins

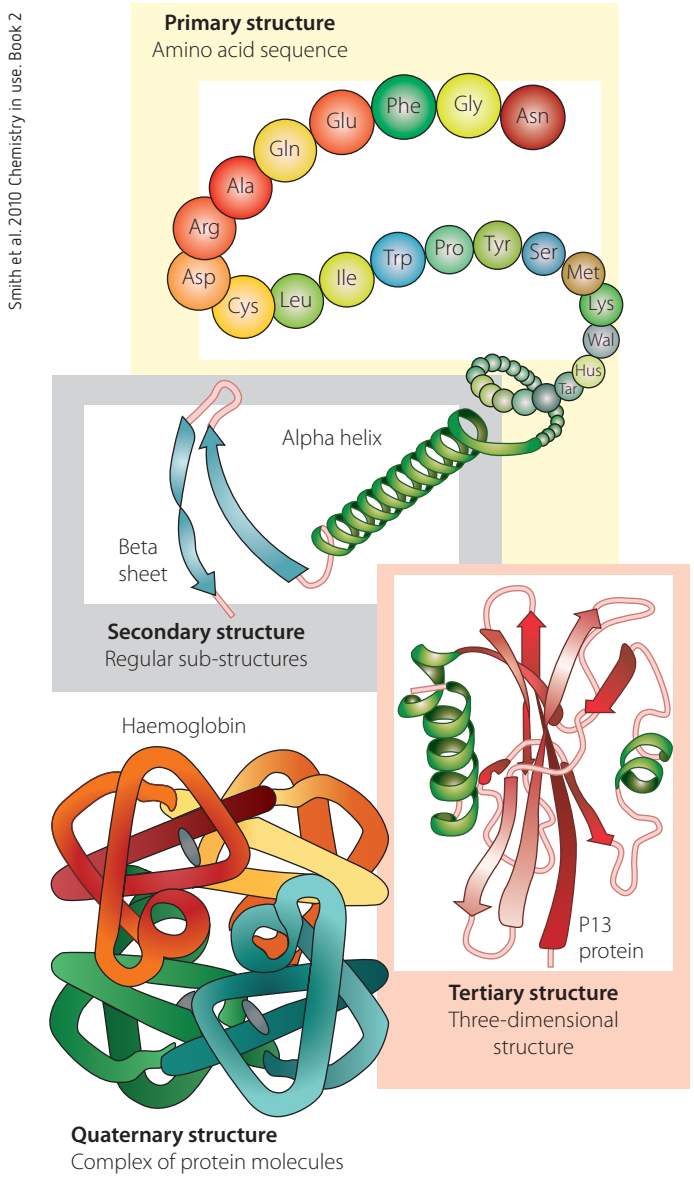


FIGURE 18.2.2 Levels of protein structure

The sequence of amino acids determines the primary structure of a protein chain. The way the protein folds to produce the secondary structure depends on this sequence.

Amino acids contain the amino (—NH_2) functional group and the carboxyl (—COOH) functional group. This means amino acids have both acidic and basic properties.

The monomer $H_2N—(CH_2)_5—COOH$, used to make nylon-6, has an amino and an acid functional group but is not classified as an amino acid, because amino acids have two specific structural features that are not present in this molecule.

The special structural features common to the 20 amino acid monomers that form proteins are:

- the amino and carboxyl functional groups are attached to the same carbon atom (called the **alpha-carbon**)
- a hydrogen attached to the alpha-carbon.

alpha-carbon
the carbon atom in an amino acid that separates the amino and carboxyl groups

The simplest amino acid is glycine, which has the structure shown in Figure 18.2.3.

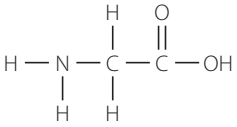


FIGURE 18.2.3
Glycine

alpha-amino acid
an amino acid with one carbon atom separating the amino and carboxyl groups

These monomers are **alpha-amino acids** because they can only form proteins when the two functional groups are joined to the same carbon atom. The general structure of an alpha-amino acid is shown in Figure 18.2.4.

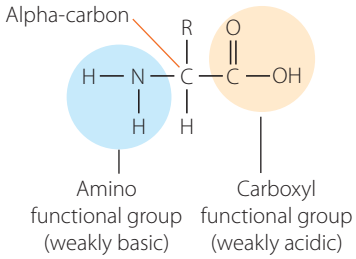


FIGURE 18.2.4 General structure of an alpha-amino acid

The 'R' group is a carbon-containing side-chain. The 20 amino acids commonly found in proteins can be categorised into three broad groups. They are amino acids with:

1. non-polar R groups
2. polar R groups capable of forming ions (generally with an additional —NH_2 or —COOH group as part of the R chain)
3. polar R groups that generally do not form ions (generally with an —OH or —SH group as part of the R chain) (Figure 18.2.5).

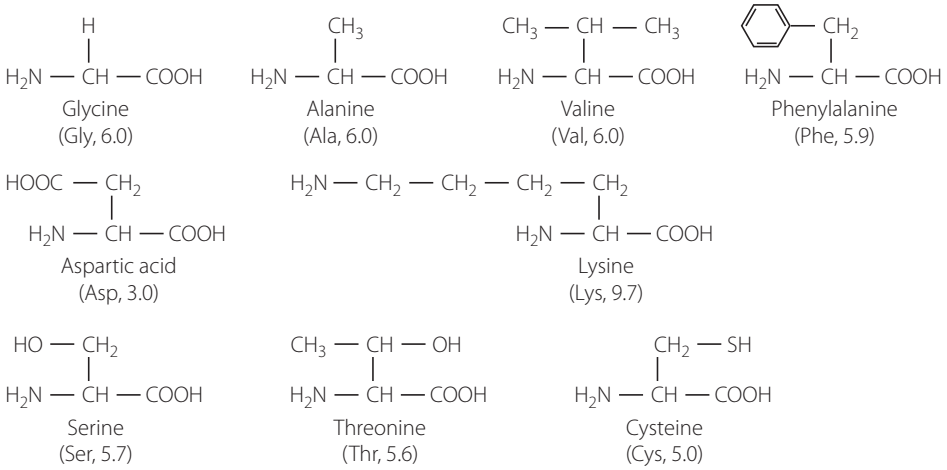


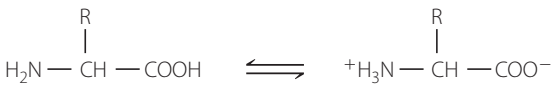
FIGURE 18.2.5 Common amino acids found in proteins. Their usual abbreviations are given in brackets along with their isoelectric points (the pH at which they exist as the neutral molecule)

Forming zwitterions

zwitterion
the form of an amino acid where the amino group is protonated at the same time as the carboxyl group is deprotonated, so that there is no net charge

The amino acids shown in Figure 18.2.5 have been written as neutral molecules. However, the acidic —COOH group tends to lose a proton to form —COO^-, while the basic amine group —NH_2 tends to gain a proton to form —NH_3^+. This results in a dipolar ion called a **zwitterion**. Therefore, in aqueous solution, amino acids exist as an equilibrium mixture of neutral molecules with the dipolar ion (Figure 18.2.6).

FIGURE 18.2.6
A zwitterion



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The dipolar structure means amino acids exhibit some of the properties of ionic substances – they form crystalline solids, have relatively high melting points and are soluble in water.

Recall that the —COOH group is a weak acid and $—NH_2$ is a weak base. This means the pH of a solution containing the amino acid affects the nature of the zwitterion. In strongly acidic solutions (e.g. pH 2–3), the $—COO^-$ group gains a proton to become —COOH while the $—NH_3^+$ does not change. So the zwitterion changes to a cation (Figure 18.2.7).

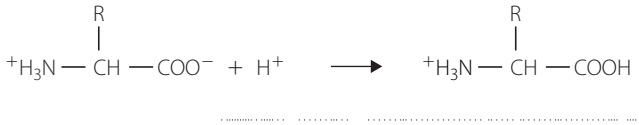


FIGURE 18.2.7 Amino acid in acid conditions

In alkaline solutions, the $—NH_3^+$ group loses a proton while the $—COO^-$ group does not change. So the zwitterion changes to an anion seen in Figure 18.2.8.

FIGURE 18.2.8 Amino acid in alkaline conditions

The pH at which an amino acid exists as an overall neutral zwitterion is called the **isoelectric point**. This is different for different amino acids because of the influence of the different R groups. At pH values less than the isoelectric point, the zwitterion will exist as the cation; and at pH values higher than the isoelectric point, the zwitterion will exist as the anion.

isoelectric point the pH value at which there is no net charge on a protein

Unlike nylons, which have a regular repeating unit, polypeptides can have various combinations of amino acids. Biochemists have developed a shorthand way of drawing them. Each of the 20 amino acids that make up the body's proteins has been given a three-letter abbreviation, as can be seen in the examples in Figure 18.2.5. The dipeptide alanylglycine, can be written as Ala–Gly. A possible sequence of a peptide with eight amino acids is Lys–Cys–Asp–Cys–Gly–Val–Val–Thr.

When hundreds to thousands of amino acid units join together, the result is a protein. So proteins are giant polypeptides. In any protein, there is still an amino group at one end and a carboxyl group at the other.

Secondary structure of proteins

The secondary structure of a protein is the way individual amino acids in the protein chain bond to other amino acids in the same or adjacent chains. The secondary structure involves folding or twisting as a result of hydrogen bonding. The arrangement is determined mainly by hydrogen bonding between non-bonding electron pairs on the oxygen of the C═O group of one amino acid and a hydrogen atom attached to the amine group of another amino acid.

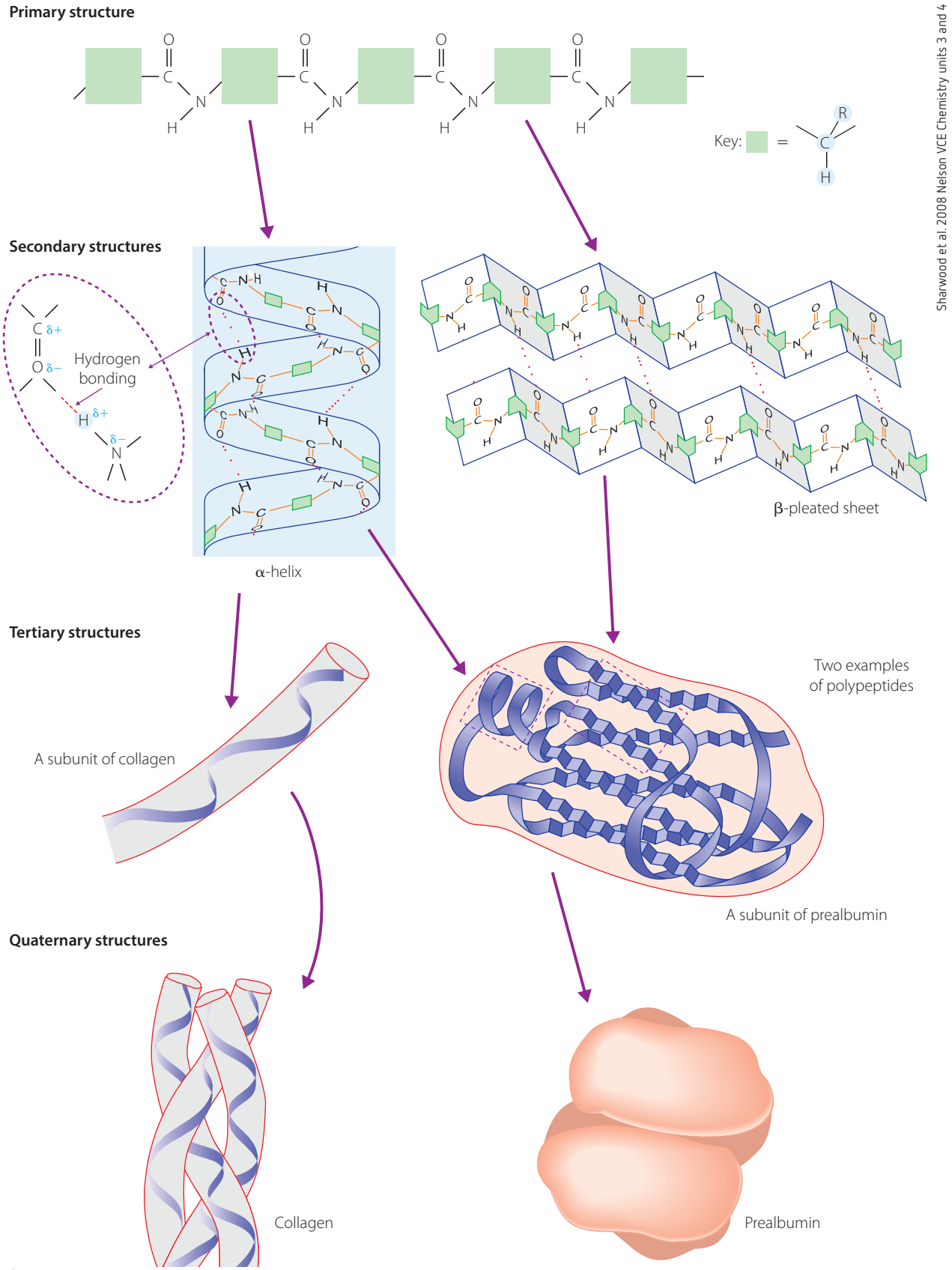
There are two common arrangements of the protein chain:

1. When the —C═O group of one amino acid forms a hydrogen bond to an —NH group four peptide links further along the chain, the result is a spiral structure called an **α-helix**.
2. When stretched regions of different chains lie alongside each other, hydrogen bonding may occur between chains, resulting in a **β-pleated sheet** structure.

α-helix or alpha helix a structure of natural proteins where the carbonyl (C═O) of one amino acid is hydrogen bonded to the amino H (N—H) of an amino acid that is four down the chain, pulling it into a helical structure, like a curled ribbon

β-pleated sheet or beta-pleated sheet two or more segments of a polypeptide chain lie alongside one another, to form a sheet-like structure held together by hydrogen bonds

These two different secondary structures are shown in Figure 18.2.9. The nature of the secondary structure of a protein is an important determinant of its functional properties. Factors such as heat, pH and the presence of salts can affect the hydrogen bonding and, therefore, the stability of the secondary structure.



Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

FIGURE 18.2.9 The structure of proteins

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Tertiary and quaternary structure

The most important level of organisation is the tertiary structure of a protein as it gives the protein its three-dimensional shape. This is the way the helices and sheets of the secondary structure fold up and interact to form a three-dimensional structure.

The overall tertiary shape may be long and narrow, which is typical of the fibrous proteins such as keratin (skin, wool, feathers) and collagen (tendons, cartilage and hides), or a roughly spherical globular shape, which is typical of insulin, haemoglobin and enzymes.

There are five types of interactions that determine the tertiary structure. These interactions occur between the R group side chains on the amino acids that make up the chain. They are:

1. dispersion forces between non-polar side chains on amino acids such as phenylalanine and valine
2. hydrogen bonding between polar side groups such as —C═O and —OH or —N—H on amino acids such as serine and asparagine, as well as hydrogen bonding between peptide groups
3. ionic attraction between ionisable side chains such as $—COO^-$ in aspartic acid and $–NH_3^-$ in lysine
4. dipole–dipole attraction between polar side groups such as serine and threonine
5. covalent bonding formed when the —SH groups on the side-chain of cysteine are oxidised to form —S—S— (disulfide) links (a form of cross-linking between chains); cysteine plays a special role in providing greater stability to many tertiary structures.

Examples of each of these links are shown in Figure 18.2.10.

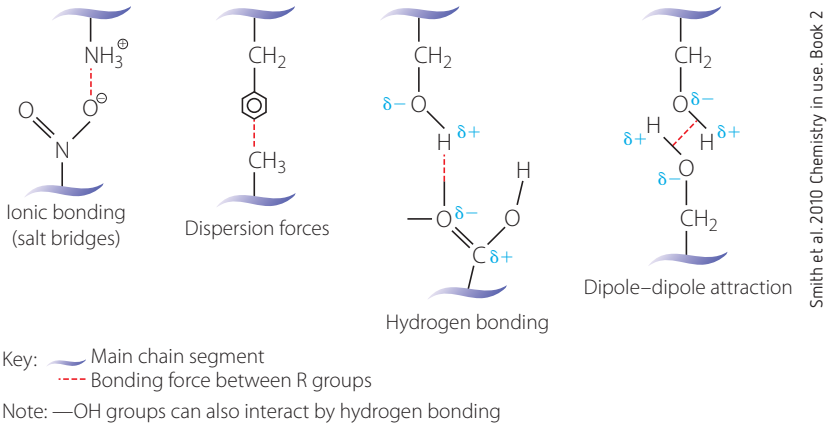


FIGURE 18.2.10 Examples of the intermolecular forces that determine the tertiary structure of a protein.

If there is more than one polypeptide chain involved, then there may be a quaternary structure, where the same intermolecular attractions cause the polypeptide chains to aggregate together in a very specific conformation. It is this three-dimensional quaternary structure of the overall protein that allows it to interact with other molecules. For example, an enzyme must have a three-dimensional structure that allows it to interact specifically with its substrate; and haemoglobin (made of four polypeptide subunits) must have the correct three-dimensional structure so it can interact with iron and oxygen.

DRUGS DESIGNED BY COMPUTER?

Our knowledge of the three-dimensional structures of complex molecules like proteins is now used to program computers to predict the action of drugs on the body. This means researchers can screen drugs before they are tested on living things, to prevent problems. Computers can also be used to design new drugs that will interact with proteins and other molecules and to speed up the development of new medicines.

SCIENCE AS A HUMAN ENDEAVOUR

SECTION REVIEW 18.2

REMEMBERING

1 **a** Draw the general structure of an amino acid and label the two functional groups of this molecule.

b Redraw the general structure from part a to show a zwitterion.

2 What are the three broad groups into which amino acids can be categorised?

3 Describe three levels of organisation of a protein and the relationship between levels.

UNDERSTANDING

4 Explain the different types of bonding that occur in the tertiary structure of a protein and categorise them from strongest to weakest.

5 What is the difference between an amide link and a peptide link?

6 Draw the structural formula of a dipeptide formed between the following amino acids and identify the link between them.

a Alanine and cysteine

b Glycine and serine

7 For each of the amino acids listed draw the structural formula of the zwitterion form of the molecule.

a Valine

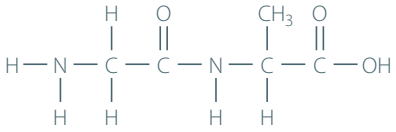
b Lysine

c Serine

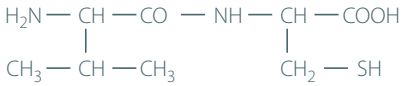
APPLYING

8 Write the equation for the hydrolysis of the dipeptides shown below and name the amino acids formed.

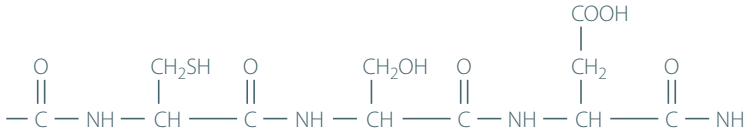
a



b



9 A section of a protein chain is shown.



a How many different amino acids reacted to produce this segment?

b Draw the structure of the amino acids identified in part a.

c Research what nylon-6 looks like. Explain the difference between this segment of a protein molecule and a segment of nylon-6.

REFLECTING

10 Predict what would happen to the secondary and tertiary structures of a protein if amino acids with polar groups were replaced with ones with non-polar groups.

18.3 Enzymes

enzyme
a biological catalyst which increases the rate of a reaction without being used up in the reaction

Every day, chemical reactions occur in your body to keep it healthy. Many of these reactions rely on **enzymes** to allow the reaction to occur at an adequate rate. An enzyme is a biological catalyst. This means that it is found in living organisms and, being a catalyst, can speed up a chemical reaction without being consumed.

Enzymes are usually large protein molecules. Enzymes are highly specific and act on a particular reaction, type of reaction or bond type by making it easier for the reaction to occur. Each enzyme has an **active site** with a shape that matches the reactant particles. When the enzyme and reactants (known as the **substrates**) bind, a change occurs that allows the reactants to form the products in a way that lowers the activation energy. Because less energy is needed for a successful collision, more particles have enough energy and therefore more collisions will result in a chemical reaction.

Our digestive system provides the nutrients we need for growth, repair and energy. The food we eat is largely made up of **carbohydrates**, proteins and **fats**. These are large organic molecules that are made up of smaller units (Table 18.3.1). The digestive system breaks down the large molecules into smaller molecules that can be absorbed into the bloodstream. In the blood, the molecules are transported to where they are needed.

active site
the area of the enzyme where it interacts directly with the substrate molecule

substrate
the molecule that is taking part in the reaction which the enzyme is catalysing

carbohydrates
food group consisting of molecules such as sugars and starches; a naturally occurring compound with the general formula $C_x(H_2O)_y$

fat
food group consisting of chains of triglyceride molecules; essential for life

TABLE 18.3.1 Nutrients in food

NUTRIENT	SMALL UNITS THAT CAN BE ABSORBED
Proteins	Amino acids
Carbohydrates	Simple sugars; e.g. glucose
Fats	Glycerol and fatty acids

Enzymes can be specific to a particular reaction, breaking a particular bond in a particular molecule (Figure 18.3.1). This means that the larger molecules are split into smaller sections. Upon binding to the enzyme at the active site, the substrate is changed in such a way as to allow the bond to be broken with less energy. The products formed are then released and the enzyme is available for further reactions.

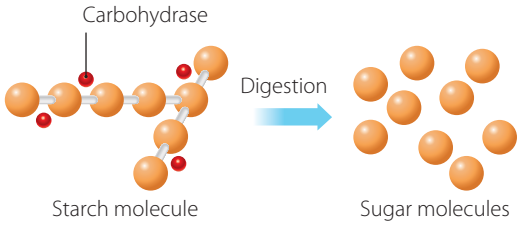


FIGURE 18.3.1 Enzymes help break complex molecules into smaller, simpler molecules that can be absorbed. For example, carbohydrase acts on starch molecules to produce sugar molecules.

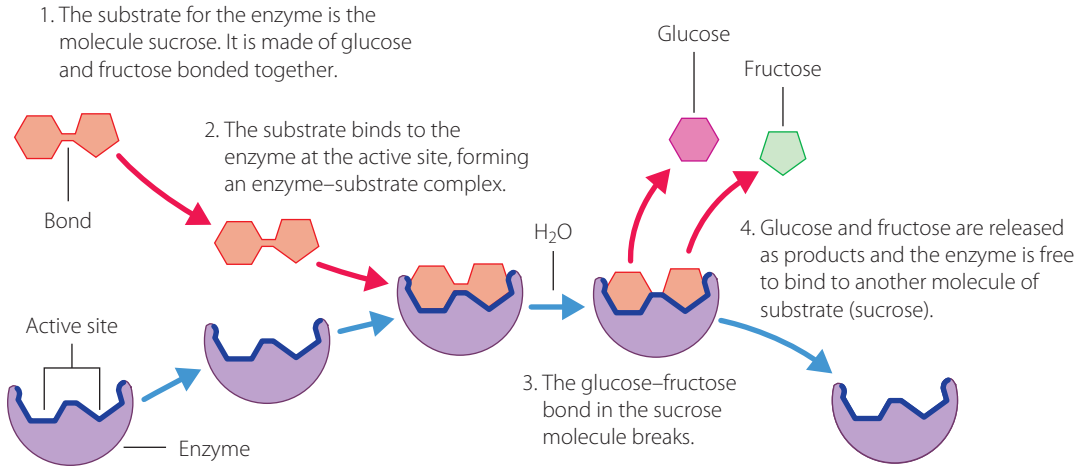


FIGURE 18.3.2 A model for an enzyme.

Table 18.3.2 lists some features of some digestive enzymes.

TABLE 18.3.2 Digestive enzymes

ENZYME	LOCATION	REACTANT	PRODUCT
Amylase	Saliva in the mouth Pancreas releases it into the small intestine	Starch (a large carbohydrate)	Maltose
Protease (pepsin)	Stomach	Proteins	Smaller proteins
Protease (trypsin)	Pancreas releases it into the small intestine	Proteins	Peptides and amino acids
Lipase	Pancreas releases it into the small intestine	Fats	Fatty acids and glycerol
Peptidase	Small intestine	Peptides (small sections of protein)	Amino acids
Sucrase	Small intestine	Sucrose (a small carbohydrate)	Glucose and fructose
Maltase	Small intestine	Maltose (a small carbohydrate)	Glucose
Lactase	Small intestine	Lactose (a small carbohydrate)	Glucose and galactose

There are thousands of different enzymes in the human body, controlling the wide range of reactions that are occurring. These include:

- carbonic anhydrase, which catalyses the reaction between carbon dioxide and water to form carbonic acid, allowing carbon dioxide to travel through the blood: $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$
- DNA polymerase, which is involved in DNA replication
- dehydrogenase, an important enzyme in the first step of cellular respiration in mitochondria, which produces energy in our bodies
- cyclin-dependent kinases, which control cell division
- tyrosinase, which triggers melanin synthesis and is important in determining skin colour.

The activity or effectiveness of enzymes can be affected by the conditions or environment in which they are found. These conditions include:

- concentration – the higher the enzyme concentration, the more substrate that can bind to an enzyme at a given time and the greater the reaction rate
- temperature – enzymes are proteins, and as such many are **denatured** above about 45°C. Above this temperature, the structure of the protein changes, changing the shape of the active site. This permanently inactivates the enzyme, as the substrate is unable to bind to the active site
- pH – different enzymes require different pH values for optimum activity; for example, the pH of the stomach is much less than the pH of the rest of the digestive system, so only specific enzymes will be activated in the stomach
- the presence of **co-enzymes** – ions or non-protein molecules, such as vitamins, that change the shape of the active site in order for the enzyme to function.

denaturing the permanent change than can occur to the structure of protein molecules when heated, or exposed to solutions of high acidity or alkalinity

co-enzymes molecules that assist the operation of enzymes

PRACTICAL ACTIVITY 18.3.1

Effect of pH and temperature on the enzyme complex rennet

Rennet is a complex of enzymes naturally found in the stomachs of mammals. It helps the coagulation of milk – separating it into a solid and a liquid component. It is especially important to help young animals digest milk. Rennet is also used in milk desserts, in the form of a setting agent known as junket. The enzymes help the milk set, forming a soft solid.

AIM

To investigate the effect of pH and temperature on the effectiveness of the enzymes in rennet

MATERIALS

- One packet of junket (enough for 65 mL of milk)
- 100 mL of milk
- Distilled water
- 1 mL of 1 mol L^{-1} hydrochloric acid (HCl)
- 1 mL of 1 mol L^{-1} acetic acid (CH_3COOH)
- 1 mL of 1 mol L^{-1} sodium acetate ($NaCH_3COO$)
- 1 mL of 1 mol L^{-1} sodium hydroxide (NaOH)
- 13 test tubes
- Test-tube rack
- Water baths at 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 70°C and 80°C
- 10 mL measuring cylinder
- Thermometer
- Stopwatch
- pH meter

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals could splash in your eyes.	Wear safety glasses at all times.
1 mol L^{-1} HCl and 1 mol L^{-1} NaOH are corrosive to skin and clothes.	Wear gloves and aprons.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

Part A: Effect of temperature

1. Place 5 mL of milk into each of eight test tubes.
2. Place one test tube in each water bath and leave it until the milk has reached the desired temperature.
3. Dissolve the junket in 15 mL of water. (You will need to keep some of this mixture for part B.)
4. Place 1 mL of junket into the first test tube, mix and record the temperature inside the test tube, and start the stopwatch immediately.
5. Stop the stopwatch when the milk has become firm. Record the time taken to set.
6. Repeat steps 4 and 5 for each of the milks at the other temperatures.

Part B: Effect of pH

7. Place 5 mL of milk into each of four test tubes.
8. Record the temperature of the milk – these should all be the same.
9. Into test tube 1, place 1 mL of distilled water.
10. Into test tube 2, place 1 mL of 1 mol L^{-1} HCl.

»

11 Into test tube 3, place 1 mL of 1 mol L^{-1} CH_3COOH.

12 Into test tube 4, place 1 mL of 1 mol L^{-1} NaOH.

13 Into test tube 5, place 1 mL of 1 mol L^{-1} $NaCH_3COO$.

14 Use the pH meter to test the pH of the milk in each test tube. Ensure that the meters are cleaned thoroughly between test tubes. Record the pH.

15 Add 1 mL of the junket solution from part A to test tube 1 and time how long it takes the milk to become firm. Record the time taken.

16 Repeat step 15 for test tubes 2–5.

RESULTS

Construct a results table like this in your notebook. Record your data in the table.

VARIABLE	TEST TUBE	TEMPERATURE (°C)	pH	TIME FOR MILK TO BECOME FIRM (MIN)
Temperature	1			
	2			
	3			
	4			
	5			
	6			
	7			
	8			
pH	1 (distilled water)			
	2 (HCl)			
	3 (CH_3COOH)			
	4 (NaOH)			
	5 ($NaCH_3COO$)			

ANALYSIS

1 Draw separate graphs for parts A and B.

2 What happened to the time taken for milk to become firm as the temperature increased?

3 What happened to the time taken for the milk to become firm as the pH increased?

4 Do these results support your understanding of the effects of temperature and pH on enzymes?

DISCUSSION

1 What aspects of the experiment increased the accuracy and reliability of the results?

2 What were the major difficulties in obtaining accurate results during the experiment?

3 How could you improve the experiment?

CONCLUSION

1 What conclusion can you make about the effect of temperature on the activity of enzymes in junket?

2 What conclusion can you make about the effect of pH on the activity of the enzymes in junket?

TAKING IT FURTHER

1 In what other ways could you investigate the action of enzymes?

2 Research the role of rennet (or rennin). Explain how your findings about the effect of temperature and pH may play a role in ensuring the enzyme's effectiveness.

SECTION REVIEW 18.3

REMEMBERING

1 Define:
   - **a** enzyme
   - **b** active site
   - **c** substrate
   - **d** denature
   - **e** co-enzyme.

2 Explain the factors that can affect the rate of a biological reaction.

UNDERSTANDING

3 Explain why enzymes are generally more effective than non-biological catalysts.

APPLYING

4 For a non-biological reaction, rate of the reaction increases as the temperature increases. We can explain this with collision theory, discussed on page 11. However, when a catalyst is involved, the relationship between temperature and rate of reaction is more complex. Explain why this is so.

18.4 Carbohydrates

Carbohydrates, which include simple sugars, are natural polymers. They are the most widely distributed and abundant compounds in the biosphere. The carbohydrate cellulose, the main component of plants, is probably the most abundant organic compound on Earth. Cellulose is a polymer found in the cell walls of plants. It is responsible for giving plants their structural strength. Cellulose is indigestible to humans but is part of the fibre needed in a balanced diet.

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FIGURE 18.4.1 Cellulose is found in the cell walls of plant cells.

Carbohydrates are a diverse group of molecules but they are all made up of the same three elements – carbon, hydrogen and oxygen – and there are always twice as many hydrogen atoms as there are oxygen atoms. The most common formula for carbohydrates is $C_6H_{12}O_6$. Carbohydrates are named because their formula can be written as $C_x(H_2O)_y$.

The structures of carbohydrates feature a ring containing carbon atoms (usually four to six) and one oxygen atom. The carbons of the ring are bonded to —OH groups and H atoms. Two or more rings may be joined together to make bigger molecules. The —OH groups participate in hydrogen bonds, which makes starch and sugar soluble in water.

Complex carbohydrates such as cellulose and starch are polymers made from simple units (sugars) called **monosaccharides**, meaning single (one) sugar, that are joined through a condensation polymerisation reaction.

monosaccharide a sugar that cannot be decomposed into simpler sugars

Monosaccharides

Monosaccharides are commonly referred to as simple sugars. They are all isomers of $C_6H_{12}O_6$. The monosaccharides glucose, fructose and galactose have different structures and properties, as shown in Figure 18.4.2.

The thick wedge-shaped bonds in the ring indicate that the plane of the ring is perpendicular to the paper. The H atoms and —OH and —CH_2OH groups attached to the ring are above and below that plane. The positioning of these groups is important because it determines which compound the structure represents. Glucose and galactose differ only in the location of one —OH group, yet they have noticeably different properties.

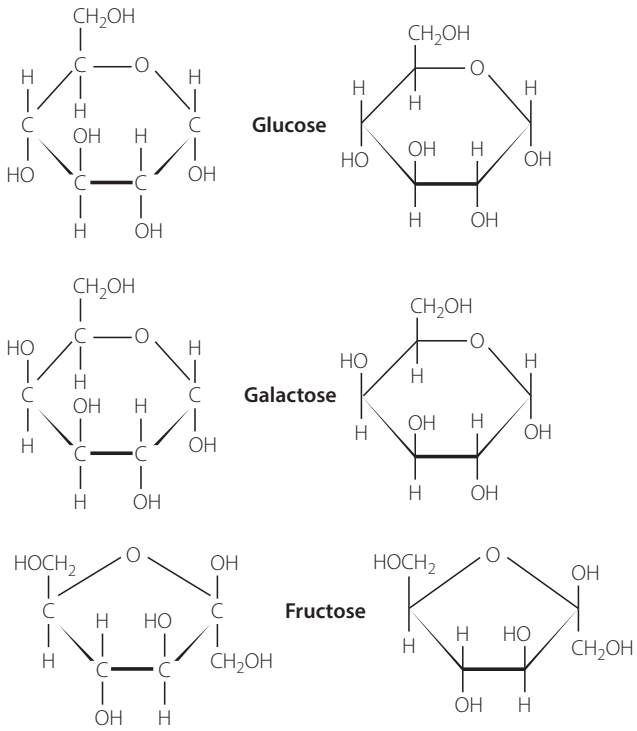

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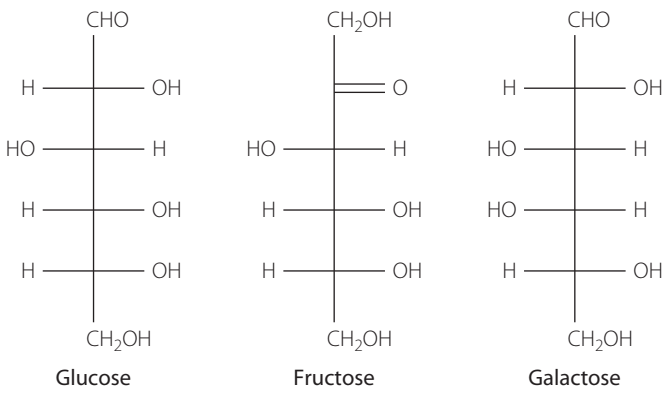
FIGURE 18.4.2 Structures of three common monosaccharides. The left-hand structures show all the atoms of the molecules; in the right-hand ones, the carbon atoms are not labelled.

Monosaccharides can also exist in a different form, where the molecules have the form of a chain rather than a ring. The structures of glucose, galactose and fructose in chain form are shown in Figure 18.4.3.

FIGURE 18.4.3 Glucose, galactose and fructose in chain form.



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When drawn in this form, we can see that the glucose and galactose molecules possess an aldehyde functional group, represented as —CHO, whereas fructose possesses a ketone functional group, represented as —C═O. Consequently, glucose and galactose are known as **aldose** sugars and fructose is a **ketose** sugar. Glucose and galactose are also sometimes known as **reducing sugars**, because of the reactions in which they subsequently participate as a result of possessing the aldehyde group. Glucose, fructose and galactose are all white crystalline, sweet-tasting compounds. Of the three, glucose is the most important in human nutrition because our bodies use it as a source of energy.

aldose
a sugar containing an aldehyde group

ketose
a sugar containing a ketone group

reducing sugar
another name for an aldose sugar

There are two isomers of glucose, called α-glucose and β-glucose, shown in Figure 18.4.4. The α form of glucose has the OH group on C1 below the plane of the ring, whereas in β-glucose it is above the plane of the ring.

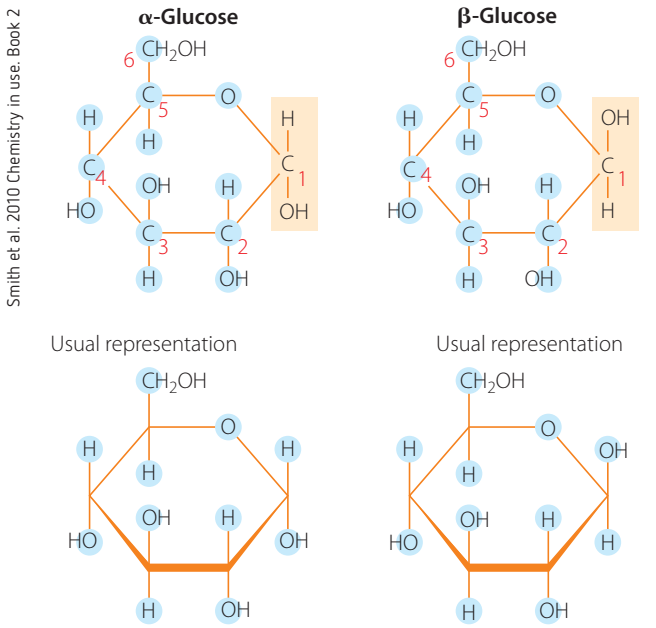

FIGURE 18.4.4 The α and β forms of glucose.

Disaccharides

Monosaccharides are the building blocks of other carbohydrates. When two monosaccharides join, they form a **disaccharide**. Common disaccharides are sucrose from cane sugar, maltose from malt and lactose from milk, their composition is shown in Table 18.4.1.

disaccharide
a sugar made from two monosaccharide units

TABLE 18.4.1 The composition of some common disaccharides

DISACCHARIDE	MONOSACCHARIDES
Sucrose	Glucose + fructose
Maltose	Glucose + glucose
Lactose	Glucose + galactose

The reaction that occurs to form the disaccharide is a condensation reaction because a water molecule is released. This can be written simply as:

$$2C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$$

While the molecular formula makes the reaction seem simple, when the structural formulas are considered the situation becomes more complicated because there are different isomers and different forms of these isomers. For example, sucrose is formed by linking the carbonyl carbons of α-glucose and β-fructose.

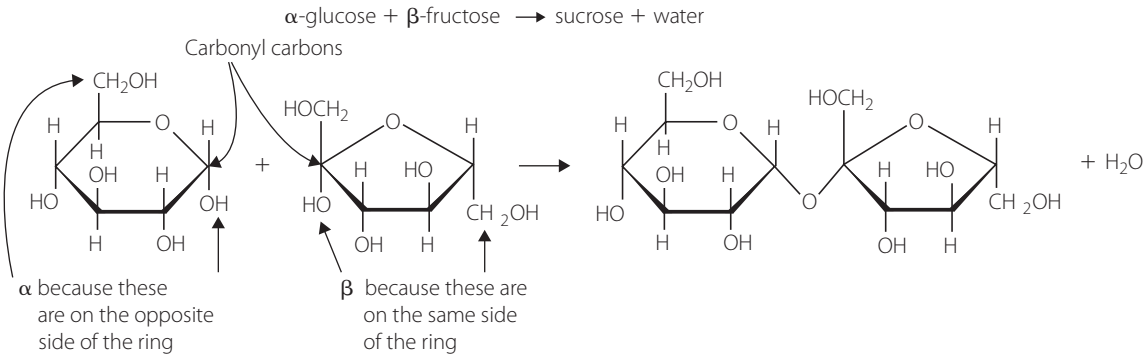

FIGURE 18.4.5 The formation of sucrose

glycosidic link
the ether bond that connects two monosaccharide units in a carbohydrate

The link that joins the monosaccharides is called a **glycosidic link**, —C—O—C—.

Maltose is produced when two glucose monomers join and lactose is produced when a glucose monomer and a galactose monomer join. These three disaccharides have different properties because of their different structures. Maltose and lactose are not as sweet as sucrose while fructose is sweeter than sucrose. Their melting points are: lactose 253°C, sucrose 186°C and maltose 160°C. They have similar densities.

Disaccharides are too large to pass through cell membranes, so they need to be broken down to their constituent monomers in the digestive system. This hydrolysis reaction is the reverse of the condensation polymerisation reaction by which they are formed and adds water to give a new —OH group to the fructose ring and —H to the oxygen on the glucose ring.

Polysaccharides

polysaccharide
a carbohydrate molecule made from many monosaccharide units

Polysaccharides are formed when hundreds or thousands of monosaccharides join through condensation polymerisation. A polysaccharide may contain only one type of monomer or different types. This gives the carbohydrate its primary structure.

Many polysaccharides form stable secondary structures because the bonding within or between polysaccharide chains means they form helices or chain-linked sheets. However, these secondary structures can often be disrupted by temperature increases, changing pH or adding a denaturing agent.

The three polysaccharides important to human life are starch and cellulose (from plants) and glycogen (from animals). These polysaccharides are all polymers of glucose but have different glycosidic links, and variable amounts of branching of the polymer chain and degree of polymerisation. As a result, these polysaccharides each have different properties and therefore different functions.

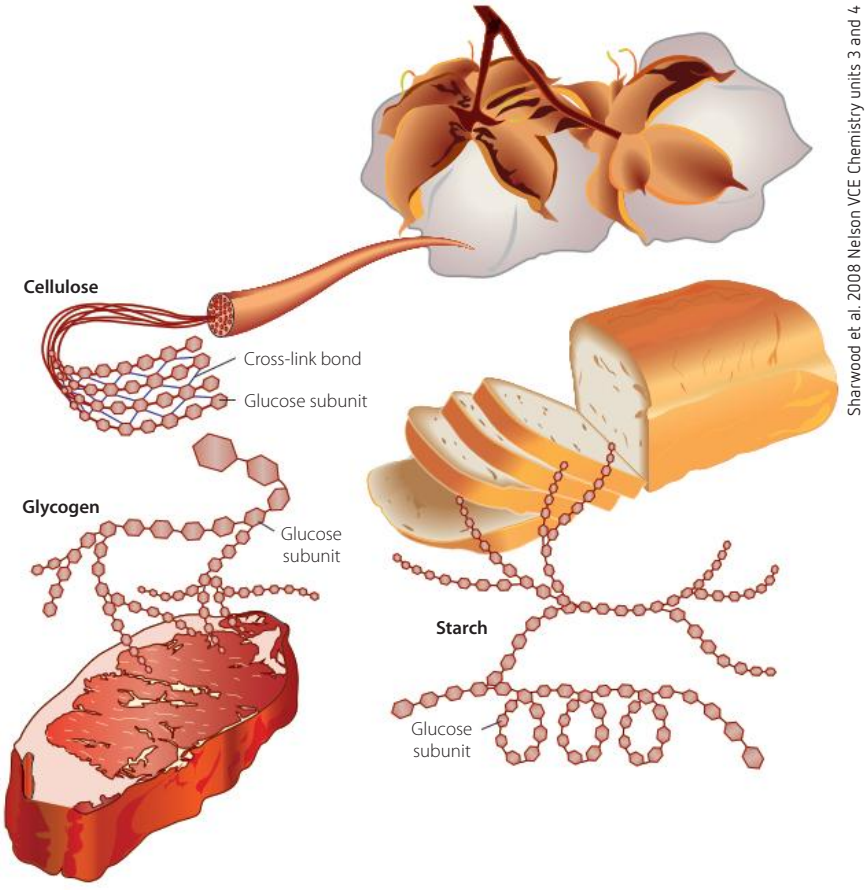

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FIGURE 18.4.6 Starch, cellulose and glycogen

Starch

Starch is found in plants, where it is used to store excess energy. Humans can digest starch, and it is an important nutrient, as it provides a source of energy for the biological processes that occur in our body.

Starch consists of long chains of α-glucose monomers. These chains take two forms: amylose and amylopectin. About 20 per cent of starch is in the form of amylose, a straight-chain polymer that can form spirals because of intra-chain hydrogen bonding. Amylopectin, which forms 80 per cent of starch, is a highly branched chain. These chains occur when one glucose molecule condenses with three other glucose molecules instead of the normal two. This part of the molecule cannot form spirals. Figure 18.4.6 shows how these two forms of starch originate as the glycosidic bonds between α-glucose molecules formed between different atoms, thus creating either the straight chains of amylose, or the branching in amylopectin.

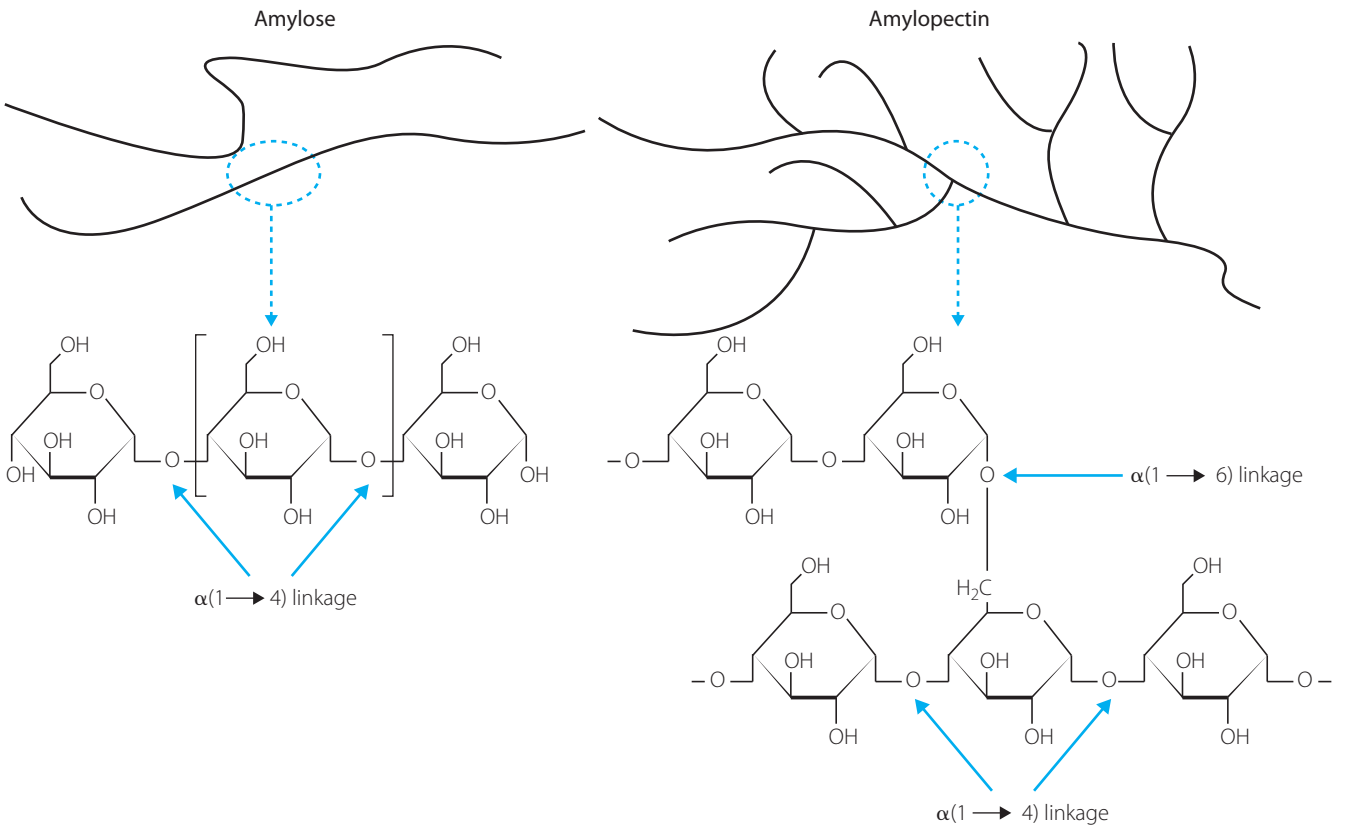


FIGURE 18.4.7 Amylose and amylopectin

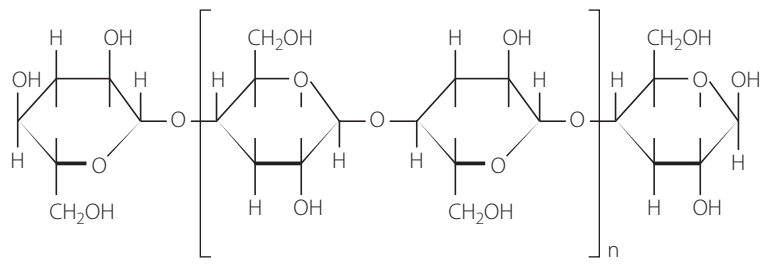
Cellulose

Cellulose is also found in plants, forming structural features such as stems and leaves. The strength of cellulose enables plants to support their own weight and withstand the forces of gravity. Many animals eat cellulose in large quantities, and it is an important part of a balanced diet for humans as it is the principal component of fibre – the indigestible material that passes through the digestive system.

Cellulose is a polymer of β-glucose, and the different orientation of the atoms in β-glucose, compared to α-glucose, means that the monomer molecules are also oriented differently in the polymer chain, as shown in Figure 18.4.7. Cellulose has a very different structure to that of starch. It consists of unbranched molecules that preferentially form hydrogen bonds with each other to form a strong cross-linked structure. Cellulose is a highly crystalline polysaccharide, and this accounts for many of its properties, such as strength, rigidity and insolubility in water.

crystalline
having a regular, ordered arrangement of atoms

FIGURE 18.4.8 The structure of cellulose



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Glycogen

Like starch, glycogen is a polymer of α-glucose, and it is used in nature as a store for the energy released through respiration. However, glycogen is formed in animals rather than in plants. It is highly branched with an **amorphous**, non-crystalline structure. The structure of glycogen is similar to that of amylopectin, but with a different frequency of branching.

amorphous without a clearly defined shape or form

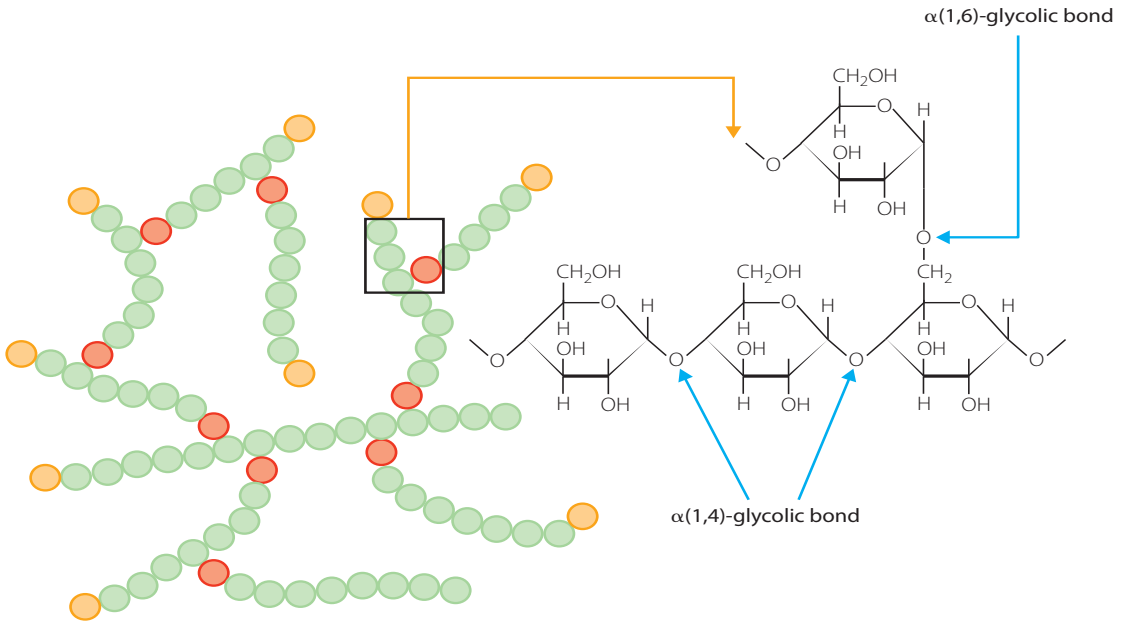


FIGURE 18.4.9 The structure of glycogen

SECTION REVIEW 18.4

REMEMBERING

1. Describe the differences between monosaccharides, disaccharides and polysaccharides.
2. Name and draw the structure of the linkage that joins monomer units together.
3. What functional group is characteristic of carbohydrates?

UNDERSTANDING

4. Explain why monosaccharides and disaccharides are soluble in water.
5. Why is the combined mass of the monosaccharides resulting from the hydrolysis of a disaccharide greater than that of the disaccharide?
6. Write the equation for the hydrolysis of sucrose.
7. Describe the differences between cellulose, starch and glycogen in terms of their structure, bonding and properties.

ANALYSING

8. Using the empirical formula for starch, $C_6H_{10}O_5$:
   - **a** calculate the percentage of oxygen and carbon in one repeating unit
   - **b** calculate the molecular weight of a molecule of starch that contained 300 monomer units
   - **c** write an equation for the hydrolysis of one unit
   - **d** write an equation for the hydrolysis of 50 units
   - **e** explain whether or not the equation is accurate and why.

18.5 Lipids

triglyceride
an ester formed from glycerol and three fatty acid molecules

oil
a lipid that is liquid at room temperature

glycerol
propane-1,2,3-triol

fatty acid
a carboxylic acid with a long hydrocarbon chain attached to a carboxyl group

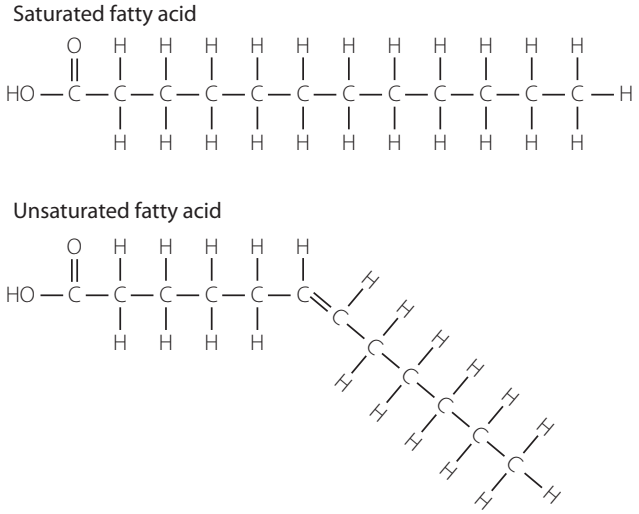
unsaturated fatty acid
a hydrocarbon molecule containing at least one C=C bond

saturated fatty acid
a hydrocarbon molecule with no C=C bond

Lipids are naturally occurring ester molecules and belong to the organic family called **triglycerides**. If they are solid at room temperature, then they are called fats. If they are liquid at room temperature, then they are **oils**.

Lipids are generally formed when 1,2,3-propanetriol (a propane molecule in which an —OH is joined to each carbon), commonly known as **glycerol**, reacts with a fatty acid molecule, in a condensation reaction. A **fatty acid** molecule consists of a carboxylic acid functional group at the end of a long hydrocarbon chain, which can contain 10–20 carbon atoms. The hydrocarbon chain may also contain carbon–carbon double bonds, in which case the molecule is described as an **unsaturated fatty acid**. If there are no double bonds between carbon atoms, the molecule is a **saturated fatty acid**. In general, lipids originating from plants are more likely to be unsaturated and in the liquid form, and lipids originating from animals will be solid and saturated.

FIGURE 18.5.1
Saturated and unsaturated fatty acids



The glycerol molecule makes up the backbone of the molecule and the fatty acids make up the tail. Each of the three alcohol groups in glycerol forms an ester link with a fatty acid, eliminating a water molecule in the process. As for all esters, this esterification reaction is reversible through hydrolysis, and during digestion these lipids are broken down to glycerol and fatty acids. These reactions are shown in Figure 18.5.2.

Saponification

Soaps and detergents are generally used as cleaning products because of their ability to remove dirt, oil and stains. This vital property is due to the structure of the soap and detergent molecules. Our knowledge of this structure has enabled us to synthesise more effective cleaning products.

Soaps are salts of fatty acids. They consist of a long hydrocarbon chain, or tail, with a carboxylate ion ($—COO^-$) at one end – this is known as the head (Figure 18.5.3). A positively charged sodium or potassium ion is bonded to the carboxylate ion, making the soap molecule a sodium (or potassium) salt.

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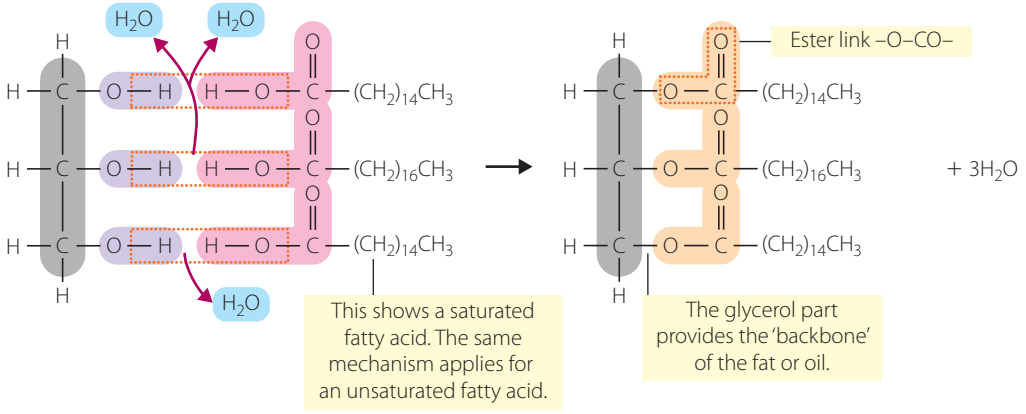
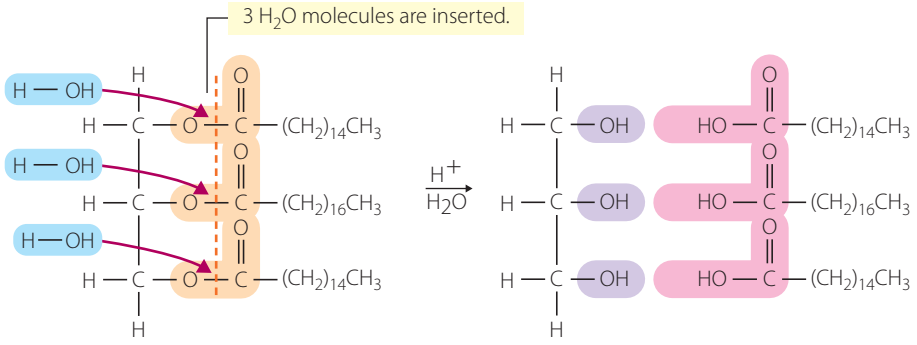
Production of a fat



$$\text{Glycerol} + 3\text{ fatty acids} \xrightarrow[\text{reaction}]{\text{Condensation}} \text{Triglyceride} + 3H_2O$$

Hydrolysis of a fat



$$\text{Triglyceride} + 3H_2O \xrightarrow[\text{reaction}]{\text{Hydrolysis}} \text{Glycerol} + 3\text{ fatty acids}$$

FIGURE 18.5.2 The production and hydrolysis of a lipid

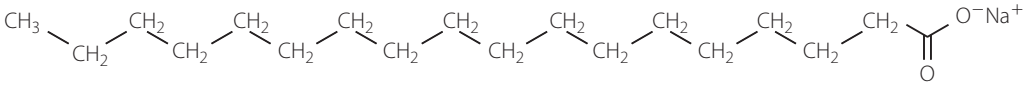


FIGURE 18.5.3 The structure of a soap molecule, showing the long hydrocarbon tail and carboxylate ion head.

Soaps are made through the hydrolysis of fats in a saponification reaction. When a triglyceride reacts with sodium (or potassium) hydroxide, the ester bonds break and glycerol and three alkyl carboxylates are formed.

Soaps are able to clean because they can bond with both polar and non-polar substances. The hydrocarbon chain, or tail, is non-polar, or hydrophobic. This part can bond to non-polar dirt and grease. The head is polar due to the presence of the carboxylate ion. It is hydrophilic – it can form bonds with water molecules.

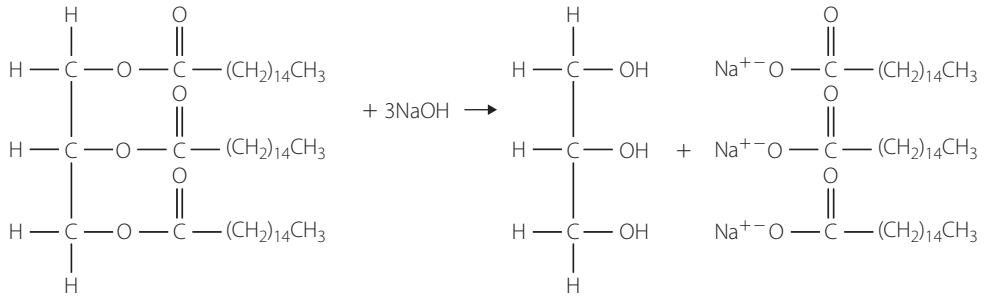


FIGURE 18.5.4 The production of soap

Soap molecules surround dirt or grease on a surface, with their hydrophobic tails embedded in the dirt or grease. This leaves the hydrophilic ends on the outside to bond with the water molecules. When the water is agitated, the water molecules pull on the soap molecules, which pull on the dirt. This lifts the dirt away from the surface and more soap molecules are able to surround it. When the soapy water is washed away, the dirt is taken with it.

One problem with soaps is that they don't lather up in water containing calcium or magnesium ions – 'hard' water. When the calcium or magnesium ions combine with the carboxylate ions on the soap, they form an insoluble product, resulting in scum. Household **detergents** do not contain the carboxylate ion and therefore do not form the precipitate.

detergent
a water-soluble agent which makes dirt and oils soluble yet, unlike a soap, does not form a scum in hard water

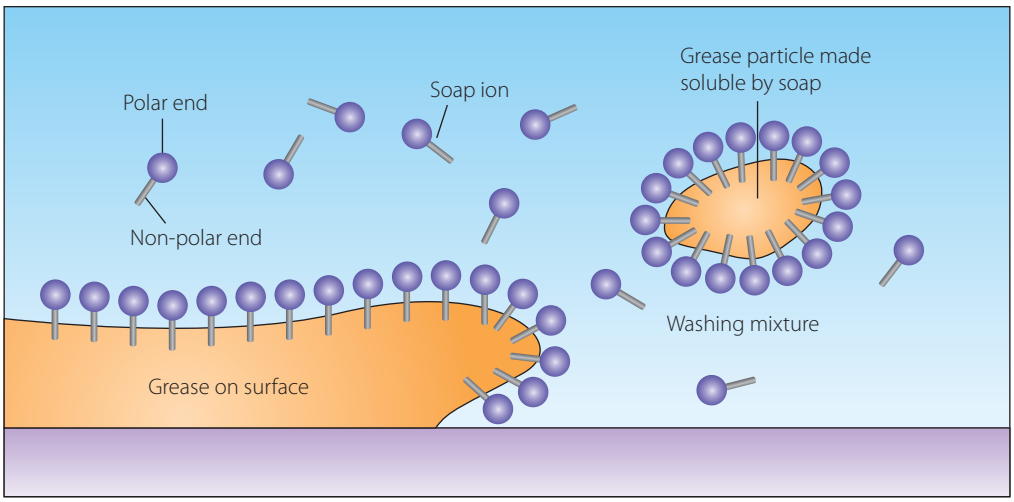


FIGURE 18.5.5 The cleaning action of soap

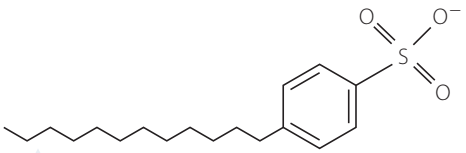


FIGURE 18.5.6 The structure of an anionic detergent

Like soaps, these detergents contain a non-polar hydrocarbon chain tail and a polar head. This means that they are able to clean by the same process as soaps. The hydrocarbon tail in detergents is an alkylbenzene, while the polar head is a sulfonate (SO_3^-) ion. These are known as anionic detergents because of the negative charge on the ion.

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SECTION REVIEW 18.5

REMEMBERING

1 Explain the difference between a fat and an oil.
2 What is the difference in structure which causes a lipid to form an oil rather than a fat?
3 What is meant by the term 'fatty acid'?

APPLYING

4 Explain how soap can remove dirt from a piece of cloth, when washing with water does not do so.
5 Explain the advantage of a detergent over a soap.

18.6 The structure and properties of synthetic polymers

It is important to distinguish between synthetic polymers and **plastic**. While all plastics are synthetic polymers, not all synthetic polymers are plastics. Plastics are malleable and pliable and capable of being moulded by heat and pressure. Chemists distinguish between polymers that can be melted and re-formed and those than cannot by using the terms **thermoplastic** and **thermosetting**.

plastic
a synthetic polymer that is malleable, pliable and capable of being moulded by heat and pressure

thermoplastic
polymers that can be melted and re-formed

thermosetting
polymers that cannot be melted and re-formed

Thermoplastic polymers soften on heating and so are easily recycled because they can be melted and remoulded. Thermoplastic polymers are used in plastic bags and plastic wrap (polyethylene), garden hoses (polyvinyl chloride) and soft-drink bottles (polyethylene terephthalate). Thermosetting polymers do not become soft or change shape on heating, so they are not easily recycled. These polymers are generally stronger, more chemically resistant and more durable than thermoplastic polymers and are used, for example, in insulating foams (polyurethane), worktop surfaces, cups and plates (melamine) and some older electrical insulators (Bakelite).

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FIGURE 18.6.1 Melamine is an example of a thermosetting plastic.

LDPE and HDPE

One of the most common addition polymerisation reactions occurs in the production of polyethene, which involves the linking of ethene molecules into long chains, as previously described in Chapter 17.

There are two types of polyethene, produced by two different processes – low-density polyethene (LDPE) and high-density polyethene (HDPE). Their different properties are a result of differences in their structures.

LDPE has significant chain branching because some of the hydrogen atoms are replaced by alkyl groups. The branches prevent the polymer chains packing closely together so there is a lot of space in the product and fewer dispersion forces between them. This leads to its low density, low melting point and greater flexibility.

HDPE consists of unbranched polyethene chains that can pack closely together in an orderly way. Because the chains are packed more closely together, this product has a higher density. There is also stronger bonding because there are more dispersion forces between chains, resulting in a higher melting point and less flexibility.

HDPE has a more ordered structure so is said to be more crystalline, while LDPE, with its more random structure, is amorphous (non-crystalline). Figure 18.6.2 shows the difference between the linear chains of HDPE and the branched chains of LDPE, while Table 18.6.1 summarises their differences.

FIGURE 18.6.2
Different arrangements of polymer chains in HDPE and LDPE

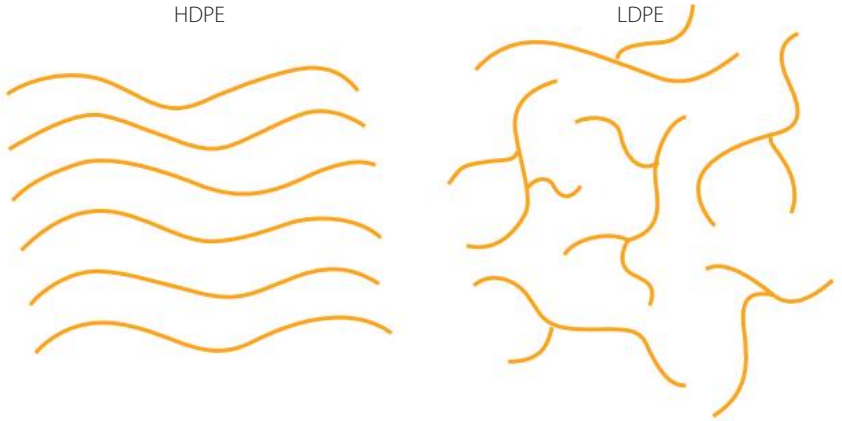

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TABLE 18.6.1 Differences in structure, properties and uses of LDPE and HDPE

POLYMER	STRUCTURE AND BONDING	PROPERTIES	USE
Low-density polyethylene (LDPE)	• Amorphous (disordered) • Branched chains • Weak bonding due to fewer dispersion forces between chains that are further apart	• Soft, flexible, transparent, • Impermeable to water vapour • Unreactive towards acids and bases • Absorbs oils and softens, • Low melting point (80–95°C) • Low tensile strength	• Plastic bags, toys, plastic food wraps, wire and cable insulation, lamination film for paper and card used in juice and milk cartons, hard disc drives
High-density polyethylene (HDPE)	• Crystalline (ordered) • Linear chains • Stronger bonding due to more dispersion forces and closeness of chains	• Denser, tougher, opaque and more rigid • Higher melting point • Greater tensile strength than LDPE • Impermeable to water vapour • Unreactive towards acids and bases	• Detergent bottles, milk and water jugs, fuel tanks for vehicles, bottle caps, food storage containers, 3D printer filament, plastic surgery

PRACTICAL ACTIVITY 18.6.1

Investigating crystalline and amorphous packing of polymer chains

The arrangement of polymer chains and the strength of interactions between adjacent chains is the reason why some plastics are soft and flexible and others are hard and rigid. If the chains can move easily past each other when the plastic is bent, then it will be flexible, but if the chains are held in place, the plastic will be rigid.

When polymer chains are packed closely together in a regular pattern, they form a crystalline area. The more crystalline areas in the polymer there are, the stronger and less flexible it is. The areas where the chains are randomly arranged, and so further apart, are called amorphous.

Many polymers have both crystalline and amorphous regions. Because polymer chains are so long, any one chain can be involved in both regions along its length.

AIM

To use spaghetti to make a model of polymer structure. (To find out more about how polymers are used see page 271.)

MATERIALS

- Spaghetti (about 100 g)
- Saucepan or large beaker
- Hot plate
- Strainer
- Water
- Transparent container with a flat base and straight sides

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Boiling water can cause serious burns.	Wear protective clothing. Use heatproof gloves to handle the container with boiling water.

RISK ASSESSMENT

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Cook the spaghetti according to the manufacturer's instructions.
2. Strain the cooked spaghetti to remove the excess water.
3. Pour the strained spaghetti into the straight-sided container and allow it to cool.
4. Once the spaghetti is cold, turn it out onto a flat surface, being sure it retains its block shape.

RESULTS

Draw a diagram or take a photo of the flat bottom of the spaghetti.

FIGURE 18.6.3 An upturned spaghetti cake

ANALYSIS

1. Identify crystalline and amorphous regions on your diagram or photo.
2. Estimate the percentage of crystallinity (that is, how much of your polymer is crystalline) in your 'polymer' and compare this with other students' results.

DISCUSSION

1. Compare how easy it is to lift a piece of spaghetti from an amorphous region and a crystalline region. Discuss this in terms of intermolecular forces.
2. Discuss whether your polymer would be more or less rigid than those of other students. Justify your answer.

CONCLUSION

Relate the properties of the amorphous and crystalline regions to the properties of LDPE and HDPE.

Atactic, syntactic and isotactic polypropene

Propene Polypropylene

FIGURE 18.6.4 Propene and polypropene

Polypropene (sometimes referred to as polypropylene) is an addition polymer of propene, which is formed in a similar process to that of polyethene. As can be seen in Figure 18.6.4, the —CH_3 group in propene which is not involved in the double bond in the propene monomer exists as a side group to the primary chain.

There are three variations of the structure of polypropene, depending on the orientation of the —CH_3 alkyl group relative to the chain. The spatial arrangement of these side groups makes a difference to the properties of the polymer.

The three possible arrangements are shown in Figure 18.6.5, where the coloured ovals represent the —CH_3 group and the hydrogen atoms have been omitted for simplicity.

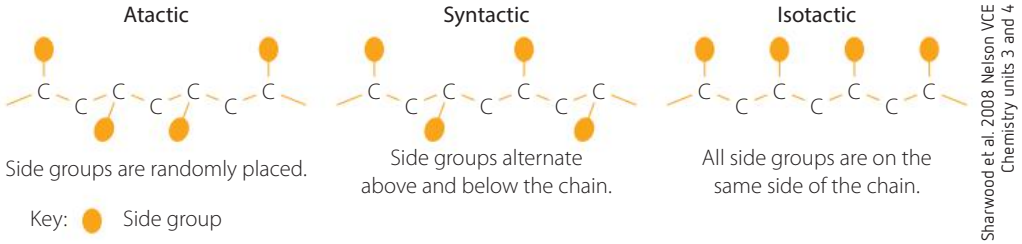

FIGURE 18.6.5 Three possible arrangements of side groups in polypropene

isotactic
a polymer where the side-chain functional groups are regularly arranged on the same side of the chain

atactic
a polymer where the side-chain functional groups are randomly arranged on the polymer chain

The regular arrangement of the —CH_3 groups on the same side of the polymer chain in the **isotactic** arrangement makes it possible for the chains to pack close together and maximise the dispersion forces between them. This means it is quite strong and hard with excellent resistance to stress, cracking and chemical reactions. It is the common form used to manufacture objects such as crates and ropes.

In the random **atactic** arrangement, the chains cannot lie close together, so the forces of attraction are weaker. This results in a softer polymer with a lower melting point. The atactic version formed during the manufacture of the isotactic polymer is considered a waste product and is a soft rubbery polymer, which has limited use mainly as a roofing material and sealant.

Syntactic polypropene has only recently been made on a large scale. In this version, the —CH_3 groups alternate above and below the chain. The regularity means the chains can pack closely, resulting in fairly strong intermolecular forces. However, its attractions are not as strong as in the isotactic version, so it is somewhat softer than the isotactic polymer, but also tough and clear. It is used in packaging and, because it is stable to gamma radiation, it has applications in medicine, such as medical tubing, bags and pouches.

The isotactic and syntactic forms of polypropylene are called stereoregular polymers. They are semicrystalline. The chains in the crystalline parts are not stretched out in a zigzag way as in polyethylene, but curl up into regular spirals, allowing even stronger bonding.

syntactic
a polymer where the side-chain functional groups alternate above and below the chain

stereoregular polymers
polymers with small, regularly ordered units in a single chain

Polytetrafluoroethene (PTFE)

Polytetrafluoroethene (PTFE) is a polymer you are probably more familiar with as Teflon. It is most commonly known as the non-stick surface on pans, but it is also used to treat carpets and fabrics to make them stain resistant and has also been used for making artificial body parts. This polymer is also very strong. It is used to make high-grade electrical insulation and pipe thread sealant. The major application, using approximately 50 per cent of PTFE production, is insulation for wiring in aerospace and computer applications.

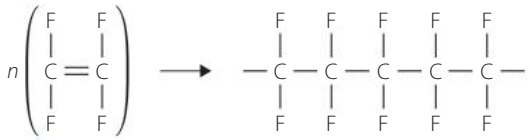

FIGURE 18.6.6 Formation of polytetrafluoroethene (PTFE)

PTFE is formed in a very similar reaction to polyethene by addition polymerisation.

This polymer has repeating units similar to those of polyethene except all the hydrogen atoms have been replaced with fluorine. Its properties are due to the polar carbon–fluorine bonds and dipole–dipole interaction between polymer chains, which make it strong and tough. It also has the third lowest coefficient of friction of any solid and is resistant to the formation of dispersion forces, which means it is the only known surface geckos cannot stick to.

Alamy Stock Photo/Zoonar GmbH

FIGURE 18.6.7 Non-stick frying pans are coated with pigmented Teflon

PRACTICAL ACTIVITY 18.6.2

How strong is Teflon?

Teflon tape is used by plumbers to make a waterproof seal between threaded iron pipes. You can buy Teflon tape at most hardware stores.

1. Cut a 20 cm piece of tape, take a firm grip on each end and stretch it a bit lengthwise. What do you observe?
2. Stretch the tape a little widthwise. What do you observe?
3. Try to break the tape by stretching it slowly lengthwise. Use as much force as you need.
4. Try to break the tape by stretching it widthwise. What do you observe?
5. Use what you know about bonding to try to explain what you observed.

SECTION REVIEW 18.6

REMEMBERING

1 **a** What is the difference between an amorphous and a crystalline polymer?

b How and why do these structural differences affect the properties of a polymer?

2 What is a copolymer?

APPLYING

3 **a** Draw the structures of three possible variations of polypropene.

b Explain why each of the different structures would have different properties.

4 Explain what density is and why HDPE has a higher density than LDPE.

ANALYSING

5 Explain why, even though they are both amorphous polymers, polyvinyl chloride forms a hard, rigid polymer, while polystyrene is hard and brittle.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Explain the following terms.

- Polymer
- Monomer
- Addition
- Condensation
- Copolymer
- Biodegradable
- Tensile strength
- Density
- Polyamide
- Alpha-amino acid
- Zwitterion
- Isoelectric point
- Enzyme
- Aldose
- Ketose
- Disaccharide
- Polysaccharide
- Crystalline
- Amorphous
- Fatty acid
- Detergent
- Plastic
- Thermoplastic
- Thermosetting
- Vulcanisation
- Isotactic
- Atactic
- Syntactic

CATEGORY QUESTIONS

2 Compare and contrast the structure and properties of LDPE and HDPE.

3 Explain the structure of a lipid, and the differences in structure between oils and fats.

ELABORATION QUESTIONS

4 Explain why the tertiary and quaternary structures of proteins are so important in the function and operation of enzymes.

5 Outline the variations that can exist in the structure of polymer molecules and explain how these variations can manifest themselves in the properties of these polymers.

END-OF-CHAPTER EXAM

End-of-chapter test

1 When fatty acids and glycerol react they form:

A a triglyceride.

B a peptide.

C an ester.

D a carbohydrate.

2 A sample of polypropene has the methyl side chains randomly arranged in relation to the chain. It is known as:

A syntactic.

B atactic.

C HDPE.

D isotactic.

3 Sections of a lipid molecule that are attracted to water molecules are known as:

A hydrophobic.

B hydrocarbon chain.

C hydrophilic.

D carbon atoms.

4 Which of the following is not an important structural feature of a polymer?

A Crystallinity

B Cross-linking

C Solubility

D Side groups

5 Essay question: Proteins, such as haemoglobin, and polysaccharides, such as cellulose, are both polymers. As such, they have some properties in common yet they vary in other properties. Compare and contrast the properties of a protein and a polysaccharide by explaining the similarities and differences between them.

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19 ANALYTICAL TECHNIQUES

Introduction

Chemists have to determine the structures of organic compounds to be able to understand how bonds are formed and how molecules react. This enables a better understanding of how biological molecules, such as enzymes, ribosomes and DNA, function. Understanding the detail down to the individual atoms has revolutionised the development of new medicines and promises advances in the early diagnosis of cancers.

The use of techniques such as chromatography, electrophoresis, mass spectroscopy, X-ray crystallography and infrared spectroscopy has led to revolutionary breakthroughs in determining the structure and function of molecules. For example, by 2014, X-ray crystallography had been associated with 28 Nobel Prizes.

Stimulus question

How can we quickly and accurately analyse the structure of molecules?

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19.1 Chromatography

chromatography technique for separation of mixtures due to differing interactions with different media

mobile phase a liquid or gas that carries the sample through a chromatography column

stationary phase a solid to which the sample molecules adsorb as they move through the chromatography column

Chapter 14 of *QScience Chemistry Units 1 & 2* provides a detailed explanation of the principles of **chromatography**, and how the data from chromatography can be used to separate and quantify the different components in a mixture. It is important, however, to examine in more detail the specific modifications to chromatography techniques that can be made in order to analyse larger organic molecules, such as proteins, and how the information from chromatography can be used in conjunction with other techniques.

Column chromatography

As previously discussed, chromatography is the process of separating a mixture of particles according to their differing affinities with two other substances: a **mobile phase** and a **stationary phase**. For larger organic molecules, this commonly occurs in a column, as can be observed in Figure 19.1.1.

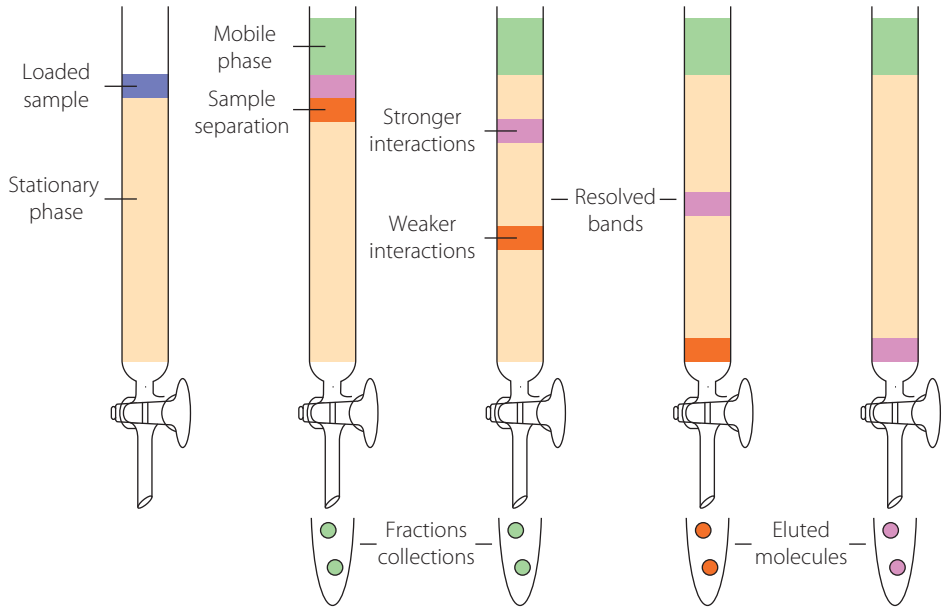


FIGURE 19.1.1 Column chromatography

In column chromatography:

1. The sample is placed at one end of a stationary phase, which is normally a solid of very fine particles, packed into a column.
2. The mobile phase, or eluent (a liquid of appropriate polarity, according to the mixture being separated) is allowed to pass through the column.
3. The different components of the sample **adsorb** to the stationary phase to different extents and also have differing solubility in the mobile phase. Therefore, the molecules from the mixture travel down the column at different rates and become separated from each other. The longer the column, the greater the separation.
4. As each **fraction** reaches the end of the column, carried by the mobile phase, it can be collected and separated from the original mixture. It may then be further analysed using one of the techniques described later in this chapter.

adsorb sticking to the surface

fraction one of the substances being separated from a mixture by chromatography

Provided the conditions (stationary phase, mobile phase, temperature, size of the column and atmospheric pressure) are kept the same, then the rate of movement of each fraction through the column should be the same. Consequently, the **retention time** (R_t the length of time required to pass through the column) is unique for each particular compound and can be used to positively identify it.

retention time
the length of time taken for a particular fraction to move through a column

Chromatography techniques for protein analysis

There are a number of variations to the column chromatography technique which can be made in order to effectively separate and analyse protein molecules.

Ion exchange chromatography

Protein molecules are charged, due to the ionisation of groups such as amino and carboxyl on the side chains which can become protonated or deprotonated according to the pH of the surrounding solution. The **isoelectric point** (pI) is the pH at which there is no net charge on a protein.

If the pH of the surrounding **buffer solution** is greater that the pI, the protein molecule will carry a net negative charge. Therefore, it will adsorb to an **anion exchange resin** stationary phase, which is positively charged. If the pH of the surrounding solution is less than the pI, the molecule will carry a net positive charge. Therefore, it will adsorb to a **cation exchange resin**, which is negatively charged.

Different proteins will adsorb differently to the stationary phase according to the extent to which they are charged. Those with more charged groups will have a greater R_t than those with fewer charged groups. Hence different protein molecules can be effectively separated.

isoelectric point
the pH value at which there is no net charge on a protein

buffer solution
a solution that maintains a constant pH when small amounts of acid and base are added

anion exchange resin
a polymer that acts as a stationary phase by attracting anions present in a solution

cation exchange resin
a polymer that acts as a stationary phase by attracting cations present in a solution

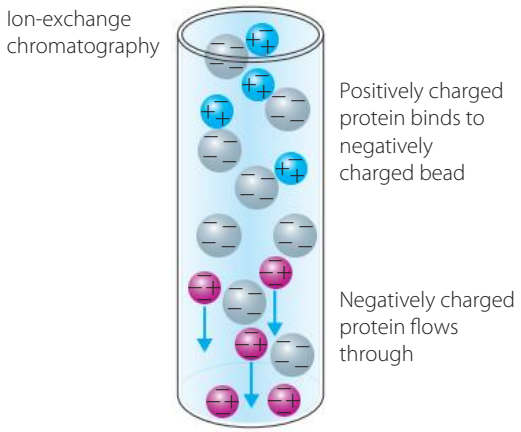


FIGURE 19.1.2 A schematic diagram of ion exchange chromatography

Ion exchange chromatography is a very powerful separation technique used to prepare samples and for analysis. It does have the disadvantage that at times the pH of the buffer solutions can affect the protein structure and cause it to denature. The extent to which this occurs depends on the specific proteins.

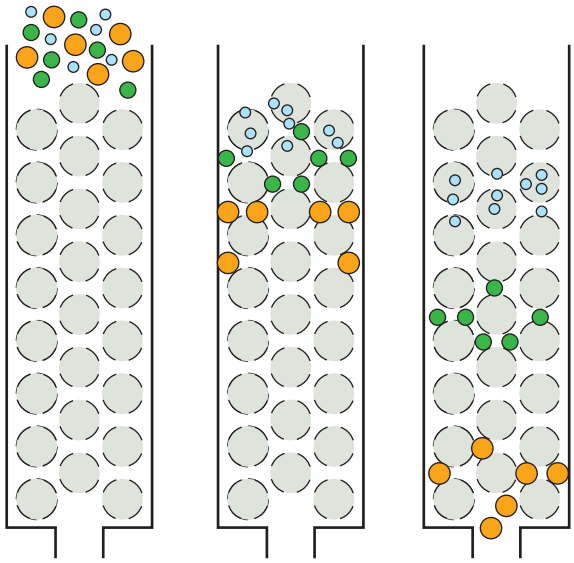
Size exclusion chromatography

Size exclusion chromatography (SEC) is a filtering technique that relies less on the interactions that occur between the sample and the mobile and stationary phases, and more on the ability of the molecules to pass through pores in the stationary phase, depending on their size.

The stationary phase usually consists of a gel containing pores of a specific size. Larger molecules do not get trapped by these pores and therefore pass through the column more quickly. The smaller the molecule, the more likely their passage through the column will be slowed by their interaction with the

pores in the stationary phase. Therefore, the R_t in the column will be inversely proportional to the size of the molecules.

FIGURE 19.1.3 A schematic diagram of SEC



Hydrophobic interaction chromatography

Hydrophobic interaction chromatography (HIC) separates molecules based on their hydrophobicity. HIC is a useful separation technique for purifying proteins while maintaining biological activity due to the use of conditions and matrices that operate under less denaturing conditions.

The principle for protein adsorption to HIC media is complementary to ion exchange and SEC. Sample molecules containing hydrophobic and hydrophilic regions are applied to a column in a solution with a very high salt concentration. This high salt concentration makes the sample less soluble; therefore, non-polar, hydrophobic regions of the molecule are adsorbed by the stationary phase. The more hydrophobic the molecule, the less salt is needed to promote binding. Usually a decreasing salt gradient is used to elute samples from the column in order of increasing hydrophobicity.

SECTION REVIEW 19.1

REMEMBERING

1 Define:
- **a** adsorb
- **b** fraction
- **c** buffer solution
- **d** ion exchange resin
- **e** retention time

2 Explain how components of a sample can be effectively separated using column chromatography.

UNDERSTANDING

3 State one reason why the technique of HIC might be preferred to ion exchange chromatography for analysing a sample of proteins.

4 Explain the relationship between R_t and molecular size in SEC.

APPLYING

5 What are the properties of proteins that have been used to develop these chromatography techniques?

19.2 Electrophoresis

The technique of **gel electrophoresis** is commonly used to separate and analyse mixtures of compounds such as protein molecules. It can provide clear information regarding the molecular mass and the composition of each protein present. It is a straightforward technique to carry out and is easily reproducible. It is also a sensitive and accurate process, and can clearly distinguish different proteins with very similar compositions.

gel electrophoresis the process of separating large charged molecules by placing them in an electric field and observing their subsequent migration through a medium such as a gel

Electrophoresis works on a very similar principle to chromatography. It can be defined as the separation of charged particles on the basis of their different rates of migration through a medium such as a gel. The gel is the equivalent of the stationary phase in chromatography. There is no mobile phase in gel electrophoresis, as the movement of the molecules is the result of the electric field that is applied across the gel, which causes a force to act on charged particles within it. The equipment is set up as shown in the schematic diagram in Figure 19.2.1.

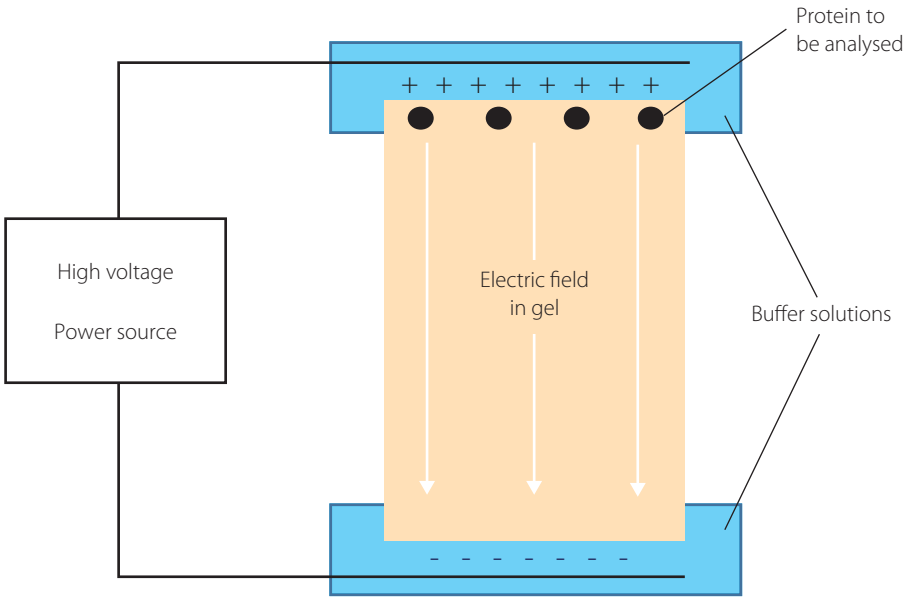


FIGURE 19.2.1 Schematic diagram of electrophoresis

In gel electrophoresis:

1. Samples of protein molecules to be analysed are introduced into wells at one end of the gel.
2. Buffer solutions at either end of the gel create a pH gradient, a gradual change in pH across the gel.
3. As a result of the buffer solution at the start of the gel, various side chains in the amino acids that comprise the peptide chains become ionised. They then interact with the **electric field** across the gel and begin to move, or migrate, across the gel.
4. The rate of migration will change according to the size of the protein molecules and the extent to which they are charged:
   - the larger the molecule, the slower it will move
   - the greater the charge on the molecule, the greater the force imposed through interaction with the electric field and so the greater the acceleration.

   Therefore, over time, different molecules in a sample will be spread across the gel because they are moving at different speeds.

electric field a region of influence around a charged particle where a force is exerted on other charged objects

5 Because of the pH gradient across the gel, eventually each protein will reach a pH that is equal to its isoelectric point. At this pH, the protein becomes neutral and so is no longer soluble. Therefore, it becomes focused into a band on the gel which can be detected, often with the assistance of UV light.

6 The sequence of bands from different protein samples can be clearly identified and then compared and contrasted with one another. Figure 19.2.2 shows the results of the electrophoresis of different samples of proteins taken from the bacterium *Shigella flexneri* at different temperatures. As the proteins all come from the same organism, there is a lot of similarity between the bands on the gel; however, on closer inspection, subtle changes can be observed, which highlights the changes that are occurring at the different temperatures.

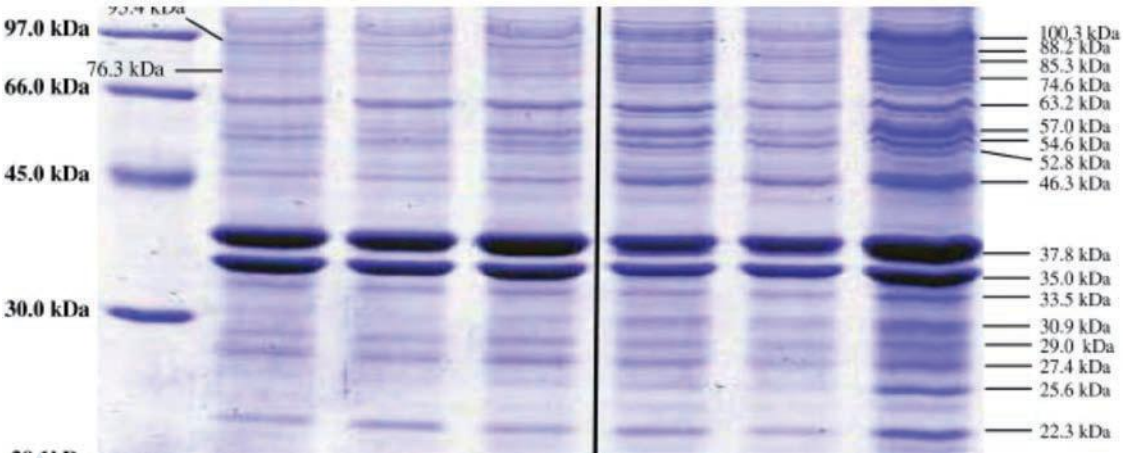


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FIGURE 19.2.2 Gel showing the outer membrane protein profiles of the *Shigella flexneri* bacterium. Channel 1 shows comparison proteins, used for reference. Channels 2–7 show protein profiles from samples at gradually increasing temperatures.

SECTION REVIEW 19.2

REMEMBERING

1 Define:
- electrophoresis
- migration
- electric field
- isoelectric point.

UNDERSTANDING

2 Explain why the electric field is necessary in electrophoresis.

3 Explain why, in electrophoresis, different protein molecules move at different speeds across the gel.

4 Explain why, in electrophoresis, it is necessary to have buffer solutions at different levels, providing a pH gradient across the gel.

REFLECTING

5 Compare and contrast the techniques of electrophoresis and chromatography. What are the similarities and differences between the two?

19.3 Mass spectrometry

Mass spectrometry can tell chemists a lot about the structure of a substance, such as the molar mass (M) and elements present, and it can detect the isotopes of an element. Using a mass spectrometer to determine the isotopic composition of an element, and therefore the relative atomic mass, is covered in more detail in Chapter 5 of *QScience Chemistry Units 1 & 2*. Mass spectrometry has many uses, from radioactively dating fossils to detecting drugs in sport supplements. Mass spectrometers are found in many locations, including on satellites, where they can identify particles intercepted in the solar wind. Mass spectrometry only requires a small amount of material but offers a wealth of information.

Principles of mass spectrometry

The mass spectrometer consists of an ionisation chamber, a path along which the particles travel and a detector (see Figure 19.3.1).

The vaporised sample is injected into the ionisation chamber where it is bombarded with high-energy electrons that can knock an electron off the molecule or atom. The resultant particle is positively charged and is called a molecular ion. Usually only one electron is knocked off, so the charge is typically 1+. If more than one electron is knocked off, then the charge corresponds to the number of electrons removed. In the original molecule, every electron was paired, so when an electron is knocked off, the resulting molecular ion has an unpaired electron. This molecule is called a radical, and is shown in Figure 19.3.2.

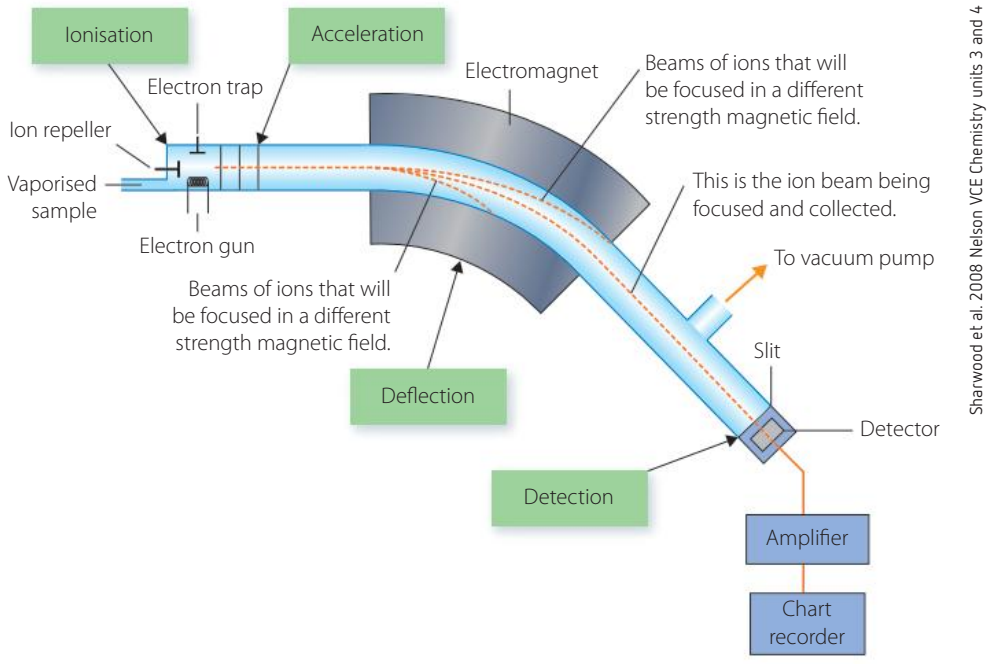
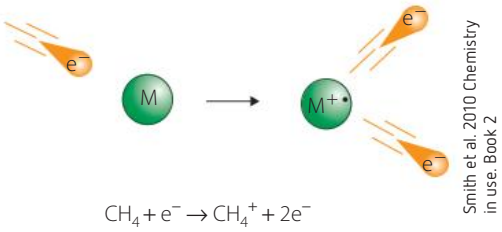


FIGURE 19.3.1 The mass spectrometer, a schematic diagram

These positive particles are accelerated along the path by an electrical field. They then pass through a magnetic field, which deflects the ions based upon mass (m) and charge (m/z). Smaller, higher charged particles are easier to deflect. By varying the strength of the magnetic field, the ions can be separated by their mass and collected by a detector. The intensity of the ion beam hitting the detector provides a measure of abundance. Only the positive ions formed will be detected, as a result of their charge. Uncharged radicals will not be detected. The results are presented as a mass spectrum: a plot of m/z versus abundance.

FIGURE 19.3.2
Formation of a positive ion by electron bombardment, M represents an atom or a molecule.



Smith et al. 2010 Chemistry in use. Book 2

SCIENCE AS A HUMAN ENDEAVOUR

DEG

In some Chinese brands of toothpaste, a chemical called DEG was used as a sweetener. However, it has now been established that DEG is toxic and its use in toothpaste has been banned. In order to enforce the ban, mass spectrometry can be used by regulators to quickly and effectively identify the presence of DEG in the toothpaste.

molecular ion
the ion formed when the molecule is ionised without being fragmented in a mass spectrometer

radical
a species formed with an unpaired, high-energy electron in an excited state.

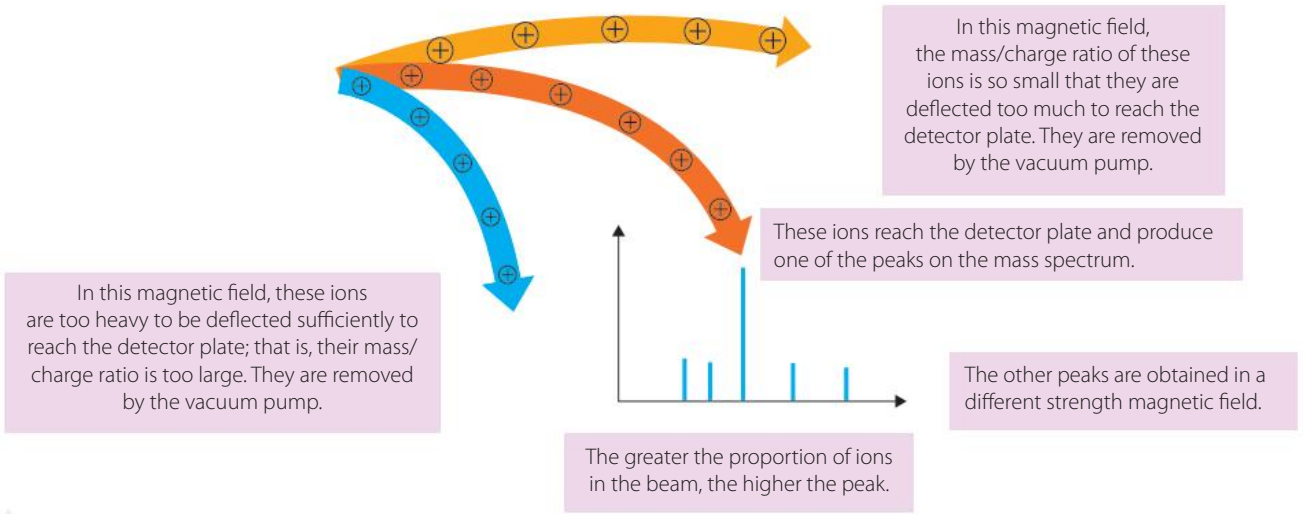
The firing of high-energy electrons onto an organic molecule can cause the molecule to fragment. The initial molecular cation can break to form a smaller cation and a free radical. A free radical still has an unpaired valence electron and is very reactive. The free radical is neutral and uncharged so it is not detected by mass spectrometry. Free radicals are denoted with a single dot, which represents the unpaired, excited electron; for example, H·.

The free radical of methane can fragment in a mass spectrometer as shown:

$$CH_4^{+\cdot} \rightarrow CH_3^+ + H\cdot$$

$$\text{or } CH_4^{+\cdot} \rightarrow CH_3\cdot + H^+$$

In these cases, the mass spectrometer would only detect the CH_3^+ and the H^+, as they are both positively charged.



Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

FIGURE 19.3.3 Focusing and collecting an ion stream

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PRACTICAL ACTIVITY 19.3.1

Using mass spectroscopy

AIM

To show how effective mass spectroscopy can be in developing a new pharmaceutical, fuel, polymer or nanomaterial

WHAT TO DO

1. In groups of two or three, discuss the different uses of mass spectroscopy in industry, and decide on which area to investigate: the production of a particular pharmaceutical, fuel, polymer or nanomaterial. This should take about 10 minutes.
2. Research the role of mass spectroscopy in the area of your choice. Find as much information as you need to show the effectiveness of mass spectroscopy.
3. You may find it helpful to browse online spectral libraries via the weblink.

19.3.1 Spectral libraries

WHAT DID YOU DISCOVER?

1. Write a brief account of what you did.
2. Prepare a short presentation aimed at 14–16-year-old students to be delivered to your class. As far as possible, every group member should take part.
3. Be prepared to answer questions and to discuss what you discovered.

Interpreting mass spectra

The plot produced by a mass spectrograph is called a mass spectrum and has a series of lines at different *m/z* (mass/charge) values along the *x*-axis. A cation will be detected at the point that corresponds to the mass of the particle, which is the atomic mass unit. The height of the peak corresponds to the abundance of the species. The most abundant peak on the spectrum is called the base peak and it is given a relative abundance of 100 per cent. The other peaks are plotted as a relative percentage to the base peak. Mass spectra have a percentage scale on the *y*-axis.

The most important peak on the mass spectrum is the molecular ion ($M^{+\cdot}$) or parent molecular ion. This molecular ion gives the molar mass of the original compound.

Fragmentation pattern

Organic molecule fragmentations provide clues to the structure of the molecule. When ethanoic acid ($C_2H_4O_2$) is injected into the mass spectrometer, a range of peaks is observed (see Figure 19.3.4). Notice that the parent ion at the *m/z* 60 peak is not the most abundant peak. The most abundant peak is the base peak at *m/z* 43. The other common peaks present are at *m/z* 45 and 15.

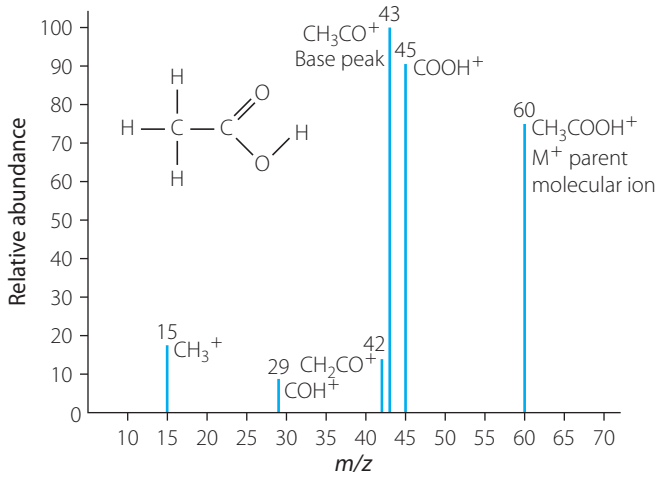
The parent ion CH_3COOH^+ has many different possibilities for fragmentation. If the bond between the two carbons breaks, then there are two possible peaks: a peak corresponding to the cation CH_3^+ at an *m/z* value of 15 and a peak corresponding to $COOH^+$ at an *m/z* value of 45. Notice that the peak at 45 is much bigger than the peak at 15. This indicates that the fragmentation:

$$CH_3COOH^+ \rightarrow CH_3^{\cdot} + COOH^+$$

is more common than:

$$CH_3COOH^+ \rightarrow CH_3^+ + COOH^{\cdot}$$

FIGURE 19.3.4
Simplified mass spectrum of ethanoic acid, CH_3COOH. Parent ion and base peak are identified



Remember that radicals are not detected by mass spectroscopy. If the covalent bond between the C and O is broken, then there are two possible fragments: CH_3CH_2 ($m/z = 29$) and OH ($m/z = 17$).

In mass spectroscopy, you can look at the peaks on the mass spectra. A peak of 15 indicates a CH_3^+ and would indicate that the methyl group is present.

Alternatively, you can look at the differences in peak values. The molecular ion has a value of 60 and there is a peak at $m/z = 45$. This difference, 15, could indicate loss of a methyl group. The peak at $m/z = 43$ is 17 less than the parent peak. This could indicate loss of an OH group. A loss of an H atom could explain a peak at $m/z = 59$.

Therefore, mass spectrometry is one technique that can be used, usually in conjunction with other techniques, to provide information about the structure of an organic molecule.

Table 19.3.1 shows common fragmentations that occur in organic molecules.

FIGURE 19.3.5
Simplified fragmentation pattern of molecular ion CH_3COOH^+

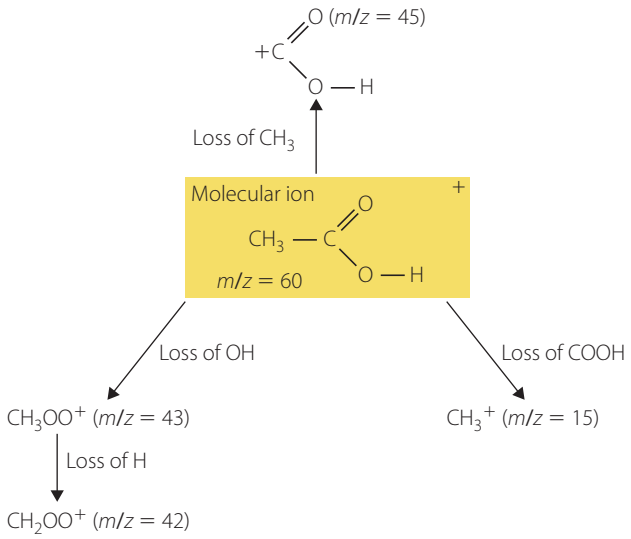


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TABLE 19.3.1 Commonly formed fragments of organic molecules

RELATIVE MASS	FRAGMENT
15	CH_3^+
17	OH^+
29	CH_2CH_3, CHO^+
31	OCH_3^+
45	COOH, $OCH_2CH_3^+$

SECTION REVIEW 19.3

REMEMBERING

1 Define:
- **a** radical
- **b** ionisation
- **c** molecular ion
- **d** mass/charge ratio
- **e** base peak.

2 Draw a simple schematic diagram of a mass spectrometer. Include labels to show what happens in each part of the instrument.

3 Which peak in a mass spectrum indicates the molecular mass of the compound?

4 When do you get a peak larger than the parent molecular ion?

UNDERSTANDING

5 Why are only cations detected in mass spectroscopy?

6 Explain how a mass spectrum can be used to help determine the structure of a compound.

APPLYING

7 Figure 19.3.6 shows the mass spectrum of ethanol.

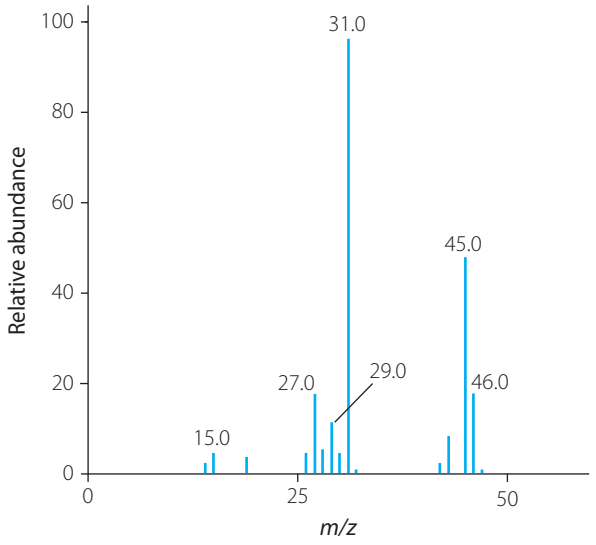
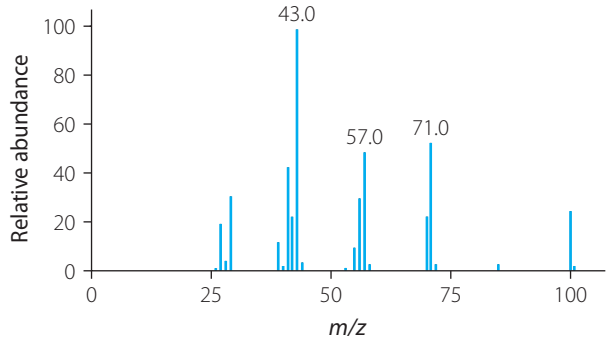


FIGURE 19.3.6 Mass spectrum of ethanol

- **a** Account for the peaks at 15, 29, 45 and 46.
- **b** What can be concluded about the peak at 31? Justify your answer.

8 Figure 19.3.7 shows the mass spectrum for C_7H_{16}. Account for the main peaks in the spectrum.

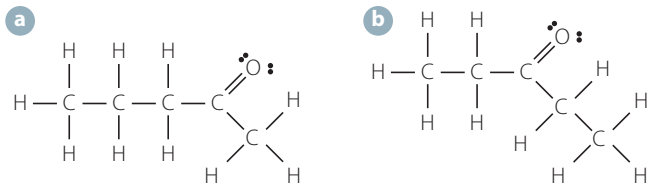
FIGURE 19.3.7 Mass spectrum for C_7H_{16}



ANALYSING

9 The chemical composition of compound X was found to be $C_5H_{10}O$. The two possible structural isomers are shown in Figure 19.3.8.

FIGURE 19.3.8 Possible structures for compound X



a What mass/charge ratio (*m/z*) would you expect for the parent ion for each isomer?

b The base peak for Structure A occurs at a mass/charge ratio of 43, whereas the mass spectrum for Structure B occurs at a mass/charge ratio of 57. Account for these two peaks.

c The mass spectrum of compound X was found to not have a peak at 29. How does this enable the structure of compound X to be determined?

10 How has medicine been advanced by the technique of mass spectrometry?

19.4 X-ray crystallography

The helical shape of one of the most famous molecules was determined by using X-ray crystallography. Rosalind Franklin's work was used to determine the structure of DNA, RNA, viruses, coal and graphite. Her image from the X-ray crystallography of the DNA crystal was key in determining the structure of DNA. Understanding the structure then helped to explain how genetic information is passed from parents to offspring.

In 1962, two Nobel Prizes were awarded to people who used X-ray crystallography to determine structure of biomolecules. The Nobel Prize for medicine went to Francis Crick, James Watson and Maurice Wilkins 'for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material'. (Dr Rosalind Franklin did not receive a Nobel Prize because she died of cancer before 1962 and the award is not given posthumously.) The Nobel Prize for chemistry went to Max Perutz and John Kendrew 'for their studies of the structures of globular proteins', namely haemoglobin and myoglobin.

Today, X-ray crystallography is still considered the most accurate method for determining structures. It is used in rational drug design and to work out the structures of proteins, enzymes and viruses. By knowing where the atoms are placed, scientists can determine how these molecules interact, thus speeding up the development of new drugs and vaccines, and saving millions of dollars.

Atoms are extremely small, with diameters of about 0.2–0.5 nm. Haemoglobin has a relative molecular mass of 67 000 and dimensions of $6.4 \times 5.5 \times 5$ nm. Ribosomes are much larger and more complex. The challenge is to distinguish individual atoms in order to resolve how molecules are put together.

Principles of X-ray diffractometry

There are four major steps in an X-ray study.

1. Obtain a crystal of the matter being studied.
2. Expose it to X-rays.
3. Record the diffraction pattern. Diffraction is the pattern observed when X-rays act as a wave and are scattered by layers of atoms within the crystals.
4. Analyse the data. Computers are used to analyse the data and propose a structure. The computers iterate (complete the measurement and recording numerous times) to produce the best structure.

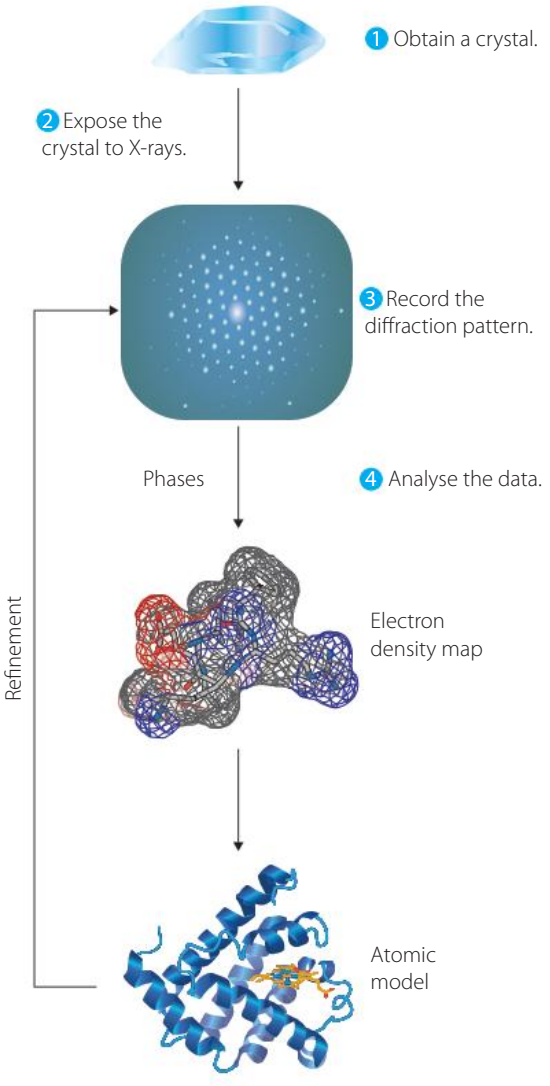


FIGURE 19.4.1 An X-ray diffraction flow chart

Producing crystals

For X-ray diffraction to work, a crystal has to be produced. A crystal is a regular array in which the molecules or atoms line up in a repeating pattern. Franklin used the sodium salt of DNA to produce a crystal for her work on DNA structure. Producing a crystal is a very difficult task. The crystal must be near perfect and small (0.1–0.5 mm).

Producing a crystal is a time-consuming task; 'small' molecules, such as cholesterol and fatty acids, are easier to produce than larger ones, such as DNA, proteins and viruses. When crystallising a biomolecule, the pH, ionic strength, nature of the precipitant, temperature and presence of cofactors or counter ions must be taken into account to grow a good-quality crystal. The crystal may even need to be stabilised by freezing in liquid nitrogen.

Typically, crystals are formed by cooling supersaturated solutions of the substance. Care must be taken to ensure that the individual crystals are big enough to be used. The Australian Synchrotron in Clayton, Victoria, is sensitive enough to use very fine crystals.

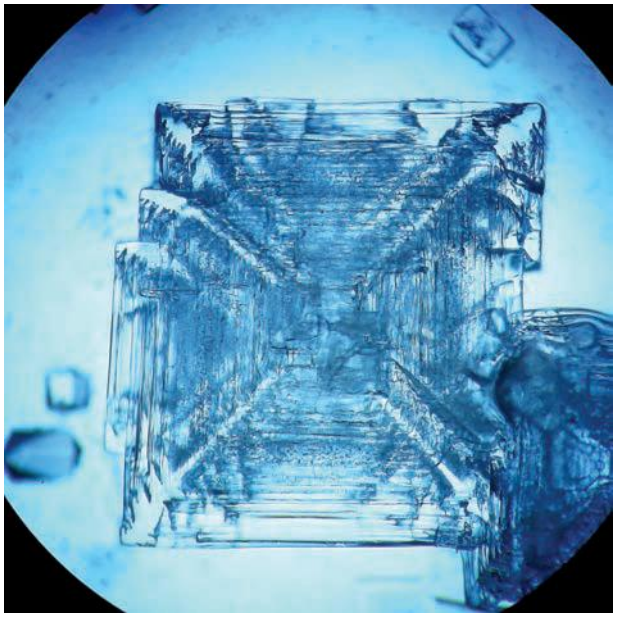


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FIGURE 19.4.2 The 1915 Nobel Prize in Physics was awarded to Sir Henry Bragg and Lawrence Bragg for the development of the X-ray spectrometer, which showed that salts, such as this potassium chloride crystal, have a regular array.

19.4.1 X-ray crystallography

19.4.2 Unsung technique

Diffraction

diffraction waves are spread when passing through a crystal

constructive interference two waves mutually reinforcing each other, producing a combined wave with amplitude equal to the sum of the constituent waves

destructive interference two waves opposing each other and negating the effect of each other

When a crystal of potassium chloride (KCl, Figure 19.4.2) is placed in the path of a beam of visible light, the light passes right through it virtually unchanged. The wavelengths in white light are much longer than the interparticle distances in KCl. But if the same crystal is exposed to X-rays, two things occur.

The energy of the X-ray is similar to the energy of the electrons in their orbitals. So a small fraction of the radiation is absorbed and re-emitted by the electron clouds of the atoms present. This effect leads to fluorescence.

The interference of scattered X-rays also leads to diffraction. **Diffraction** is the apparent scattering of waves when they encounter objects in their path. This is seen when sunlight hits a thin layer of oil on water or in soap bubbles (Figure 19.4.3). The incident light will be reflected from the top and the bottom of the oil layer. The beams from the bottom must have travelled a further distance. If the two waves come together, then the crests of the waves may reinforce each other. This is called **constructive interference**. If one crest is out of phase with the other, then they will cancel each other out. This is called **destructive interference**.

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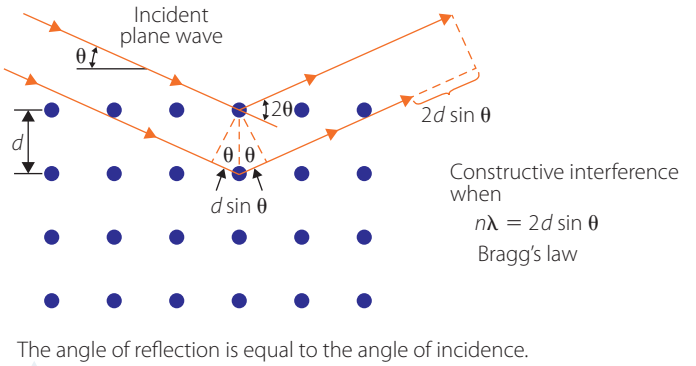
FIGURE 19.4.3 Diffraction in a soap bubble



The angle of reflection is equal to the angle of incidence.

FIGURE 19.4.4 Reflection in a crystal

For each crystal, there will only be certain **angles of incidence** that allow constructive interference. At these angles, a relatively strong reflection is observed (Figure 19.4.4). At the other angles, no scattered beam will be seen.

angles of incidence the angle a beam of radiation makes with a line perpendicular to the surface

Diffraction occurs when the object has a similar dimension to the wavelength being used. X-rays are used because their wavelength is very similar to the distance between atoms (Figure 19.4.5). The electrons are primarily responsible for the scattering of X-rays. The electron density (number of electrons in a given volume) determines how strongly an atom scatters X-rays.

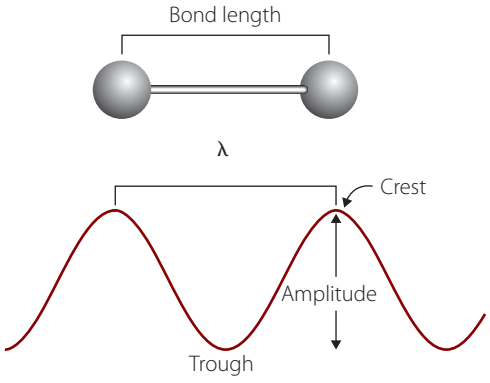


FIGURE 19.4.5 The wavelength of the X-rays is approximately equal to the bond length between atoms.

Interpreting diffraction patterns

Early experimenters such as Lawrence Bragg had to calculate the dimensions between the ions without computers, manually turning the crystals and calculating the intensity between each layer to build up a three-dimensional view. With a lot of time and calculation, they could show that diamonds have tetrahedral carbons and salt crystals consist of atomic lattices and not, as had been imagined, molecular ones.

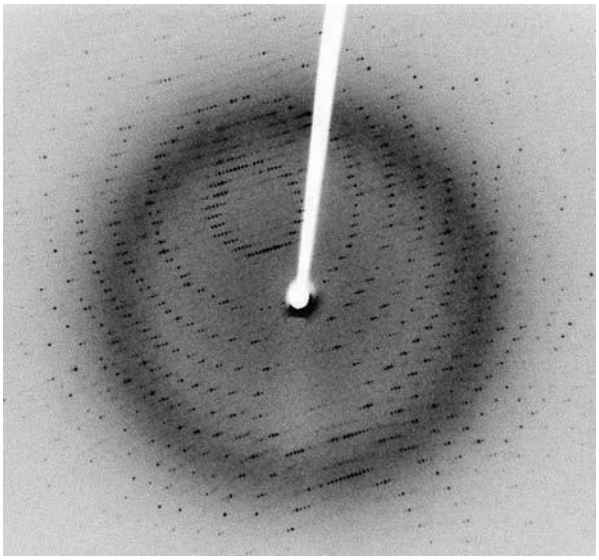
19.4.3 The Bragg equation

LAWRENCE BRAGG

The youngest ever Science Nobel laureate is Lawrence Bragg, born in South Australia. In 1915, at the age of 25, he and his father Sir William Bragg received the Nobel Prize in Physics for their work in X-ray crystallography. William Bragg and others thought X-rays were particles. Diffraction patterns were observed but no one could work out how they were formed. Lawrence explained the diffraction patterns in the three-dimensional layers of the crystal, formulating his Bragg equation and confirming that X-rays are waves.

SCIENCE AS A HUMAN ENDEAVOUR

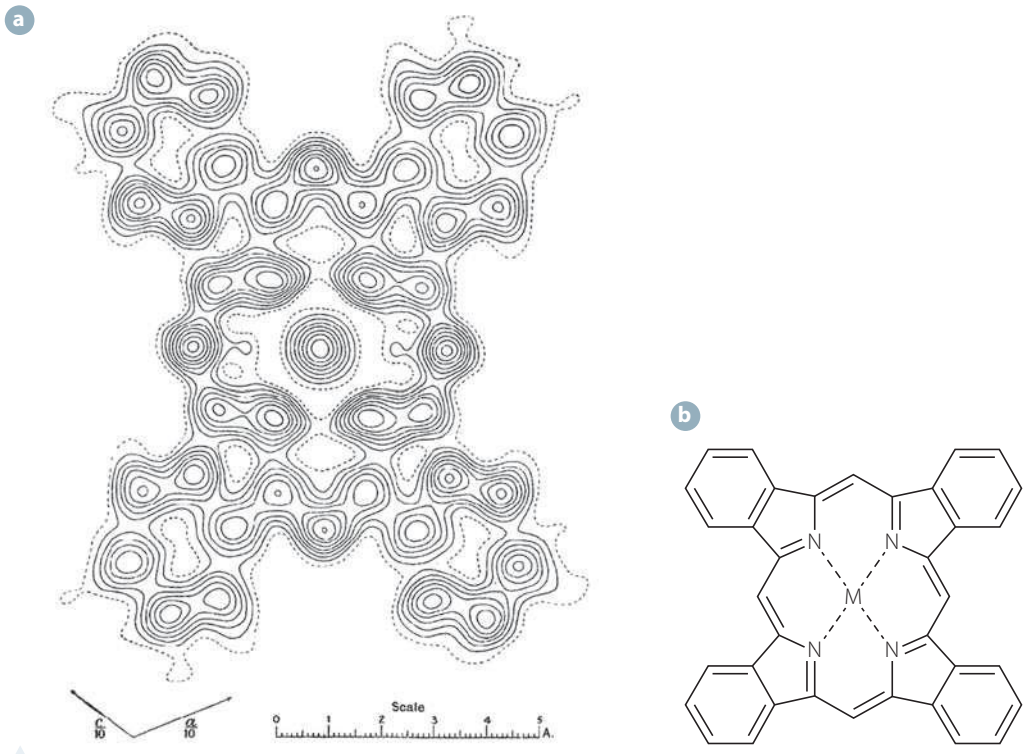
FIGURE 19.4.6 An X-ray diffraction pattern



Jeff Dahl / Wikimedia Commons / CC-BY-SA-3.0

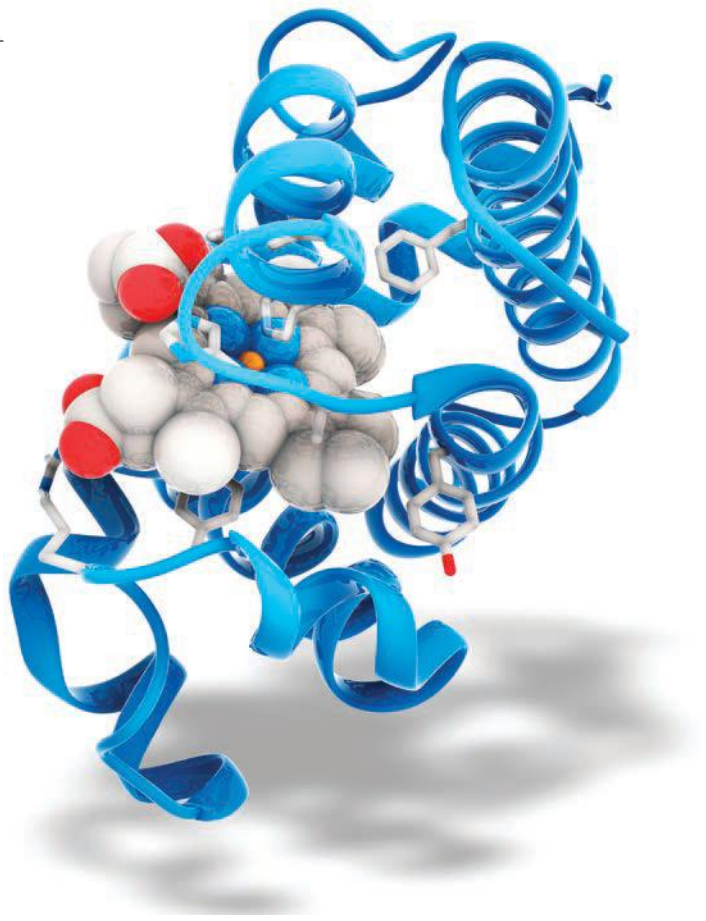
Today, the crystal in the X-ray machine is automatically rotated to produce diffraction patterns. Detectors measure hundreds of reflections at once, reducing the time needed from weeks to days. With intense light sources such as the synchrotron, the time needed to collect data is reduced further, to seconds.

From the diffraction pattern, an electron density map can be made. This allows the distance between the atoms to be calculated so that bond length and bond angles can be determined.



a Reproduced from J. M. Robertson and I. Woodward, An X-ray study of the phthalocyanines. Part III. Quantitative structure determination of nickel phthalocyanine, J. Chem. Soc., 1937, 219. With permission of The Royal Society of Chemistry.; **b** Deb Smith.

FIGURE 19.4.7 **a** The resultant electron density map and **b** determined structure (M = metal atom). Atoms with higher atomic numbers have more electrons and so scatter X-rays more effectively. Electron density maps provide the location of atoms relative to each other, allowing the bond angles and lengths to be determined. Note that hydrogen atoms are not often located due to their small size.



Ramon andrade 3dciencia / science photo

FIGURE 19.4.8 The three-dimensional structure of the biomolecule myoglobin, as determined by X-ray crystallography

SECTION REVIEW 19.4

REMEMBERING

1 What part of the electromagnetic spectrum is used to determine the bond lengths between atoms in proteins?

2 What factors affect the quality of crystals?

UNDERSTANDING

3 Describe a process that could be used to make a crystal of NaCl.

4 What is one advantage and one disadvantage of X-ray crystallography compared to other techniques?

5 Why would a crystal of a ribosome be more difficult to prepare than an ionic salt?

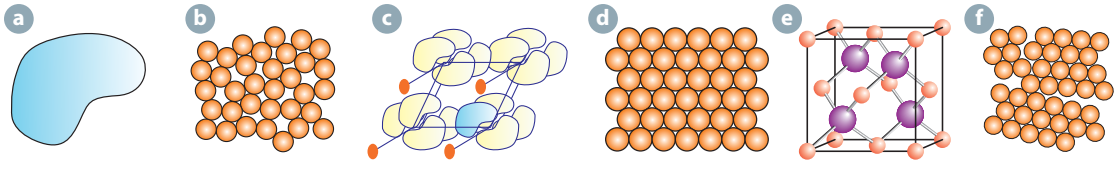
APPLYING

6 Would the crystals prepared for X-ray crystallography have the same shape if produced under different conditions?

7 What areas of research is X-ray crystallography used for?

ANALYSING

8 Crystals must have a regular array. Which of the following shapes would not make a good crystal? (More than one answer may be correct.)



19.5 Infrared spectroscopy

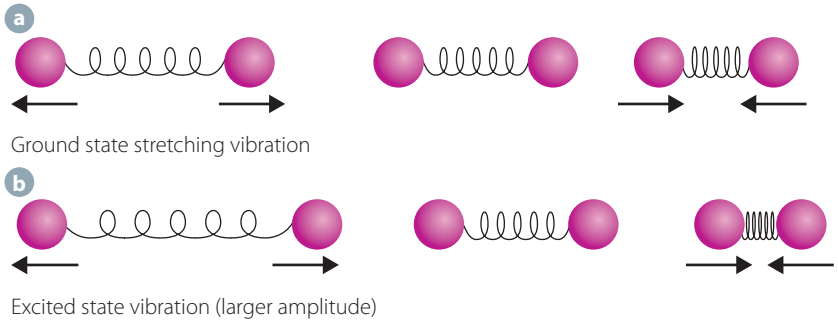
Infrared (IR) spectroscopy is a useful technique for determining the bonds or functional groups that are present or absent in a compound. It is a relatively cheap and easy technique, and is used in industrial applications for monitoring the chemical pathways, in forensic examinations and in drug development.

Principles of IR spectroscopy

Molecules are constantly moving. The two basic modes of vibration are stretching and bending. A simple diatomic molecule is like two heavy spheres connected by a spring; the spheres can vibrate backwards and forwards around their equilibrium position, as shown in Figure 19.5.1. In polyatomic molecules, such as water, the general vibration modes are shown in Figure 19.5.2.

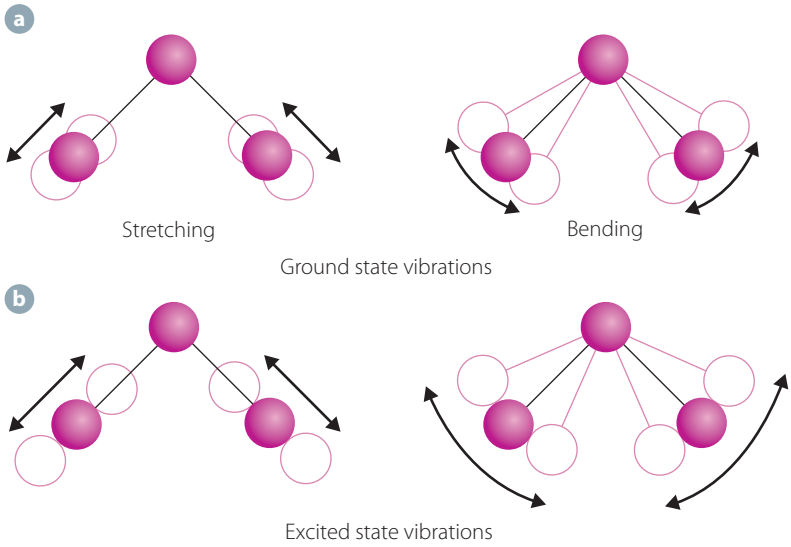
The vibrations may be symmetrical or asymmetrical. A molecule can absorb infrared energy and change to a higher energy vibration mode. The molecules will now vibrate with more energy and amplitude. The spring will be stretched to greater lengths and compressed more, as shown in Figure 19.5.1b and 19.5.2b. When bending vibrations are excited, the change in angle is greater, as shown in Figure 19.5.2b. This is not true for diatomic molecules such as O_2 and N_2; these molecules cannot be detected by IR spectroscopy.

FIGURE 19.5.1
Vibrations for **a** ground state and **b** excited state of a diatomic molecule



Smith et al. 2010 Chemistry in use. Book 2

FIGURE 19.5.2
a Ground and **b** excited states of two of the vibrations that occur in triatomic molecules



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The energy absorbed depends upon the bond length, the bond strength and the atom's size. Heavier atoms require more energy to increase vibration. Double bonds require more energy than single bonds to increase vibration. Measurement of the absorbance will determine which bonds are present. Typical absorption values are shown in Table 19.5.1.

A sample is placed in a cell that is in a beam of infrared radiation. A number of different frequencies are absorbed by the compound. The percentage transmitted is recorded against the energy of the frequency. The *x*-axis is the wavenumber (cm^{-1}), which is the inverse of wavelength (cm). The *x*-axis of the infrared spectrum always shows a dramatic change.

Unlike the earlier spectra, infrared spectra consist of a series of troughs from a base line; the spectra looks 'upside down'. The *y*-axis is the percentage of light transmitted. The base line shows 100 per cent of the light still being transmitted.

INQUIRING FURTHER

Find out how IR spectroscopy is being used by people with diabetes as a non-invasive way to measure blood sugar levels.

19.5.1 Infrared spectra

TABLE 19.5.1 Characteristic infrared absorption frequencies of some common functional groups

CLASS OF COMPOUND AND BOND	BAND POSITIONS (cm^{-1})
Alkanes, alkyl groups	
C—H	2850–2960
Alkenes	
—C—H	3020–3100
—C=C	1650–1670
Alkyl halides	
C— Cl	600–800
C—Br	500–600
C—I	500
Alcohols	
—O—H	3400–3650 (strong, broad)
—C—O	1050–1150
Amines	
N—H	3310–3500
C—N	1030–1230
Carbonyl compounds (e.g. carboxylic acids, esters)	
C=O	1670–1780
Carboxylic acids	
—O—H	2500–3100 (strong, broad)

Interpreting infrared spectra

To interpret infrared spectra, you look for key troughs or absorption bands. Infrared spectra include a large number of bands that are ignored when interpreting the data, because they are caused by the many different vibrational modes of the molecules that do not provide useful information. The key area to examine is in the higher wavenumber region. Notice in the spectra in Figure 19.5.3 that the *x*-axis has a change of scale. The troughs to the right of around 1400 cm^{-1} are called the fingerprint region.

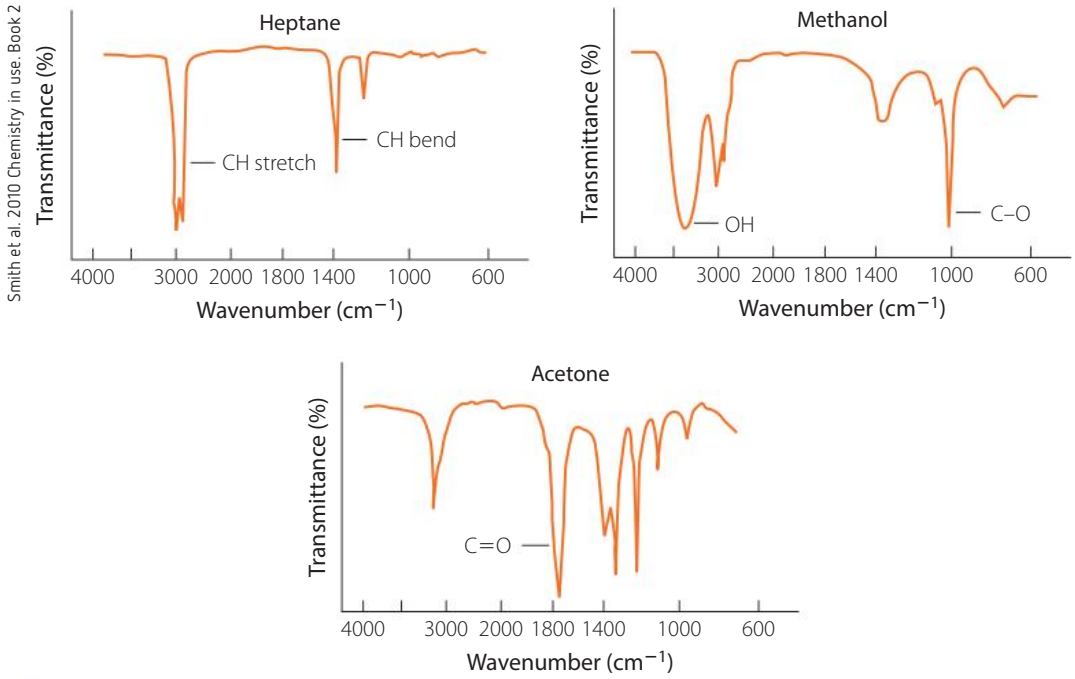


FIGURE 19.5.3 Infrared spectra of heptane, methanol and propanone (CH_3COCH_3). The broad trough at around 3200 cm^{-1} is characteristic of an alcohol —OH stretch. The vibrations that cause the major absorption bands are identified.

19.5.2 Spectroscopy in a suitcase

Almost every organic molecule has a —C—H bond (where a hydrogen is attached to a carbon), which absorbs somewhere in the range from 2800–3000 cm^{-1}. This trough does not provide much information. Neither does the band due to a —C—C bond.

The —O—H bond, as found in alcohols, typically absorbs at 3000–3500 cm^{-1}. This is usually broad and characteristic of all —O—H bonds. The —C═O bond at 1700 cm^{-1} is also very useful. The presence of a broad trough at 3000 cm^{-1} could indicate that the compound is an alcohol. But when it is also present with a band at 1700 cm^{-1}, the compound could be a carboxylic acid.

fingerprint region region of absorption of 1400 cm^{-1} or less, where it is difficult to assign absorption peaks to specific bonds; the only way of using the information from this region is to compare the overall absorption spectrum to a library standard, to identify the molecule

Spectra fingerprint region

The region less than around 1400 cm^{-1} is called the **fingerprint region** and is unique to a compound. It can be used to confirm the identity of the unknown compound by comparing it to a known sample. The fingerprint region can also indicate whether the sample is pure, if it matches that of a pure standard. The trough may be of different intensities due to the concentration differences between the two samples.

PRACTICAL ACTIVITY 19.5.1

Matching structures

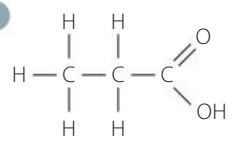
AIM

To identify structures from infrared and mass spectra data provided

PROCEDURE

1 Examine the six molecules a–f and the six spectra 1–6 (4–6 are over the page).

a



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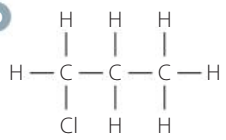

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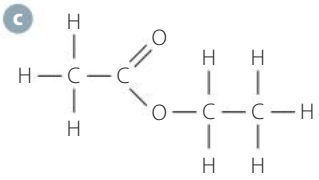

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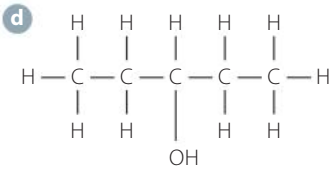

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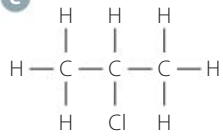

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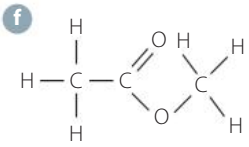
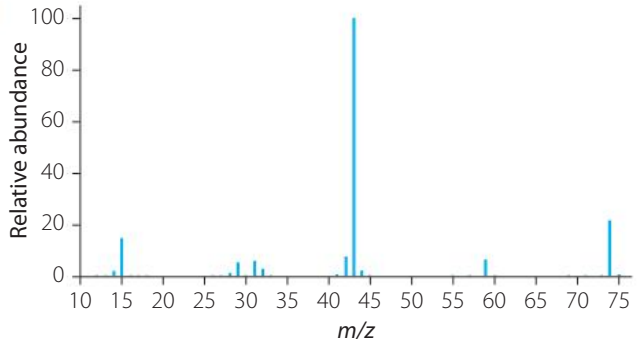


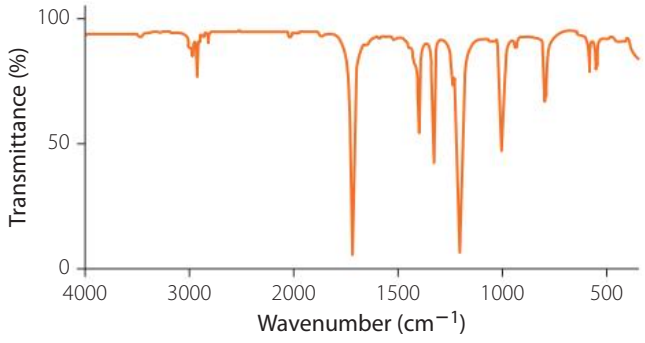
2 Match the spectra to the organic molecules. (Hint: Calculate the molar mass.)

3 Look for possible common fragments.

4 Look for key functional groups in the infrared spectra.

1





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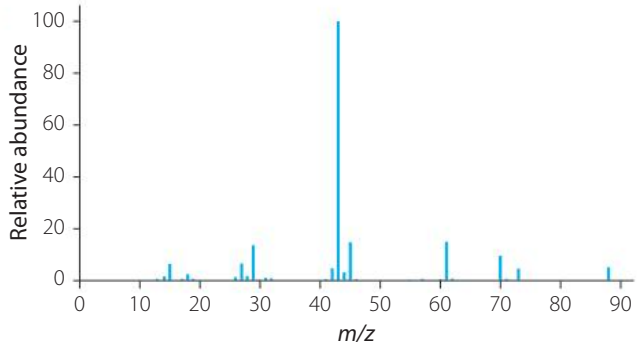

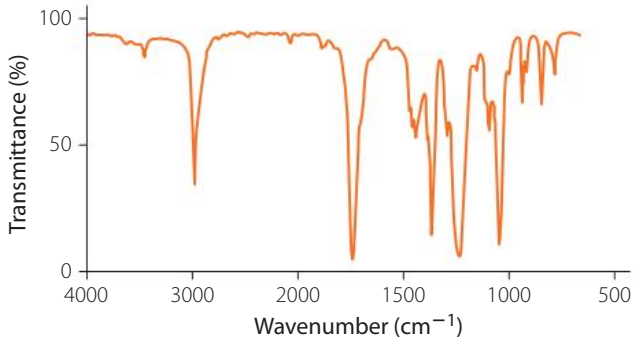

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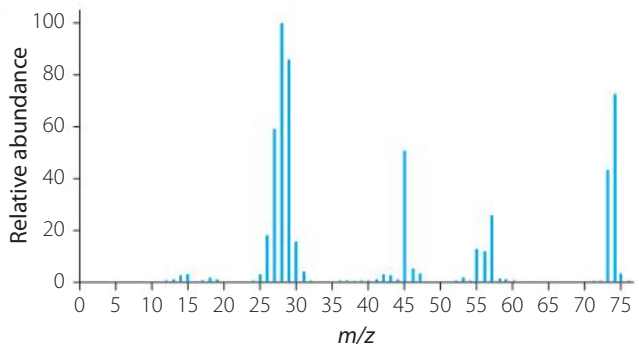

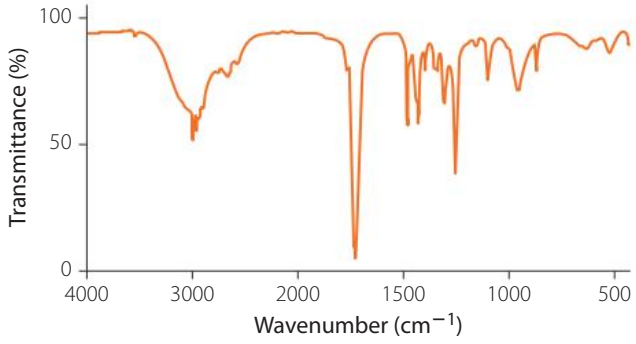

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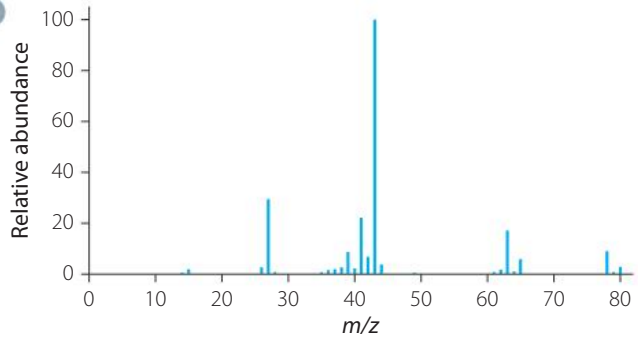

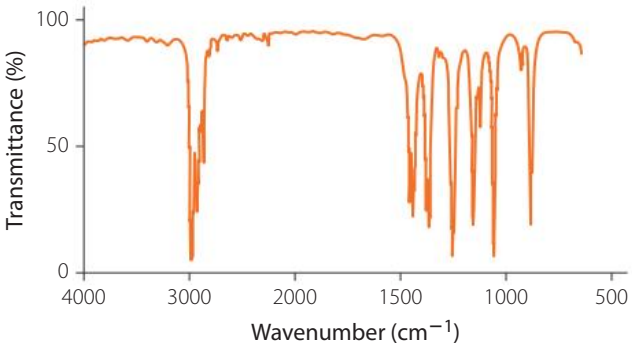

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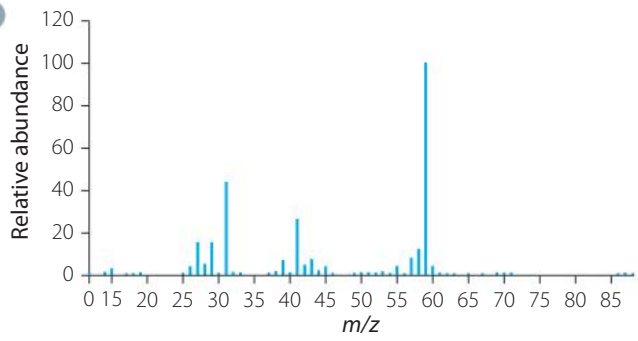

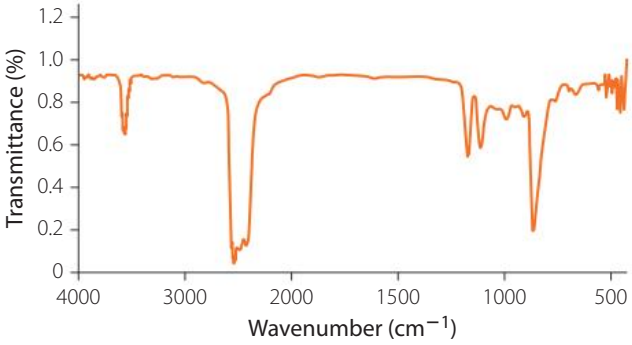

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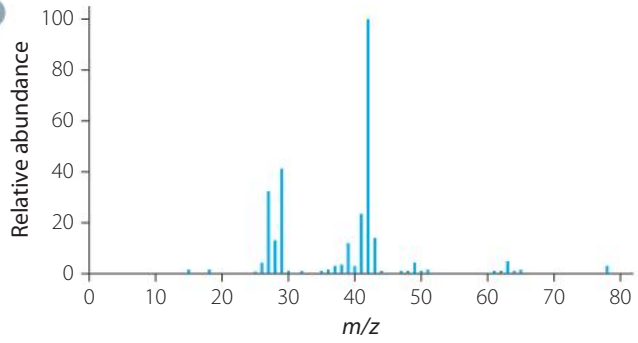
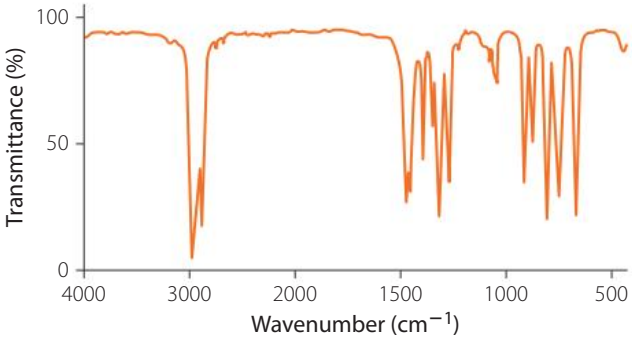




WHAT DID YOU DISCOVER?

1. Which spectra belong to each compound?
2. Give the correct IUPAC name for each compound.

SECTION REVIEW 19.5

REMEMBERING

1. Why is infrared light absorbed by some molecules?
2. Why is IR spectroscopy sometimes referred to as vibrational spectroscopy?
3. Explain what is meant by the 'fingerprint region' and why it is so named.

UNDERSTANDING

4. Group the following compounds into those that would show or not show a broad peak at 3300 cm^{-1}: 1-propanol, 2-propanol, ethane, ethanol, ethanoic acid, methanoic (formic) acid, ethyl ethanoate, butanoic acid, 1-chloroethane, 1-methylamine.

APPLYING

5 Two compounds, X and Y, react with sulfuric acid to produce a compound that smells like nail polish remover (methyl ethanoate). A student tried to make this compound.

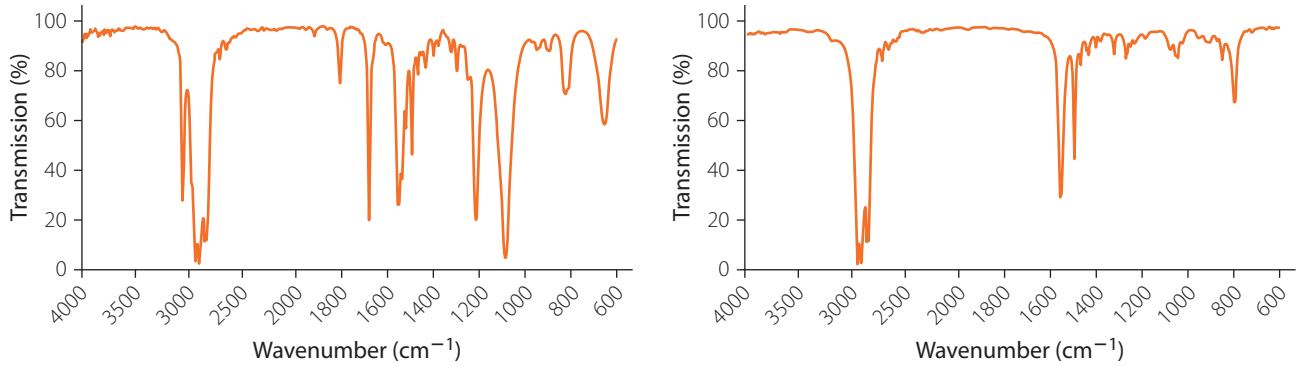
- **a** What would she see in the infrared spectrum to distinguish between X and Y?
- **b** What would she see in the infrared spectrum for methyl ethanoate?
- **c** How would she be able to say that the sample is pure?

6 How could IR spectroscopy be used to distinguish between the following pairs of compounds?

- **a** Ethane and propane
- **b** Ethanol and propanol
- **c** 2-chloropropane and iodomethane
- **d** 1-propanol and propanoic acid

ANALYSING

7 Compare the two spectra below. Decide which spectra is of 1-hexene and which is of hexane, and justify your decision. Account for the main absorption bands.



19.6 Combining analytical techniques

Although a lot of information can be obtained by a single technique, much more information can be gained by combining techniques. Each technique provides one piece of the puzzle that is used to determine the whole structure. In 2002, the Nobel Prize in Chemistry was awarded for the development of a mass spectrometric analysis (John B. Fenn and Koichi Tanaka) and for the development of nuclear magnetic resonance (NMR) for biological macromolecules (Kurt Wüthrich). Their work determined the three-dimensional picture of what proteins look like in solution and enabled their function in the cell to be understood.

When you only have a small amount of sample, it is important to maximise the amount of information you can obtain from the techniques. The improved sensitivity of instruments over time has meant that more information can now be obtained. Precious artworks can be tested for authenticity by gas chromatography, mass spectrometry and IR spectroscopy; the pigments, glues and even the wooden frames can be analysed to determine if they originate from the same era.

Manufacturers have now combined gas chromatographs and mass spectrometers into one instrument: the GC-MS. The GC separates the components and then they pass into the MS. In the MS they are fragmented so that each component can have its structure unravelled.

TABLE 19.6.1 Characteristic infrared absorption frequencies of some common functional groups

TECHNIQUE	MAIN FEATURE	WHAT IT DOES	ADVANTAGES	DISADVANTAGES
X-ray diffractions	X-rays are scattered by crystals and result in a diffraction pattern.	Determines distances between the nuclei and the angles	Accurate and sensitive measurement of the distance between nuclei	Very expensive to buy and operate Crystals needed
Mass spectrometry	High-energy electrons produce cations, which are separated due to mass/charge.	Determines molar mass, isotopic abundances	Very sensitive Small sample size	Very expensive to buy and operate
IR spectroscopy	Infrared radiation increases the energy of the vibrational modes of the organic molecule.	Determines functional groups present	Huge range of analytes and small sample size	Moderately expensive
High-pressure liquid chromatography/ gas chromatography	Organic compounds are separated based on different adsorption and desorption rates between the mobile and the stationary phases.	Separates components	Relatively cheap Good compromise between price and resolution	Specialist operators needed

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1. Which technique would be the easiest to use to distinguish carbohydrates, esters, carboxylic acids and amino acids?
2. Which technique would be best to distinguish a range of carboxylic acids?
3. Why do NMR spectroscopy and X-ray crystallography dominate the Nobel Prize awards?
4. Which technique is the best for determining the molar mass of a compound?
5. Why is the molar mass for an element as given on the periodic table not a whole number?
6. What bonding is involved in the formation of crystals for X-ray crystallography?
7. What characteristic peaks would you expect in a mass spectrum of a chloroalkane?

CATEGORY QUESTIONS

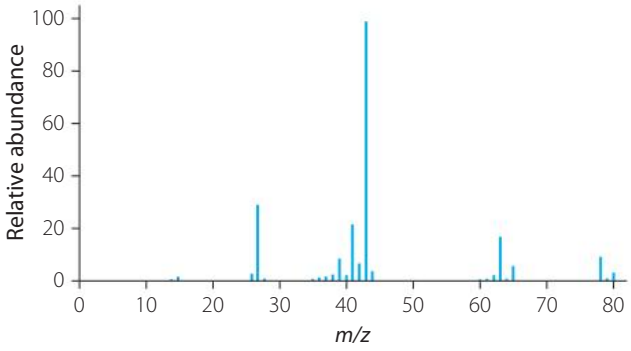
8. Infrared and mass spectra can be used to determine the structures of molecules. How do these techniques differ in this task? Is just one of these sufficient?
9. Aspirin is produced from the reaction of salicylic acid and ethanoic anhydride. Copy and complete the following table to show whether each technique is suitable for determining whether aspirin has been produced, evidence for the presence of aspirin and how you would use this technique to determine that the sample is pure.

TECHNIQUE	IS TECHNIQUE SUITABLE?	EVIDENCE THAT WOULD BE PRESENT	HOW THIS TECHNIQUE COULD DETERMINE IF SAMPLE WAS PURE
IR spectroscopy			
NMR spectroscopy			
X-ray crystallography			
Mass spectrometry			
UV–vis spectroscopy			
HPLC/GC			

ELABORATION QUESTIONS

10. A compound was formed from the reaction of an alkene and HCl. The compound was 46% carbon and 9% hydrogen.
    - **a** Determine the empirical formula for the compound.
    - **b** Examine the mass spectrum (Figure 19.7.1, on the next page) of the compound. What is the molecular formula for the compound?
    - **c** Why is the parent peak not the peak with the largest *m/z* value in this case?
    - **d** Draw the possible isomers for the compound.
    - **e** Account for peaks at 43, 63 and 65.
    - **f** Use the mass spectrum to decide which one is the most likely isomer.
11. In court, criminals may claim that they were producing a perfume and not an illicit drug. How would infrared analysis help forensic scientists discredit this claim? Would it be an advantage to take samples from the clandestine laboratory over time?

FIGURE 19.7.1 Mass spectrum of unknown compound



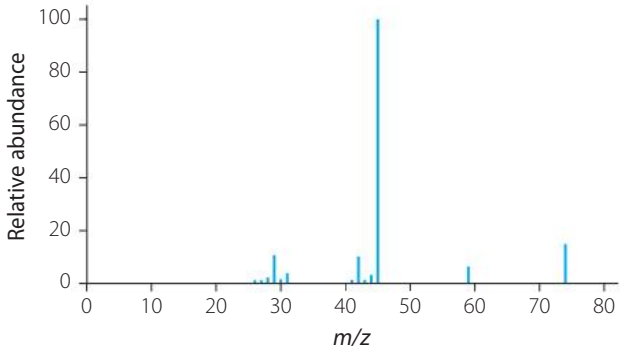
12 What differences would you expect in a mass spectrum of 1-propanol and 2-propanol?

13 X is an organic compound composed of carbon, hydrogen and oxygen. It contains 48.63% carbon and 8.18% hydrogen by mass.

a Calculate the empirical formula of X.

b The mass spectrum for X is shown in Figure 19.7.2.

FIGURE 19.7.2 Mass spectrum of compound X

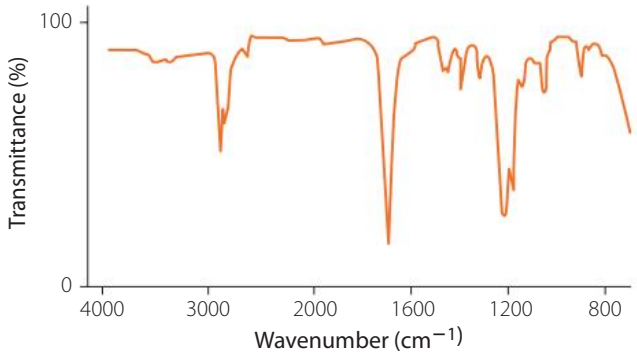


i Deduce, giving a reason, the molecular formula of X.

ii Identify the formulas of the fragment ions with *m/z* values of 45 and 29.

c The infrared spectrum of X is shown in Figure 19.7.3.

FIGURE 19.7.3 Infrared spectrum of compound X



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i Explain why X is not a carboxylic acid.

ii Identify, giving reasons, three bonds that are present in X.

d Deduce the most likely structural formula of X based on your answers to parts b and c. State the name of X and give one use of compounds belonging to this homologous series.

e State and explain the number of peaks compound X will show in its low-resolution H^{-1} NMR spectrum.

f State the names of two compounds that could react together to produce X. Identify the type of reaction and give an equation for the reaction.

g Give structural formulas for two possible isomers of X.

EVIDENCE QUESTIONS

14 Analyse the peaks for the mass spectrum in Figure 19.7.4. Is it 1,2-ethanediol?

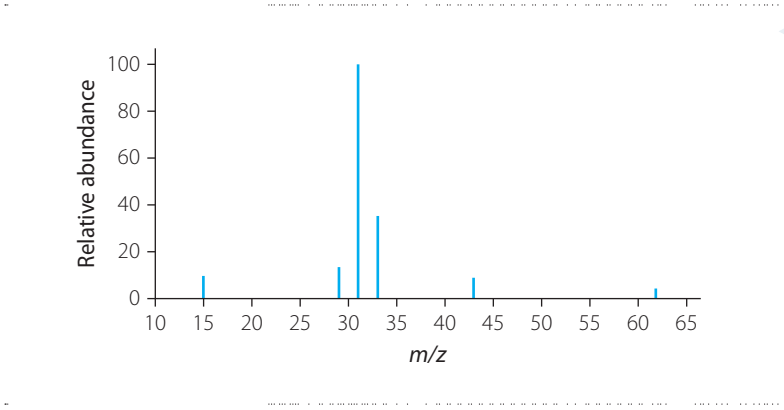
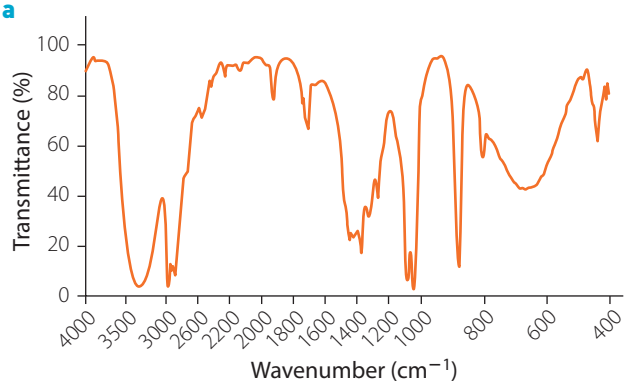


FIGURE 19.7.4 Mass spectrum

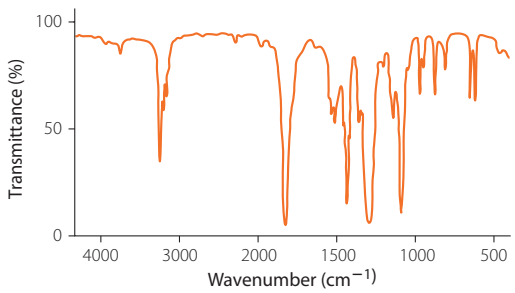
15 Salicyclic acid and acetic (ethanoic) anhydride react to form aspirin. This reaction does not go to completion. The salicyclic acid remaining will react with aqueous $FeCl_3$ to form a purple compound, $FeCl_3$. How can the purity of the product be quantified by IR spectroscopy?

16 Compare the following infrared and mass spectra. Assign ethanol, ethanoic acid or ethyl ethanoate to the correct spectra.

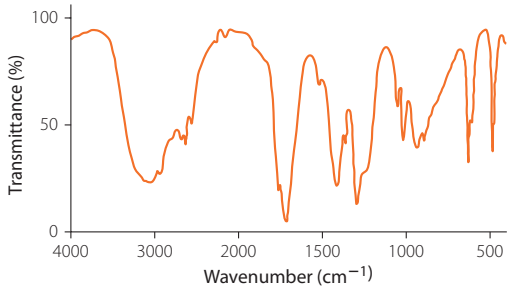
a



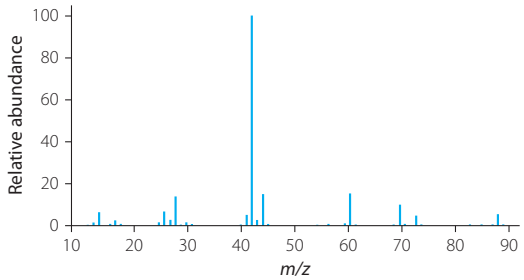
b



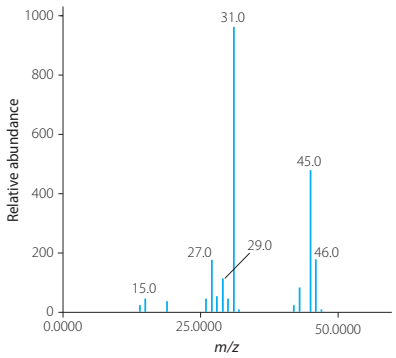
c



d



e



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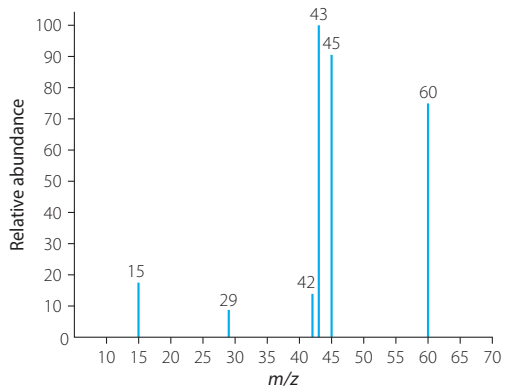

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END-OF-CHAPTER EXAM

End-of-chapter test

1 Protein X and protein Y have been combined in a mixture in the ratio 30% X : 70% Y. Protein X has approximately half the molecular mass of protein Y. The mixture is separated using gas–liquid chromatography.

When comparing the peaks for the two proteins on the chromatogram obtained, it would be expected that the peak for protein Y has:

A a shorter R_t and a larger peak area.

B a shorter R_t and a smaller peak area.

C a longer R_t and a larger peak area.

D a longer R_t and a smaller peak area.

2 Which one of the following analytical techniques involves the motion of ions of different mass in a magnetic field?

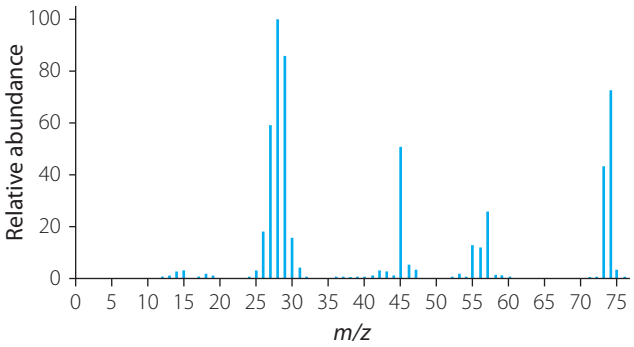
A Gas chromatography

B Thin layer chromatography

C Mass spectroscopy

D IR spectroscopy

3 The mass spectrum of propanoic acid is shown below.



What fragment must have been lost from the molecular ion to account for the high peak at *m/z* 73?

A H

B H^+

C H_2

D H_2^+

4 Black ink is made by mixing other coloured inks: cyan, magenta and yellow. The best way to show that black ink is made up of cyan, magenta and yellow would be to use:

A mass spectroscopy.

B IR spectroscopy.

C X-ray crystallography.

D thin layer chromatography.

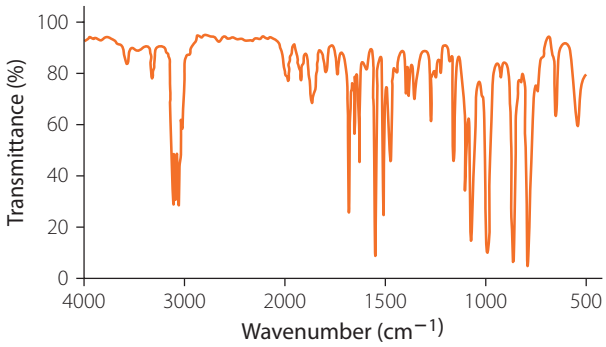
5 Two chemicals, A and B, have the same chemical composition: 54.55% C, 9.9% H, 10.7% N and the remainder oxygen.

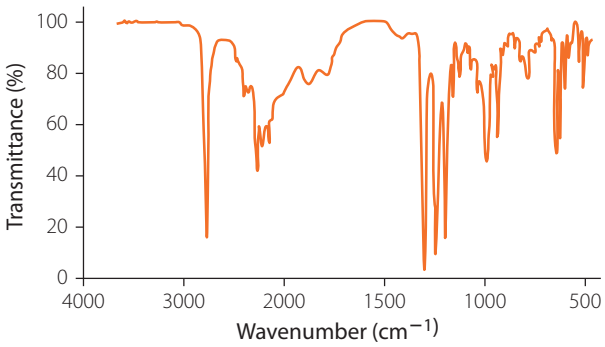
a Calculate the empirical formula for the chemicals A and B.

As they have the same composition and therefore, empirical formula, a chemist carried out chemical tests to try to distinguish them. Both chemicals A and B reacted with acids and bases.

b What is the likely class of compounds that chemicals A and B belong to?

The chemist started to think that A and B were the same sample. So she ran infrared spectra on both and obtained the following spectra.





c Explain why the IR spectra confirm that they are not the same sample.

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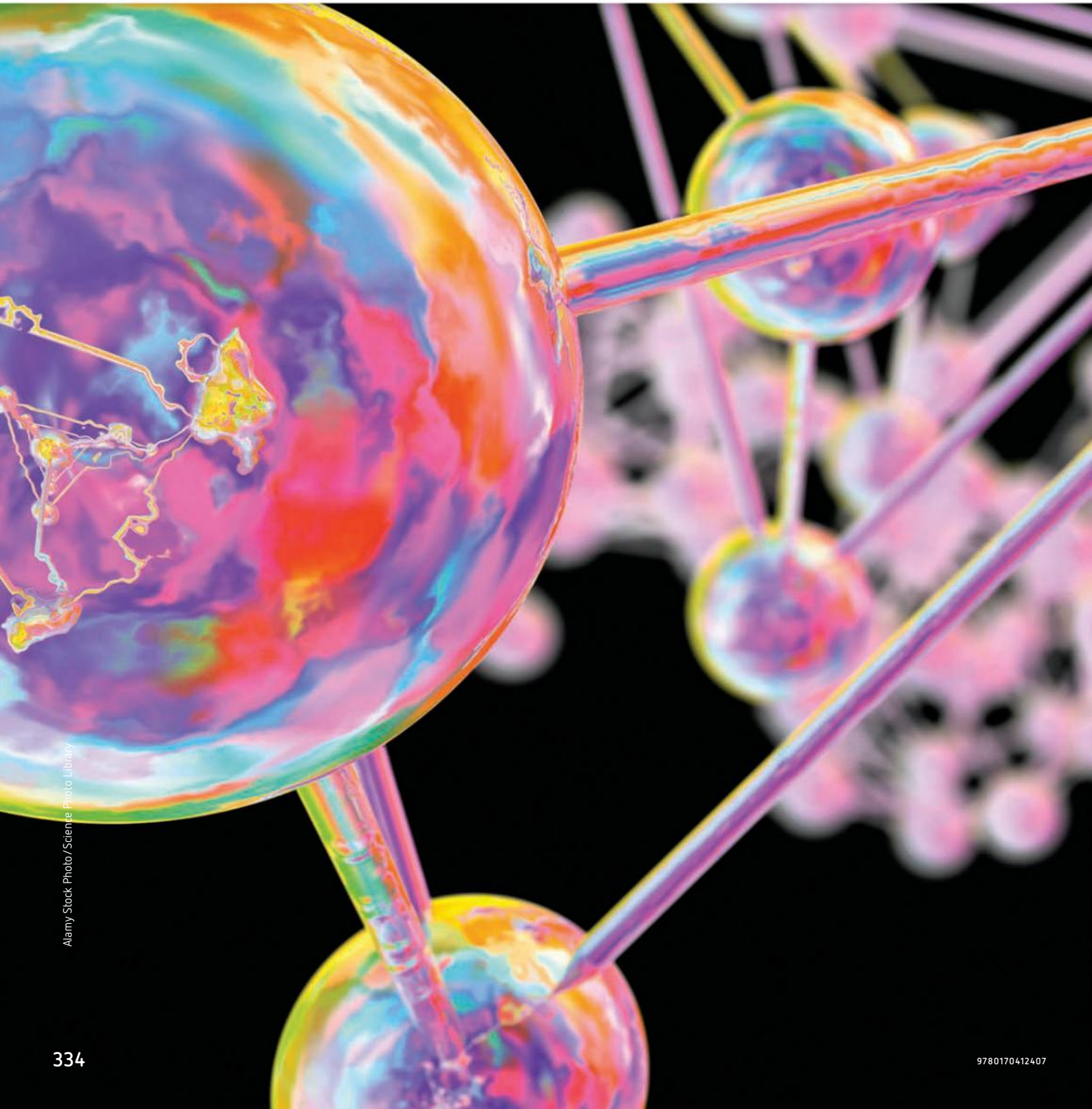
» UNIT FOUR

STRUCTURE, SYNTHESIS AND DESIGN



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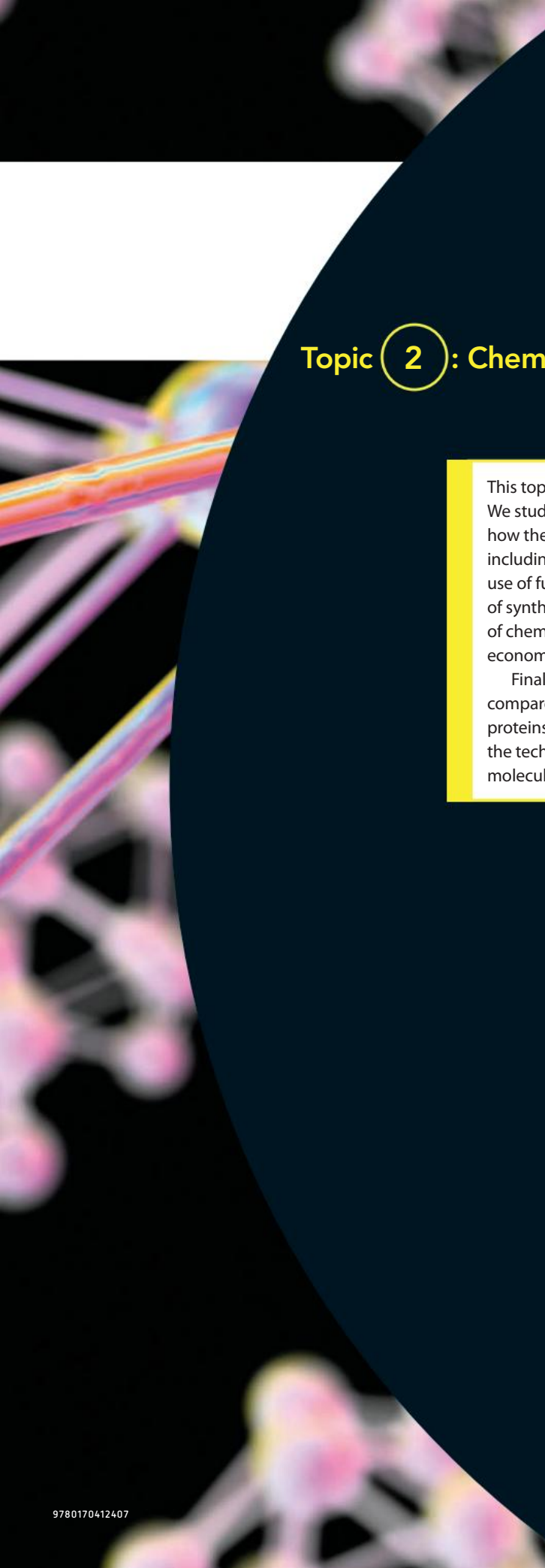

Topic 2: Chemical synthesis and design

STIMULUS QUESTION

This topic examines the synthesis and manufacture of new molecules. We study factors such as rate of production and equilibrium yield to learn how these can be manipulated. We look at a number of specific reactions including using enzymes to produce biodiesel and bioethanol, and the use of fuel cells that use hydrogen. We also examine the potential impact of synthetic processes on the environment and how our knowledge of chemistry can be used to minimise negative effects while still being economically viable.

Finally, we examine the production of synthetic polymers and plastics and compare and contrast this with the production of natural polymers such as proteins and carbohydrates. We also examine molecular manufacturing and the techniques that can be used to accurately design and construct specific molecules, and the applications they can have.

SCIENCE AS A HUMAN ENDEAVOUR

Students should be given opportunities to investigate:

- green synthesis methods and atom economy
- biofuel synthesis
- development of molecular manufacturing processes.

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20 SYNTHESIS REACTIONS

Introduction

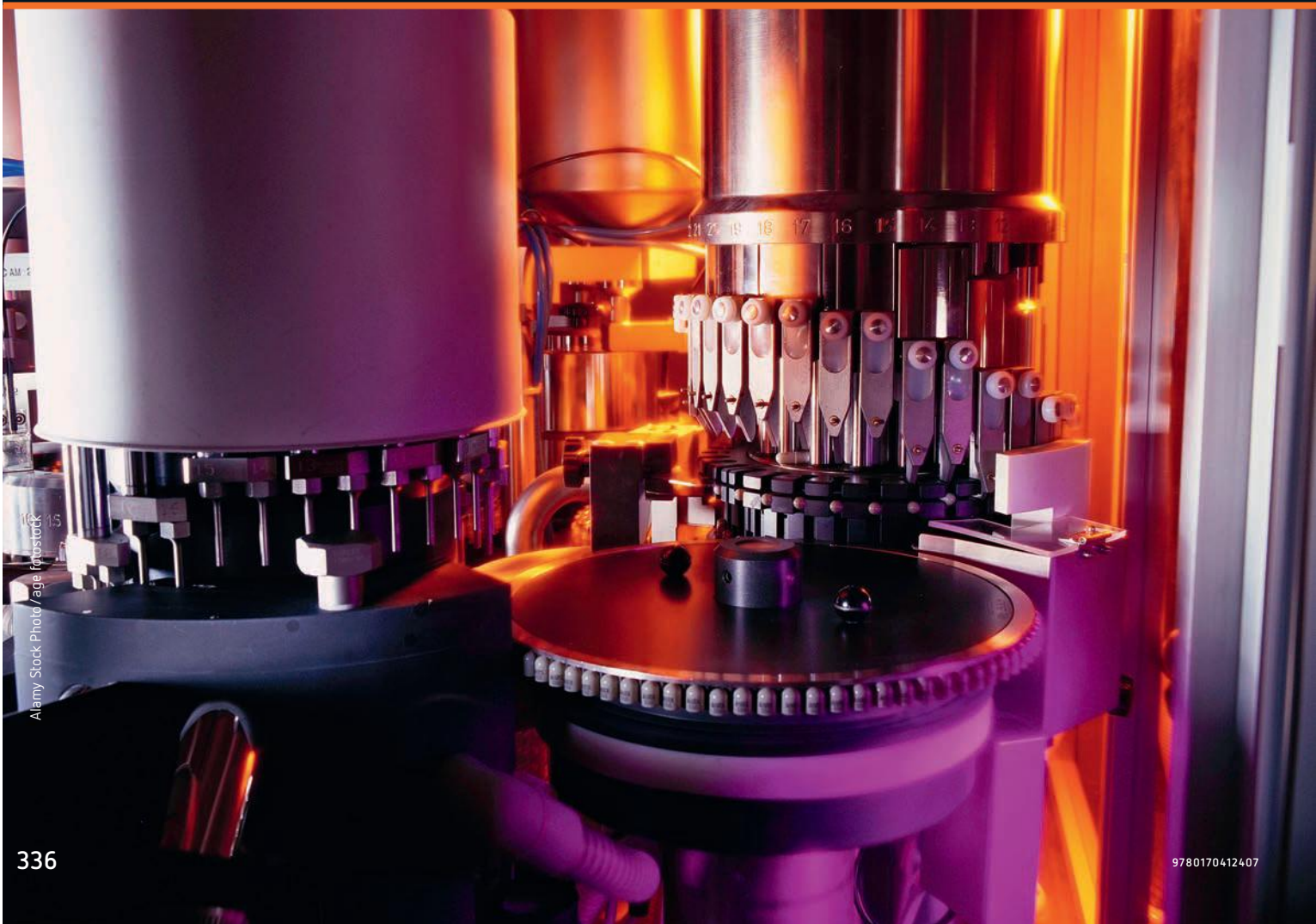
Can you imagine life without plastic? No plastic bags or PVC pipes, no plastic bottles or ice-cream containers. Many of the things we use every day are made from plastics. More specifically, they are made by applying chemistry techniques to manufacture new products. The manufacturing processes need to be safe, sustainable and cost-effective, and the knowledge of chemists and chemical engineers is critical in ensuring that this is the case.

Stimulus questions

How can we maximise the production of a chemical?

How can we produce chemicals with minimum waste?

How can we ensure that chemical manufacturing processes are safe for workers and the environment?



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20.1 Using chemical synthesis

Chemical **synthesis** involves the selection of particular reagents to form a product with specific properties. Today, a huge variety of substances are produced by chemical synthesis, including pharmaceuticals, fuels, cosmetics and cleaning products. First a desired product is identified, and then the reactants and **reaction pathway** are developed. In each case, the aim is to produce the product as economically and safely as possible with the least wastage.

synthesis
to create a product artificially rather than find it occurring naturally

reaction pathway
a series of reactions leading to a specific outcome or product

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FIGURE 20.1.1 Aspirin tablets are synthesised using chemistry.

Aspirin is a pharmaceutical drug that is commonly used to alleviate pain and fever. Its use dates back centuries when people would eat ground-up willow bark to ease aches, pain and fever. The bark contains the compound salicin, which the body converts to salicylic acid. Unfortunately, salicylic acid can irritate the stomach. It was surmised that this side effect was due to the acidic nature of salicylic acid and scientists looked for a way of modifying the molecule to reduce the acidity while maintaining the compound's activity. After much research and testing, it was found that changing salicylic acid to the ester acetylsalicylic acid achieved the desired result. Aspirin is now manufactured on a huge scale using synthesis reactions.

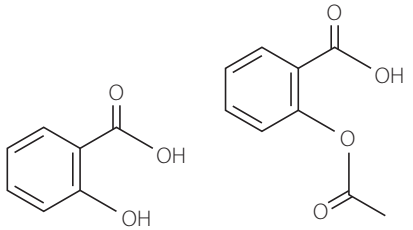

FIGURE 20.1.2 Aspirin tablets are synthesised chemically.

Penicillin is another pharmaceutical drug that is produced by synthesis reactions. Penicillin, discovered by Alexander Fleming in 1928, was originally collected from the *Penicillium* fungus. However, in 1948, John C. Sheehan began nine years of research into manufacturing synthetic penicillin. Although his method was not suitable for mass production, one of the **intermediates** produced could be altered to form a variety of different forms of penicillin that are still used today, including ampicillin (Figure 20.1.3).

intermediates
species formed during a reaction pathway as precursors to the desired product

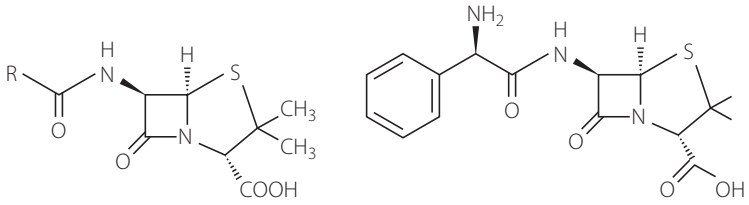

FIGURE 20.1.3 Structure of penicillin and ampicillin antibiotics, which are used to treat bacterial infections

SCIENCE AS A HUMAN ENDEAVOUR

QUININE

Quinine is an important drug for the treatment of malaria, and therefore is responsible for saving many lives. Its original source was the bark of the *Cinchona officinalis* tree from South America. A decrease in the number of these trees increased the price of quinine. In 1856, 18-year-old William Perkin attempted to synthesise quinine in his laboratory at home. Although he was not successful, his attempt led to research into the necessary reaction, and 88 years later, R. B. Woodward and W. E. Doering finally achieved the synthesis of quinine.

SECTION REVIEW 20.1

REMEMBERING

1 Define:
- **a** synthesis
- **b** reaction pathway
- **c** intermediates.

APPLYING

2 Carry out further research into the development of the production of aspirin. What were the challenges that arose and how were they overcome?

20.2 Factors to consider in designing a chemical synthesis

The design of a chemical synthesis is affected by a number of factors. Often, the process is commercially driven; therefore, the object is to produce the chemical as efficiently and cheaply as possible, without compromising on safety or environmental factors. In most cases, synthesis involves more than one step, and there may be more than one possible pathway or **reaction mechanism**. There are many factors to consider when deciding on the appropriate procedure; for example, other possible products, availability and cost of reactants, and the conditions required for the reaction.

reaction mechanism an understanding and description of how a reaction has taken place

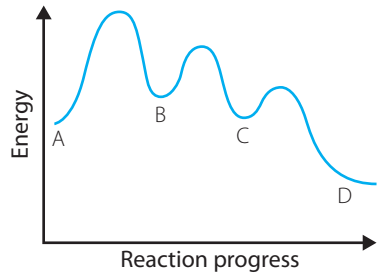

FIGURE 20.2.1 Energy profile diagram for a multistep reaction

In a multistep reaction, each step will have its own reactants, products and activation energy. These will affect the speed of the reaction and the chemicals available for the next step. Along the pathway, the products of one step may be used as reactants for another step. Therefore, these products are used up during the process. These chemicals are known as intermediates. An energy profile diagram can be used to represent the stages of the reaction (Figure 20.2.1).

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In Figure 20.2.1:

- A is a reactant
- B and C are intermediates
- D is a product.

When choosing the most appropriate procedure, scientists will also consider any side reactions that may occur and take steps to prevent these happening. This will maximise the purity of the product.

Maximising the yield of a reaction

When we perform calculations in chemistry, it is often assumed that all the reactants will react to form the products. In reality, this does not always happen. The yield of a reaction refers to the amount of product actually produced from the reactants. A reaction with a high yield will produce a large amount of product from the reactants.

In industry, it is desirable to make as much of the product as possible. To facilitate this, the conditions would be managed so that the position of equilibrium lies as far to the right as possible. This means that at equilibrium, there will be a much higher proportion of products than reactants, and also, that a high proportion of the reactants have *become* products. The conditions required will vary depending on the reaction; however, there are some common features.

- The removal of the product: by decreasing the concentration of a product the forward reaction will be favoured, shifting equilibrium to the right.
- Recycling of reactants that have not been used: by recycling the unused reactants, there is less wastage and the concentration of a reactant is increased. This favours the forward reaction, shifting equilibrium to the right.
- Conducting the reaction at an appropriate temperature: the temperature chosen should favour the forward reaction so that equilibrium lies as far to the right as possible. At the same time, the effect on the rate of the reaction and the cost of heating should be considered.
- Choosing a suitable pressure for a system including gases: the pressure of a gaseous system will affect the position of equilibrium; therefore, the pressure used should favour the forward reaction so that equilibrium lies as far to the right as possible. However, the effect on the rate of the reaction, cost and safety should also be considered.
- A catalyst is often used to increase the rate of production of the product. While this does not increase the yield directly, it will mean that the product is produced in a shorter time. It might also mean that the reaction can occur at a sufficiently productive rate at a lower temperature. In this case, if the reaction is exothermic, the lower temperature will also result in a higher yield.

Calculating the theoretical yield: limiting reactants

The theoretical yield is the amount of product that can theoretically be produced from the reactants. It is based on the assumption that the reactants react with 100 per cent efficiency. In reality, many factors affect how much product is produced. One of these factors is the amount of each reactant. As soon as one reactant runs out, the reaction can no longer proceed and no more product can be made. This reactant is known as the **limiting reagent**. The other reactants are the **excess reagents**.

limiting reagent
the reactant molecule that is completely used up during a reaction

excess reagent
the reactant which is still remaining after a reaction is complete

There are many different methods for determining which chemical is the limiting reactant. In each case, the number of moles of each reactant is compared to the stoichiometrical ratios needed in the reaction. One method is demonstrated in Worked example 20.2.1.

Once the limiting reactant has been determined, it is used to calculate the number of moles, and then the mass, volume or concentration of the product.

WORKED EXAMPLE 20.2.1

The synthesis of paracetamol ($C_8H_9NO_2$) is a three-step process, with the final step being the reaction between 4-aminophenol (C_6H_7NO) and ethanoic anhydride ($C_4H_6O_3$):

$$C_6H_7NO + C_4H_6O_3 \rightarrow C_8H_9NO_2 + C_2H_4O_2$$

If 0.5 g of 4-aminophenol reacts with 0.4 g of ethanoic anhydride, what is the mass of paracetamol that can be produced?

ANSWER

1 Calculate the number of moles of each reactant.

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

$$n(C_6H_7NO) = \frac{0.5}{109.1} = 0.004\,58 \text{ mol}$$

$$n(C_4H_6O_3) = \frac{0.4}{102.1} = 0.003\,92 \text{ mol}$$

2 Determine the stoichiometric ratio (SR), using the coefficients from the equation, and the actual ratio (AR), using the moles calculated. Make sure that the same reactant is on top for both ratios.

$$SR = \frac{1}{1} = 1$$

$$AR = \frac{0.004\,58}{0.003\,92} = 1.168$$

3 Determine which reactant is limiting. If AR > SR, the reactant on the denominator is limiting. If SR > AR, the reactant on the top in limiting.

AR > SR, so the reactant in the denominator is limiting. Therefore, $C_4H_6O_3$ is limiting.

4 Use the moles of the limiting reactant to calculate the number of moles of the product that can be produced.

$$n(C_8H_9NO_2) = n(C_4H_6O_3)$$

$$n(C_8H_9NO_2) = 0.003\,92 \text{ mol}$$

5 Use the number of moles of the product to calculate the mass of the product that can be produced.

$$m = nM$$

$$m(C_8H_9NO_2) = 0.00392 \times 151.163 = 0.593 \text{ g}$$

The mass of paracetamol is 0.593 g.

standard temperature and pressure (STP) a measurement commonly used when performing calculations on gases, such as gas density; the standard temperature is 273 Kelvin (0° Celsius) and the standard pressure is 1atm pressure.

TRY THESE YOURSELF

a What mass of ammonia can be produced from 5.0 L of hydrogen gas and 3.0 L of nitrogen gas at standard temperature and pressure?

b What mass of sulfur trioxide can be produced from 1 kg of sulfur dioxide and 1 kg of oxygen gas?

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

20.2.1 Percentage yield

The yield is usually given as a percentage of the possible yield. A yield of 90 per cent means that only 90 per cent of the amount of products that can be theoretically produced from the reactants is produced. To calculate this percentage we need to:

- use stoichiometry to calculate the amount of product that can theoretically be produced from the reactants
- know the amount of product actually produced.

Then calculate the percentage yield:

percentage yield the percentage of the maximum possible amount of product from a reaction that has actually been produced

$$\text{Percentage yield} = \frac{\text{Actual mass}}{\text{Theoretical mass}} \times 100$$

WORKED EXAMPLE 20.2.2

If 5.0 g of sulfur reacts with excess oxygen to produce 7.5077g of sulfur dioxide, what is the percentage yield for the reaction?

ANSWER

1 Write a balanced equation.

$$S + O_2 \rightarrow SO_2$$

2 Calculate the amount of product that can theoretically be produced from the reactants.

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

$$n(S) = \frac{5.0}{32.06} = 0.156 \text{ mol}$$

$$n(SO_2) = 0.156$$

$$m = n \times M$$

$$m(SO_2) = 0.156 \times (32.06 + 2 \times 16)$$

$$= 9.99 \text{ g}$$

This is the theoretical yield or mass.

3 Calculate the percentage yield using the theoretical yield or mass that you have calculated and the actual yield or mass given in the question.

$$\% \text{ yield} = \frac{\text{actual mass}}{\text{theoretical mass}} \times 100$$

$$= \frac{7.50}{9.99} \times 100$$

$$= 75.1\%$$

Percentage yield is 75.1%

TRY THESE YOURSELF

a The synthesis of aspirin (acetylsalicylic acid) involves the reaction:

$C_7H_6O_3$	+	$C_4H_6O_3$	→	$C_9H_8O_4$	+	$C_2H_4O_2$
salicylic acid		ethanoic anhydride		aspirin acetylsalicylic acid		acetic acid

If 25.0 g of acetylsalicylic acid is produced when 30.0 g of salicylic acid reacts, calculate the percentage yield for the reaction.

b Producing ammonia in the Haber process is typically carried out at approximately 450°C and 200 atm. At this temperature and pressure, 35.0 L of nitrogen gas produces 1.50 kg of ammonia. Calculate the percentage yield for the reaction.

PRACTICAL ACTIVITY 20.2.1

Percentage yield of carbon dioxide

Carbon dioxide is produced during the reaction between calcium carbonate and hydrochloric acid. In an open test tube, this gas will escape the solution and the mass lost will be reflected in the loss of mass of the solution. Using this understanding, we can measure the mass of carbon dioxide produced and thus the percentage yield for the reaction.

AIM

To determine the percentage yield of carbon dioxide in the reaction between calcium carbonate and hydrochloric acid

EQUIPMENT

- Calcium carbonate chips (approximately 2 g)
- 0.5 mol L^{-1} hydrochloric acid
- One large test tube
- Electronic balance
- 10 mL pipette

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Chemicals could splash onto your skin or eyes.	Wear safety glasses and wash your hands at the end of the experiment.
0.5 mol L^{-1} HCl is corrosive to skin and clothing.	Wear gloves, safety glasses and an apron.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Weigh approximately 2 g of calcium carbonate chips. Record the actual mass.
2. Accurately measure 10 mL of 0.5 mol L^{-1} hydrochloric acid with a pipette.
3. Pour the acid into the large test tube.
4. Accurately measure the mass of the acid and test tube.
5. Add the calcium carbonate chips to the acid and record any observations.
6. When there is no longer any visible reaction, weigh the test tube and its contents.
7. If there is time, repeat the experiment or collate the class results.

RESULTS

Record your results in a suitable table. If you are doing multiple trials or collating the class results, ensure that you include room for all trials as well as the average.

ANALYSIS

1. Write a balanced equation for the reaction.
2. Calculate the number of moles of each reactant used in the reaction.
3. Determine which reactant was the limiting reactant. Did your observations support this?
4. Calculate the mass of carbon dioxide that would theoretically be produced from the reactants.
5. Use your results to calculate the mass of carbon dioxide actually produced in your experiment.
6. Calculate the percentage yield for the reaction.

DISCUSSION

1. What assumption was made in determining the mass of carbon dioxide produced in this reaction?
2. Suggest some reasons why the reaction was not 100 per cent efficient.
3. What were some areas where errors or inaccuracies may have occurred during the experiment?
4. Suggest some ways to improve the method.

CONCLUSION

What did you conclude regarding the percentage yield in the production of carbon dioxide in this reaction?

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PRACTICAL ACTIVITY 20.2.2

Calculating the percentage yield

To calculate the percentage yield for a reaction, it is necessary to measure the amount of product produced from a known amount of reactants. In this practical activity, you will design and conduct an experiment to determine the percentage yield of the reaction between magnesium and oxygen:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

WHAT IS YOUR AIM?

What are you trying to achieve with this practical activity?

WHAT WILL YOU NEED?

Carefully plan what you will need to conduct the practical activity. List the items in detail, making note of the size, quantity, type and concentration, where applicable.

WHAT ARE THE RISKS?

Carefully consider the risks associated with the practical activity. Find the safety data sheet (SDS) for any chemicals and consider the appropriate actions to minimise any risks. Complete the table below and get your teacher's approval before conducting the practical activity.

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?

HOW WILL YOU CARRY OUT THE ACTIVITY?

List the steps that you will take during the practical activity. Ensure your procedure is clear, concise and detailed.

WHAT RESULTS WILL YOU COLLECT?

1. Ensure that you are collecting all the necessary data needed to be able to fulfil your aim of calculating the percentage yield.
2. Prepare a table to effectively organise the data that you collect during the practical activity.

HOW WILL YOU ANALYSE YOUR RESULTS?

List the steps that you will take to use the data that you have collected. Ensure your calculations are clear, correct and that they allow you to calculate the percentage yield.

WHAT HAVE YOU FOUND?

What is the percentage yield for the reaction between magnesium and oxygen?

IDEAS FOR IMPROVEMENT OR FURTHER INVESTIGATION

1. How could you improve your method to obtain more accurate results?
2. What could you do to further investigate the percentage yield for this reaction?

SECTION REVIEW 20.2

REMEMBERING

1 What is the difference between the rate of the reaction and the yield of the reaction?

2 Where should equilibrium lie to maximise the yield of the reaction?

UNDERSTANDING

3 What is the maximum yield that is possible for a reaction?

4 Why is it important to remove the product to maximise the yield of a reaction?

APPLYING

5 In the synthesis of aluminium chloride, 25.0 g of aluminium hydroxide reacts with hydrochloric acid. If 20.0 g of aluminium chloride is produced, what is the percentage yield for the reaction?

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

6 Chlorobenzene is used in the production of a range of chemicals, including dyes. Its production can occur through the substitution reaction of benzene with chlorine:

$$C_6H_6(l) + Cl_2(g) \rightarrow C_6H_5Cl(s) + HCl(g)$$

Calculate the percentage yield for the reaction if 90.0 g of benzene produces 125 g of chlorobenzene.

7 In the synthesis of hydrochloric acid, 3.0 kg of chlorine gas is placed in a chamber with 150 g of hydrogen gas.

a Write a balanced equation for the reaction.

b What conditions would favour a high rate of production?

c Given that this is an exothermic reaction, what conditions would increase the yield of HCl?

d What is the limiting reactant in this reaction?

20.3 Designing optimal processes

When designing the reaction conditions, the rate at which the yield is produced must also be considered. In an ideal situation, the reaction would have a high yield and this would be produced at a fast rate. As a result, a large amount of product is produced in a short time, thus maximising profit and minimising wastage. However, a compromise must often be reached between the yield and rate of the reaction when one condition has opposite effects on the yield and rate. Two examples of this are the Haber process and the contact process.

The Haber process

Haber process the industrial production of ammonia

The Haber process is the main method for the production of nitrogen-based fertilisers. It was developed in 1915 and involves the reaction of nitrogen and hydrogen to form ammonia. The ammonia produced is then used as a feedstock for the production of fertilisers. An industrial plant can produce around 1000 tonnes of ammonia a day. To produce chemicals at this level, chemists have worked to make the reactions as efficient as possible while making as much profit as they can.

To produce ammonia, nitrogen and hydrogen gases are reacted together in the presence of a catalyst, at a temperature of 400°C and a pressure of 250 atm. The exothermic equilibrium reaction equation is:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4\,kJ\,mol^{-1}$$

As with most industrial syntheses, the aim is to maximise the amount of ammonia produced in a given time at the lowest cost. Conditions are chosen that maximise the yield and rate while being cost efficient. Both yield and rate are affected by temperature and pressure. Figure 20.3.1 illustrates the effect of temperature and pressure on the equilibrium yield of ammonia. A high yield is promoted by high

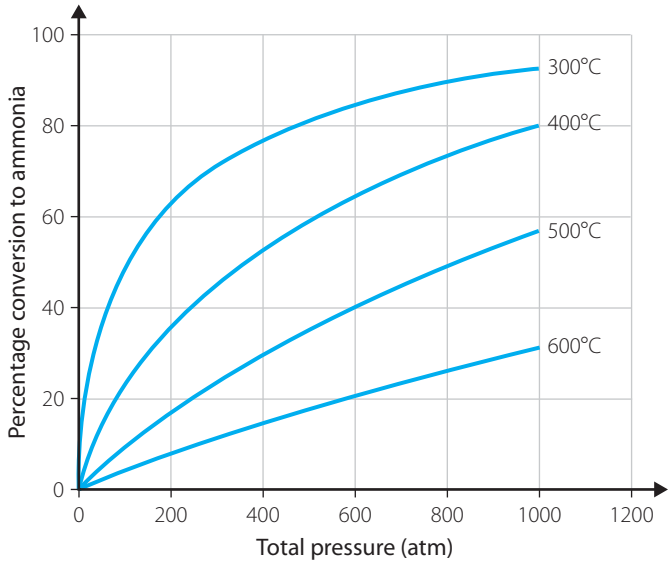


FIGURE 20.3.1 The effect of pressure and temperature on the equilibrium yield of ammonia

20.3.1 Haber process

pressure and low temperature; however, in deciding on the optimum value for each of these variables, the cost and the reaction rate also need to be considered.

Temperature

Increasing the temperature will increase the rate of the reaction because more particles will have sufficient energy for a successful collision.

Decreasing the temperature will increase the yield because decreasing the temperature favours the exothermic reaction, as described by Le Chatelier's principle. In the Haber process, the exothermic reaction is the forward reaction; therefore, decreasing the temperature will increase the yield of ammonia.

Cost must also be considered. It is very expensive to heat chemicals to extreme temperatures and so any benefits may be offset by the cost.

Therefore, a compromise is made between rate, yield and cost. A temperature of 400–450°C ensures that enough ammonia is produced in an adequate time.

Pressure

The rate of the reaction is increased by increasing the pressure of the system because this increases the concentration of the reactants and therefore the number of collisions.

Yield is also increased by increasing the pressure. Higher pressures favour the reaction that produces the least number of gaseous molecules. In the Haber process, this is the forward reaction and the yield of ammonia is increased.

Although a higher pressure increases both the yield and rate, extreme pressures have associated risks and cost. It is very expensive to produce and maintain a very high pressure. There is also the risk of explosions if the pressure is greater than the container can withstand.

A pressure of approximately 200 atm provides a balance between the high rate and yield, and the cost and risks associated with even higher pressures.

Catalysts

Catalysts do not affect the yield of the reaction, but they can affect the rate. In the Haber process, an iron/iron oxide catalyst is used with a small amount of potassium oxide and aluminium oxide. This provides an alternative pathway for the reaction with a lower activation energy. Therefore, more particles will have sufficient energy for a successful collision, and the rate of reaction will be faster. Consequently, with the use of a catalyst, the reaction can be carried out at a lower temperature, thus enabling a higher yield.

20.3.2 Control an ammonia plant

Haber process apparatus

A diagram showing the equipment and method used in the Haber process can be seen in Figure 20.3.2.

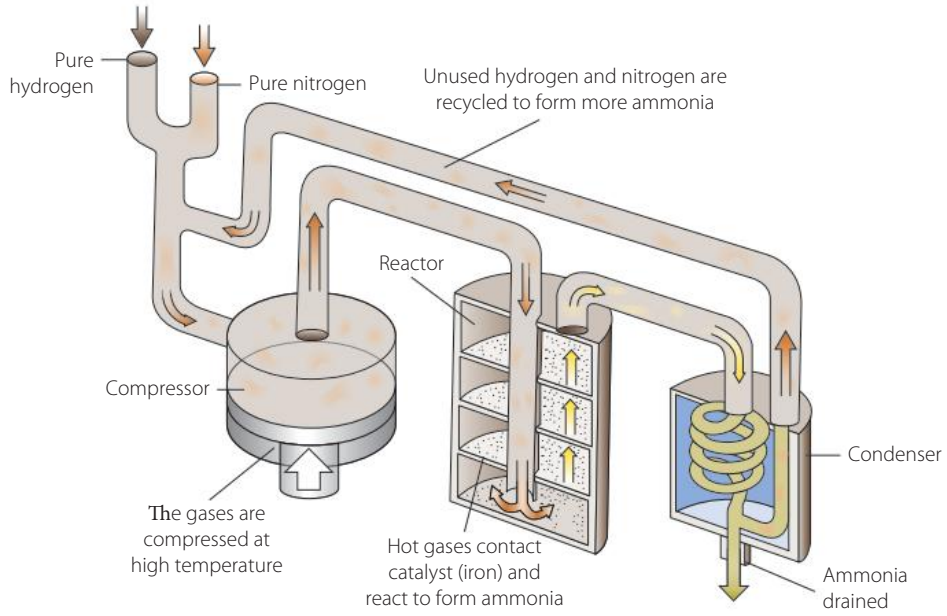
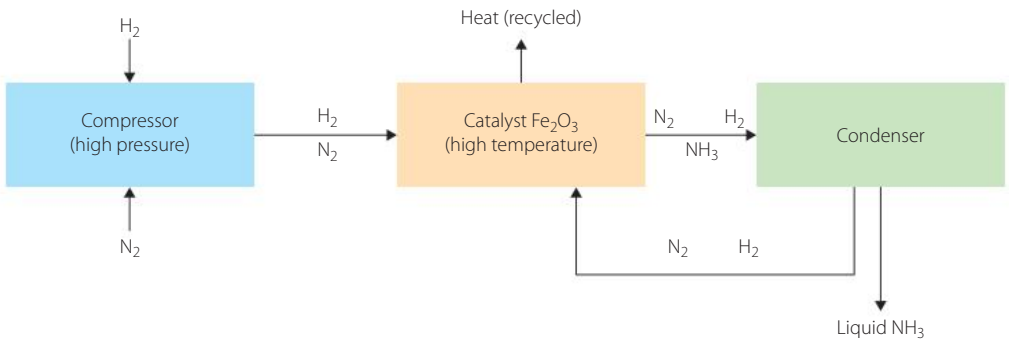


FIGURE 20.3.2 The industrial production of ammonia

- Nitrogen is sourced from the atmosphere, while the hydrogen is usually gained from methane, in a process known as steam reforming.
- The nitrogen and hydrogen gases are heated to a temperature of 400°C and fed into a compressor which raises the pressure to 200 atm. These are the optimal 'compromise' values, providing a sufficient yield of ammonia, at an acceptable reaction rate and at an economically viable cost.
- The gases are passed over beds of iron catalysts. The catalyst lowers the activation energy required for this reaction and thus increases the rate of ammonia formation. As the gases pass over the catalyst, only about 15 per cent are converted to ammonia. The remaining gases are cooled, and fed back over the catalyst beds. Due to this recycling, around 97 per cent of the nitrogen and hydrogen is eventually converted to ammonia.
- The gas mixture of ammonia and any unreacted nitrogen and hydrogen passes into a condenser, where it is cooled. The ammonia has the highest boiling point so it is condensed first, leaving the nitrogen and hydrogen gases to be fed back into the reactor for further conversion.

Figure 20.3.3 summarises this process in a flow chart.

FIGURE 20.3.3
A flow chart illustrating the Haber process



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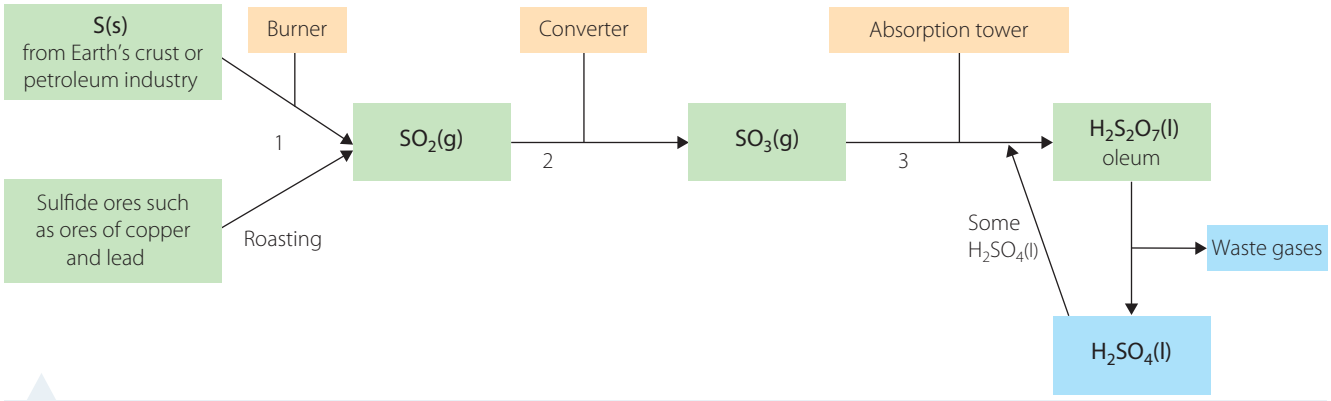
The contact process

20.3.3 Contact process

Sulfuric acid is one of the most important chemicals produced and used worldwide; it is used in the production of metal, paints, fertilisers, car batteries, detergents, dyes, fibres and in agriculture.

It is produced by the **contact process**. This starts with sulfur or a sulfide, which undergoes a number of reactions to produce the acid. Figure 20.3.4 shows a schematic diagram of the contact process.

contact process the industrial production of sulfuric acid



Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

FIGURE 20.3.4 The stages of sulfuric acid production

Step 1

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

or

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

In the first step, air is used as the source of oxygen. This is cheap and readily available. An excess of air is used, which provides the oxygen needed for the second step as well. This makes the process more efficient as the two reactants for the second step are already mixed together. However, the amount of air is controlled so that the ratio of sulfur dioxide to oxygen is 1:1.

Step 2

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -196\,kJ\,mol^{-1}$$

Step 2 of the contact process is the most significant in the design of the process and is where most consideration needs to be given to the reaction conditions in order to optimise the production of SO_3, and therefore of sulfuric acid. Several factors need to be considered, as discussed below.

Stoichiometric ratio of reactants

From the equation for the second step, you can see that the stoichiometric ratio of the two reactants is $2\,SO_2 : 1\,O_2$. Therefore, the 1:1 ratio provided gives an excess of oxygen gas. This has the combined effect of increasing the reaction rate and increasing the yield of sulfur trioxide.

The reaction rate is increased because of the increased concentration of the reactant, thereby increasing the number of collisions between reactant particles. By increasing the concentration of a reactant, the rate of the forward reaction will also increase because of the increased number of collisions. This will shift equilibrium to the right and therefore increase the yield of sulfur trioxide.

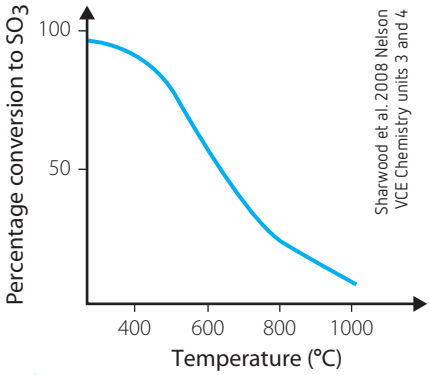


FIGURE 20.3.5 Yield of sulfur trioxide against temperature

Temperature

The combustion of sulfur dioxide in the second step is an exothermic reaction. An increase in temperature would lead to an increase in the rate of reaction due to the increased percentage of particles with enough energy for a successful collision. However, an increase in temperature would favour the endothermic reaction, which in this case is the reverse reaction. This would lead to a decreased yield of sulfur trioxide. Figure 20.3.5 shows how the yield of sulfur trioxide depends on temperature.

Therefore, a compromise temperature of 400–450°C is used. This allows a relatively high yield of sulfur trioxide to be produced in a relatively short time.

Pressure

The pressure of the chamber for the second reaction is 1–2 atm. A higher pressure increases both the rate of the reaction and the yield of sulfur trioxide. The rate of the reaction increases due to the increased concentration of the reactants and therefore the number of collisions between the particles. As there are more gaseous molecules in the reactants than the products, an increased pressure will increase the rate of the forward reaction more than the reverse. Therefore, equilibrium will shift to the right, increasing the yield of sulfur trioxide. However, it is very expensive to produce and maintain a high pressure safely; this cost outweighs the benefits gained. Therefore, a lower pressure is used.

Catalysts

The aim of the process is to produce as much sulfuric acid as quickly as possible. For this reason, a catalyst of vanadium oxide (V_2O_5) is used in the second step. Although this does not affect the yield of sulfur trioxide, it increases the rate at which it is produced, thereby increasing the rate of the next step.

Step 3

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

If we consider the previous two steps, it would seem counterproductive to add sulfuric acid when this is the desired product. If water was added directly to the sulfur trioxide, then sulfuric acid would be produced. However, this reaction is uncontrollable and will produce a fog of sulfuric acid. By dissolving the sulfur trioxide in the sulfuric acid first, the reaction can be controlled and the sulfuric acid produced can be collected efficiently. When we consider the molecules of sulfuric acid added and produced, it is clear that all of the sulfuric acid added is retrieved in the products, in addition to the new sulfuric acid produced.

SECTION REVIEW 20.3

REMEMBERING

1. Write a balanced equation to represent the Haber process and indicate the reaction conditions that are used for optimal production of ammonia.
2. Write a balanced equation to represent the contact process and indicate the reaction conditions that are used for optimal production of sulfuric acid.

UNDERSTANDING

3. Use Le Chatelier's principle to explain why temperature affects yield in the production of ammonia.
4. Use Le Chatelier's principle to explain why pressure affects yield in the production of sulfuric acid.

5 Explain why the molar ratio of reactant molecules is an important consideration in both the Haber and contact processes.

6 Explain why the use of a catalyst is critical to both the Haber and contact processes.

APPLYING

7 From what you have learned regarding the Haber and contact processes, summarise the factors that need to be considered in designing the industrial production of a chemical.

20.4 Synthesis of fuels

Carbohydrates are fuels that provide an energy source for living things. The oxidation of glucose in cells provides most of the energy needed for life. As well as needing fuel for life, we also rely on fuels to produce electricity and power vehicles.

Most fuels are organic compounds. Coal and crude oil, carbohydrates, proteins and fats are all fuel sources used for particular purposes.

Most transport fuels are derived from crude oil. Crude oil is a mixture of many different hydrocarbons and is classed as a fossil fuel because it is formed by the decomposition of prehistoric living things. Since crude oil is a mixture of hydrocarbons, it is processed by fractional distillation.

Fractional distillation cannot produce enough petrol to meet all transport needs, so some of the heavier fractions that have carbon chains with 15–25 carbon atoms are subjected to catalytic cracking. Catalytic cracking is a decomposition reaction in which larger molecules are broken down into smaller molecules.

In 2013, it was estimated that there were 1.3 trillion barrels of proven oil reserve left in the world's major fields, which at present rates of consumption will last 40 years. By 2040, production levels may be down to 15 million barrels per day, around 20 per cent of what we currently consume. It is likely that by then the world's population will be twice as large, and more of it industrialised (and therefore even more oil dependent).

We need new sources of fuels to supplement and eventually replace the current fossil fuels. Two categories of alternative fuels are biofuels and hydrogen. **Biofuels** are produced from renewable sources such as crops rather than from fossil fuels. Biofuels are classified as renewable sources of fuels because they can be continually produced from crops, algae or animal wastes. The two main biofuels currently used in Australia are ethanol and biodiesel. Ethanol is only used in Australia as a fuel additive, E10, which is a mixture of unleaded fuel and 10 per cent ethanol.

biofuels
fuels produced from plants, algae or animal waste

Synthesis of ethanol

There are two main processes used for synthesising ethanol: fermentation and hydration of ethene.

The most common method for the production of ethanol in beverages is fermentation. This process is increasingly being used to produce fuel alcohol and, since 2007, Australia has tripled its production of fuel ethanol through the fermentation process.

Fermentation

For fermentation:

- a suitable grain or fruit is mashed up with water
- an appropriate yeast strain is added
- air is excluded
- the mixture is kept at 37°C.

Enzymes in the mixture convert any starch or sucrose to glucose and fructose, and then the yeast consume the monosaccharides and produce ethanol.

The equation for the fermentation of glucose ($C_6H_{12}O_6$) is:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

disproportionation reaction typically a redox reaction, where a molecule is transformed into two or more dissimilar products

The overall reaction involving fermentation is a **disproportionation reaction** in which carbon atoms from the glucose are simultaneously reduced in the formation of ethanol and oxidised in the formation of carbon dioxide.

FIGURE 20.4.1 Part of Wilmar's bioethanol Sarina distillery in North Queensland, which produces 60 million litres of bioethanol per year by fermenting molasses, a by-product of sugar production

Hydration of ethene

catalytic cracking the process of heating larger organic molecules and converting them into smaller, more useful molecules

The most common method of producing ethanol in the developed world is the hydration of ethene, which is produced through the **catalytic cracking** of products from crude oil. Because of the low costs of ethene as a raw material, approximately 95 per cent of the industrial ethanol made in the developed world is produced in this way. However, ethanol produced by this method is not considered a biofuel because it does not come from a crop.

This is an addition reaction and can be represented in the following equation:

$$\underset{\text{Ethene}}{CH_2{=}CH_2(g)} + H_2O(g) \rightarrow \underset{\text{Ethanol}}{CH_3CH_2OH(l)} \quad \Delta H = -45\,\text{kJ mol}^{-1}$$

As this reaction is exothermic, a high yield is favoured by a low temperature. However, at low temperatures, the rate would be too slow. A temperature of approximately 300°C only gives a yield of about 5 per cent.

As the number of product molecules is less than the reactant molecules, the yield is also favoured using a high pressure of 60–70 atm. Consequently, increasing the pressure and using a catalyst of phosphoric acid increases both the yield and rate of production of ethanol.

Synthesis of biodiesel

20.4.1 Biodiesel production in Australia

Biodiesel can be produced from almost any fatty acid, including corn, palm, coconut, sunflower and peanut oils. Most biodiesel currently produced uses waste vegetable oil from restaurants, chip shops and industrial food producers, which means the cost is kept down and the fuel can compete favourably with fossil diesel.

Diesel is a fuel with a long hydrocarbon chain of 8–21 carbons. Biodiesel is similar, but is an ester, containing two oxygens. This is because it comes from plant or animal fats, which are triglycerides.

These react with a short-chain alcohol, usually methanol or ethanol, to produce an ester (the diesel) and glycerol. This process is called **transesterification**.

transesterification the process of converting one ester into another; for example, in the industrial production of biodiesel, converting a lipid into methyl esters of fatty acids, and by replacing the glycerol with methanol

The reaction with methanol is shown below. In the equation, the letter R represents a long hydrocarbon chain.

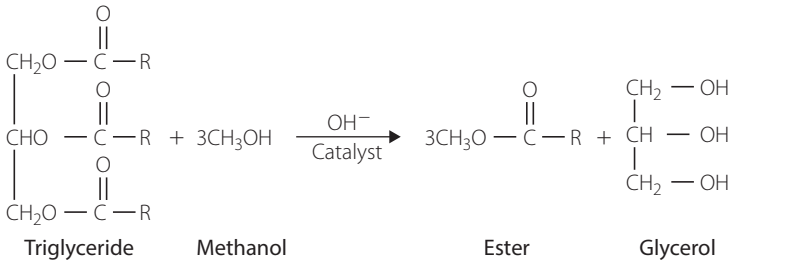


FIGURE 20.4.2 Transesterification: the production of biodiesel

Once the reaction is complete, the two products can be separated by gravity, because the glycerol is denser than the biodiesel. The biodiesel is purified and is then ready for use.

A catalyst is used in the production of biodiesel to facilitate a rapid reaction rate. Three main catalysts are used:

- base catalysts
- acid catalysts
- enzymes.

Almost all biodiesel production uses a strong base, often sodium or potassium hydroxide. This method is effective because it is the most economical, has a 98 per cent conversion yield and requires low temperatures. However, it produces high temperatures, which is a safety risk, and forms soap, which reduces the yield of the ester. In addition, it is expensive to purify the glycerol due to the presence of the base.

Alternatively, an enzyme, or biological catalyst, can be used. Lipase catalyses the breakdown of fats and can be used to increase the rate of the reaction. This method overcomes the problem of soap production and enables a higher yield of biodiesel. However, the enzymes are expensive to produce.

Another factor to consider is the yield of biodiesel. This is maximised by ensuring that the alcohol is in excess, which favours the forward reaction and therefore the production of diesel.

Hydrogen in fuel cells

As discussed in Chapter 12, when we think of fuels as a source of energy, we often think of the combustion reactions where chemical energy is converted to heat energy. However, a fuel cell is an electrochemical device. It converts chemical energy directly into electrical energy, through a process which is oxidation, although not combustion.

Since a **fuel cell** is a type of galvanic cell, it has the same structure: an anode, a cathode, an electrolyte and the flow of electrons through an external circuit. However, what distinguishes a fuel cell from other cells is that fuel and oxygen are continuously fed into the cell; the electrodes do not need to be replaced.

fuel cell a galvanic cell that generates electricity from a chemical reaction, but where there is a continuous supply of fuel and also removal of products

The most important design feature in a fuel cell is the membrane that separates the electrodes. It allows molecules and ions to migrate across it, in order for the electrode reactions to occur, as chemicals and ions produced at the cathode are often used at the anode and vice versa. However, the membrane does not conduct the electrons which must travel via an external circuit so that they can be harnessed as electricity. A key development in fuel cell technology is the improvement in the design of membranes, so that they work ever more efficiently.

The most commonly used fuel in a fuel cell is hydrogen, although short-chain alkanes have also been used. Hydrogen can be obtained from a number of sources, including an electrolytic cell, where it is obtained from the electrolysis of water powered by solar energy. Hydrogen is highly flammable and so needs to be stored carefully. However, if contained successfully, hydrogen is effectively a store of energy. It can be produced using solar energy during the day, and then can produce electricity via the fuel cell when required.

INQUIRING FURTHER

CSIRO have developed a microfuel cell that uses methanol, a high-energy density fuel that undergoes a chemical reaction with oxygen to produce an electric current. Research the benefits of this microfuel cell.

In most fuel cells, hydrogen is oxidised at the anode and oxygen is reduced at the cathode. A by-product of the fuel cell is the production of water. Hence, the overall reaction that is taking place is:

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

However, different types of fuel cells can differ in the type of electrolyte used, and this can therefore alter the specific reactions occurring at each electrode. The two most commonly used electrolytes are acid, such as phosphoric acid, and alkaline, such as potassium hydroxide.

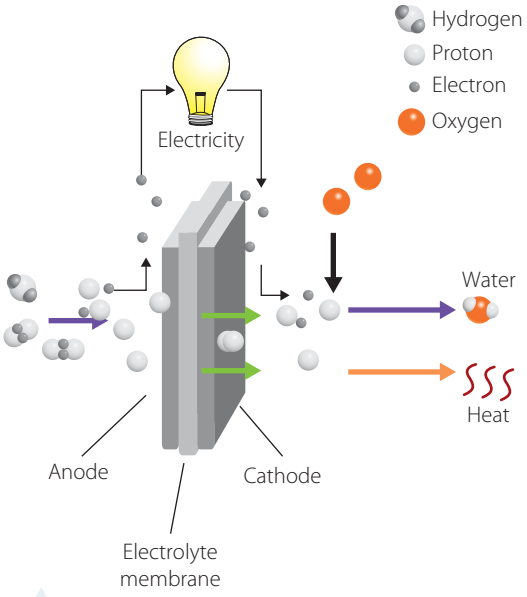


FIGURE 20.4.3 A simplified hydrogen fuel cell

Acid electrolyte

With an acid electrolyte, the reactions at the electrodes are:

$$\text{Anode:} \quad 2H_2(g) \rightarrow 4H^+(aq) + 4e^- \quad E^\circ = +0.00\,V$$

$$\text{Cathode:} \quad O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E^\circ = +1.23\,V$$

A schematic diagram for a hydrogen fuel cell with an acid electrolyte is shown in Figure 20.4.3.

Alkaline electrolyte

With an alkaline electrolyte, the reactions in the fuel cell are:

$$\text{Cathode:} \quad O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \quad E^\circ = +0.40\,V$$

$$\text{Anode:} \quad 2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^- \quad E^\circ = -0.83\ V$$

It should be noted that the overall cell potential is still 1.23 V, identical to that with the acid electrolyte, as the overall reaction is also the same. A schematic diagram of the alkaline hydrogen fuel cell is shown in Figure 20.4.4.

Again, the fuel cell is compartmentalised. The hydrogen and oxygen are on opposite sides with the electrolyte in the middle compartment. The electrodes are porous to allow the gas molecules to pass through. They are lined with a catalyst that assists with the breaking of bonds in the gaseous molecules. The most commonly used catalyst is platinum, although rhodium and nickel are also used. The use of a platinum catalyst is one of the main costs of a fuel cell.

Fuel cells can be stacked together to increase the total cell voltage, just as batteries are added in series to increase the total voltage output. The water produced must be removed from the cell; otherwise, the electrolyte will become diluted, which will affect the efficiency of the cell.

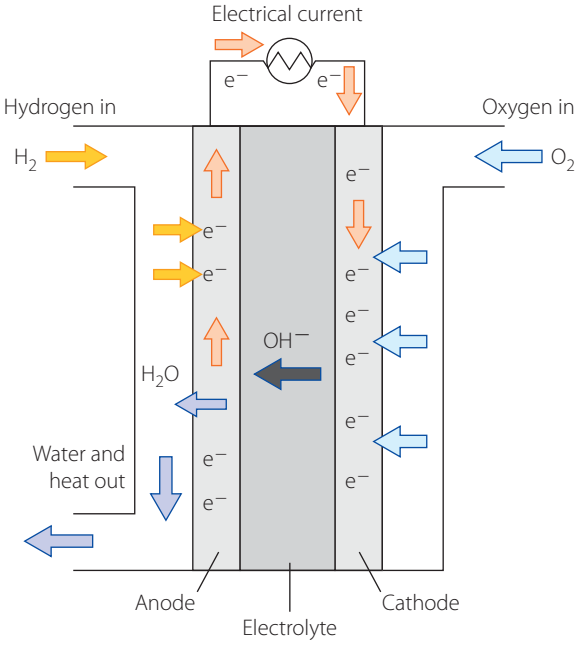


FIGURE 20.4.4
A simplified alkaline hydrogen fuel cell

SECTION REVIEW 20.4

REMEMBERING

1. What is a biofuel?
2. Why are biofuels produced?
3. What is a fuel cell?
4. Identify the energy transformation that occurs in a fuel cell.
5. What is a catalyst?
6. Identify the most common catalyst used in fuel cells.

UNDERSTANDING

7. Name the two types of chemical reactions through which ethanol is produced.
8. Should the ethanol produced through both the reactions given in answer to Question 7 be considered a biofuel? Why or why not?
9. Write the half-reactions for the fermentation of glucose to ethanol and water. Label each half-reaction as oxidation or reduction.
10. Draw a diagram showing the production of biodiesel using ethanol instead of methanol.
11. A fuel cell releases only a small voltage. How can this be used to provide the energy for a car?
12. Describe the chemistry of a fuel cell.

REFLECTING

13. Is biodiesel a better fuel than fossil diesel? Explain why or why not.
14. Discuss some of the current issues related to the use of fuel cells and the research that is being undertaken to address these issues.
15. Discuss the impact of the use of fuel cells on society and the environment.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define:
- Haber process
- contact process
- biofuels
- catalytic cracking
- transesterification
- fuel cell.

2 State the aim of synthesis reactions.

CATEGORY QUESTIONS

3 Explain how using a catalyst is critical to the industrial production of ammonia.

4 Name two biofuels and the type of reactions by which they are synthesised.

ELABORATION QUESTIONS

5 Explain why equilibrium is important in synthesis reactions.

6 The following reaction is an exothermic reaction:

$$CaO(s) + H_2O(l) \rightleftharpoons Ca(OH)_2(s)$$

Describe the effect on the yield of the reaction if the temperature is decreased.

7 During the production of oxygen gas by the electrolysis of water, 100 mL reacts producing 65.0 g of oxygen gas.

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

Calculate the percentage yield of the reaction.

EVIDENCE QUESTIONS

8 Why is the ethanol produced by fermentation considered to be a biofuel, yet the ethanol produced by hydration of ethene is not?

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END-OF-CHAPTER EXAM

End-of-chapter test

1 An alkaline hydrogen–oxygen fuel cell has the overall equation:

$$O_2(g) + 2H_2(g) \rightleftharpoons 2H_2O(l)$$

In this fuel cell, the species reacting at the cathode would be:

A $O_2(g)$ and $H^+(aq)$.

B $H_2(g)$ only.

C $O_2(g)$ and $H_2O(l)$.

D $H_2(g)$ and $OH^-(aq)$.

Questions 2 and 3 relate to the Haber process, the equation for which is:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\,kJ\,mol^{-1}$$

2 Which of the following will increase the rate of reaction?

A Increasing the temperature of the system

B Decreasing the concentration of $NH_3(g)$

C Increasing the volume of the system

D Decreasing the temperature of the system

3 Which set of conditions would achieve the maximum yield of ammonia?

A High temperature and high pressure

B Low temperature and high pressure

C High temperature and low pressure

D Low temperature and low pressure

4 Figure 20.5.1 shows a flow chart of the industrial production of methanol. The following information is also provided.

- In Reactor 1, the following reactions occur at 800°C and 30 atm of pressure and with a nickel catalyst:

$$CH_4(g) + H_2O \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +208\,kJ\,mol^{-1}$$

$$CO(g) + H_2O \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H = -41\,kJ\,mol^{-1}$$

- In Reactor 2, the following reaction occurs at 1000°C and 30 atm of pressure with a nickel catalyst:

$$2CH_4(g) + O_2 \rightleftharpoons 2CO(g) + 4H_2(g) \quad \Delta H = -36\,kJ\,mol^{-1}$$

- In the methanol reactor, the following reaction occurs at 350°C and 300 atm of pressure:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) \quad \Delta H = -103\,kJ\,mol^{-1}$$

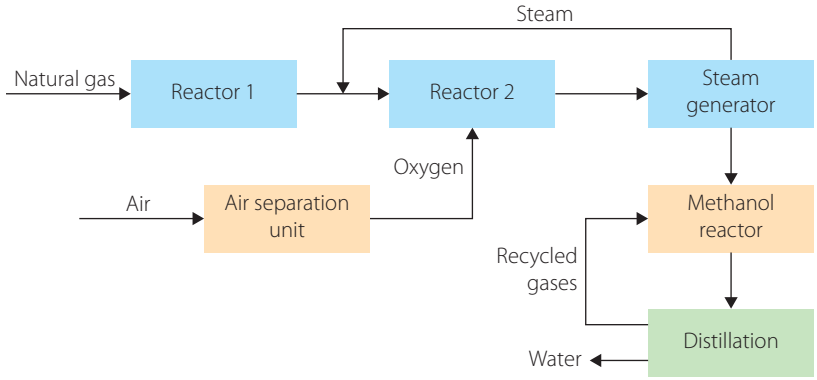

FIGURE 20.5.1 Flow chart of methanol production

Answer the questions below to fully analyse the chemical production of methanol.

a Identify the raw materials, waste products and by-products if they exist. Explain why you identified the chemicals as you did.

b Explain why the step in the air separation unit is necessary.

c Write the formulas of the chemicals that are moving for each step of the process.

d Identify places where chemicals can be recycled and what gases would be recycled in the different stages.

e Identify and explain the areas of the production process that would require high energy, medium energy and low energy.

f Identify areas where energy could be recycled.

g Explain why catalysts are used in the production of methanol.

h Explain why the reaction in the methanol reactor occurs at high pressure.

21 GREEN CHEMISTRY

Introduction

Chemistry is a natural science, practised in the real world, with the capacity to affect the environment both positively and negatively. There are a number of steps that chemists and chemical engineers take to minimise the negative impact of their work on the environment. With careful planning and awareness, their practice can be made significantly more sustainable and therefore also more responsible.

Stimulus question

What can be done to reduce the impact of a chemical process on the environment?

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21.1 Introduction to green chemistry

Green chemistry is a relatively new area of chemistry that aims to reduce the impact of chemical processes on the environment by reducing or eliminating the use or production of hazardous substances. As we learn more about the impact of chemicals on the environment, the importance of green chemistry becomes more evident.

US Environmental Protection Agency

FIGURE 21.1.1 The US Environmental Protection Agency's logo for green chemistry

Green chemistry requires that all aspects of chemical production be analysed to ensure that nothing potentially harmful is used or produced. This is the philosophy of 'prevention is better than cure'. Previously, additional steps were used to deal with the hazardous chemicals after their production. Green chemistry means that they are not produced in the first place.

The idea of green chemistry originated with the *US Federal Pollution Prevention Act* in 1990. This act included a hierarchy associated with pollution.

1. Prevent pollution.
2. Treat chemicals to make them safe prior to disposal.
3. Dispose of untreated chemicals safely.

If it is not possible to achieve the first point in the hierarchy, then you move to the next point. If this is not possible, then the third point is followed. More specifically, when designing a process, the aim is to ensure there is no pollution. If hazardous products are produced, then they should be treated before they are disposed of. If it is not possible to treat the chemicals, then they should be disposed of in a safe manner.

By following this hierarchy when designing reactions, scientists can implement green chemistry as they will be reducing or eliminating human and environmental exposure to the hazardous chemicals.

PRACTICAL ACTIVITY 21.1.1

Building a better bleach

21.1.1 Building a better bleach

AIM

To gain a better understanding of green chemistry by considering the production of bleaching agents

YOU WILL NEED

Access to the internet

WHAT TO DO

1. Use the weblink to access and read the article about chemicals used to treat stains on our clothes.
2. In small groups, discuss how the change to hydrogen peroxide to treat stains is an example of green chemistry.

WHAT DID YOU DISCOVER?

Write a paragraph summarising your discussion.

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21.2 Principles of green chemistry

When scientists are designing synthesis reactions, they should adhere to the 12 principles of green chemistry. These principles address the different stages of reactions and the areas where hazardous substances may be used or generated.

1. Prevent waste: by not producing waste, there is no waste to clean up at the end of the process.
2. Maximise atom economy: **atom economy** refers to the amount of reagent atoms that are present in the desired product. By maximising the number of atoms used that are in the desired product, there are fewer atoms left over at the end of the process. This reduces waste.
3. Design less hazardous chemical syntheses: design the synthesis process to use and generate chemicals that are not hazardous to humans or the environment.
4. Design safer chemicals and products: if the chemicals that are being designed are hazardous, then the process is going against the principles of green chemistry. The aim is to design and produce chemicals that are equally effective but less hazardous.
5. Use safer solvents and reaction conditions: when additional chemicals are required for the process, use safe ones.
6. Increase energy efficiency: high temperatures and pressures require energy. Therefore, use room temperature and pressure where possible to reduce energy consumption.
7. Use renewable reactants: consider the types of reactants used. Renewable reactants can be replenished and using waste products of other processes will also be greener chemistry.
8. Avoid using chemical derivatives: chemical derivatives have had to go through previous processes, thus using more reactants and reactions.
9. Use catalysts: catalysts are effective in small quantities and can be reused. This means less use of chemicals.
10. Design chemicals that will degrade: degradable products will mean fewer chemicals in the environment.
11. Prevent pollution: monitor the reaction in real time to control the reaction and avoid by-products.
12. Minimise the potential of chemical accidents: choose chemicals, including their phases, which minimise the chance of accidents, including explosions, fires and chemical release to the environment.

atom economy
the efficiency of a chemical reaction; the greatest efficiency is where the greatest percentage of atoms in the reactant end up in the product

GREENING IBUPROFEN

SCIENCE AS A HUMAN ENDEAVOUR

Ibuprofen is an analgesic commonly used in pain relief. It was originally synthesised by The Boots Company in a six-step method with an atom economy of only 40.0 per cent. This meant that there was a large amount of wastage in the process.

In the mid-1980s, a number of companies combined to form the BHC Company with the aim of producing a greener synthesis of ibuprofen. They created a three-step method with much less wastage and an atom economy of 77 per cent.

The significance of this development was recognised, with the BHC Company receiving both the coveted Kirkpatrick Chemical Engineering Achievement Award in 1993 and the Presidential Green Chemistry Challenge Award in 1997.

21.3 Atom economy

KEY FORMULA

$$\text{Atom economy} = \frac{\text{mass of atoms in desired product}}{\text{mass of atoms in the reactants}} \times 100$$

Atom economy refers to the mass of reactants that contribute to the desired product. The greater the atom economy, the less wastage of atoms and the greener the chemistry.

The importance of atom economy was recognised in 1998 when Professor Barry Trost was awarded the Presidential Green Chemistry Challenge Award. His work developed the ideas of reducing the use of non-renewable sources, reducing the amount of waste and decreasing the number of steps used to synthesise the desired product. These steps combine to increase the proportion of reactant atoms in the desired product, thereby increasing the atom economy and decreasing the waste atoms.

atom economy
the efficiency of a chemical reaction; the greatest efficiency is where the greatest percentage of atoms in the reactant end up in the product

WORKED EXAMPLE 21.3.1

Calculate the atom economy in the following reaction, used to synthesise calcium oxide:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

ANSWER

1 Calculate the molar mass of the reactants.

$$M(CaCO_3) = 40.1 + 12.01 + (3 \times 16)$$
$$= 100.11$$

2 Calculate the molar mass of the desired product.

$$M(CaO) = 40.1 + 16$$
$$= 56.1$$

3 Calculate the atom economy. (Note: Multiply the molar mass of each reactant or product by its coefficient.)

$$\text{Atom economy} = \frac{56.1}{100.11} \times 100 = 56\%$$

$$\text{Atom economy} = 56.0\%$$

TRY THESE YOURSELF

a Calculate the atom economy for the synthesis of ammonia in the Haber process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

b What is the atom economy in the following reaction, used to produce ethene?

$$C_{10}H_{22} \rightarrow C_2H_4 + C_8H_{18}$$

PRACTICAL ACTIVITY 21.3.1

Modelling atom economy

AIM

To use the combustion of methane to model atom economy in the production of carbon dioxide

EQUIPMENT

- Molecular model kit
- Calculator

PROCEDURE

1. Write the balanced equation for the combustion of methane.
2. Use the molecular model kit to make molecular models of the reactants.
3. Calculate the molecular mass of the total reactants.
4. Use your models of methane and oxygen to 'react' and form carbon dioxide and water in the appropriate proportions, as shown in your equation.
5. Calculate the molecular mass of the carbon dioxide produced.
6. Observe the atoms in the water – these atoms are waste as they are not part of the desired product.
7. Calculate the atom economy for the reaction.

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RESULTS/DISCUSSION

1. Would you consider this reaction to be an example of green chemistry?
2. Your calculations assumed that there was a 100 per cent yield in the reaction. What would happen to the atom economy if the yield was lower?

SECTION REVIEW 21.1–3

REMEMBERING

1. Define 'green chemistry'.
2. List the steps in the hierarchy to be followed in green chemistry.

UNDERSTANDING

3. Choose one of the 12 principles of green chemistry. Explain how implementing this principle makes a chemical process more environmentally friendly.

APPLYING

4. Calculate the atom economy for one of the reactions involved in extracting iron:

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(l) + 3CO_2(g)$$

REFLECTING

5. Discuss the importance of green chemistry, and the implications if green chemistry is not used during synthesis reactions.

21.4 Case study: the greening of the wine industry

The wine industry is aiming to reduce the use of chemicals in winemaking and viticulture. A particular environmental concern for the wine industry is contaminated waste water. Actions taken to reduce this contamination include:

- minimising the caustic chemicals used for cleaning
- using less hazardous chemicals as pesticides in the vineyard.

Reducing energy use and waste will also make wineries more sustainable. Using chemicals that are less hazardous as pesticides appears to be effective in controlling the vine mealybug, which sits under the bark of the vine. Traditionally, large amounts of organophosphates have been applied to ensure direct contact with the pest. Some companies have now developed a safer alternative by using the female mealybug's pheromones. Pheromones are molecules that insects use to attract other insects of their species. Male mealybugs were attracted to pheromone traps containing a lethal pesticide. The pheromone had some additional benefits: it also attracted the natural predators to the mealybugs and the natural predator populations were preserved, thus reducing the need for an additional pesticide spray later in the season.

Cork alternatives

Traditionally, winemakers used cork to seal the bottle. Cork is a natural product derived from the bark of the cork oak tree. However, occasionally the wine would react with the cork, which would spoil the drink's flavour. Additionally, the supply of quality cork from 1980 became very limited and

Marekusz/Dreamstime.com

FIGURE 21.4.1 Corks are no longer the preferred method of sealing bottles in Australia.

cork taint rates increased. In 2000, winemakers from the Clare Valley in South Australia released their riesling wines under screw cap. Now the majority of Australian and New Zealand wines use screw caps. However, cork manufacturers claim that cork is more sustainable.

Bottle alternatives

Glass is the traditional material used for wine containers. Glass can be recycled, but it is heavy. This means the energy and carbon footprint used in transporting the bottles is high. Lighter weight materials such as the plastic PET (polyethylene teraphthalate) could be used for bottles. These have to be treated with an oxygen barrier to enhance shelf life. The bottles weigh about 50 grams, which is about 10 per cent of the weight of a glass bottle. Another alternative is the wine cask. This holds 80 per cent more wine and is less than two-thirds the weight of the equivalent volume of a glass bottled wine. The wine cask released by the Yalumba winery in 2013 has a carbon footprint that is 13 per cent of that of a glass bottle.

Global warming: facing the challenges

Wine production relies on the quality of the grapes, which depends upon the climate they are grown in. Generally, cooler climates are preferred for wine production; those that are warm enough to stop frosts

Courtesy of Lee Hannah and Patrick Roehrdanz

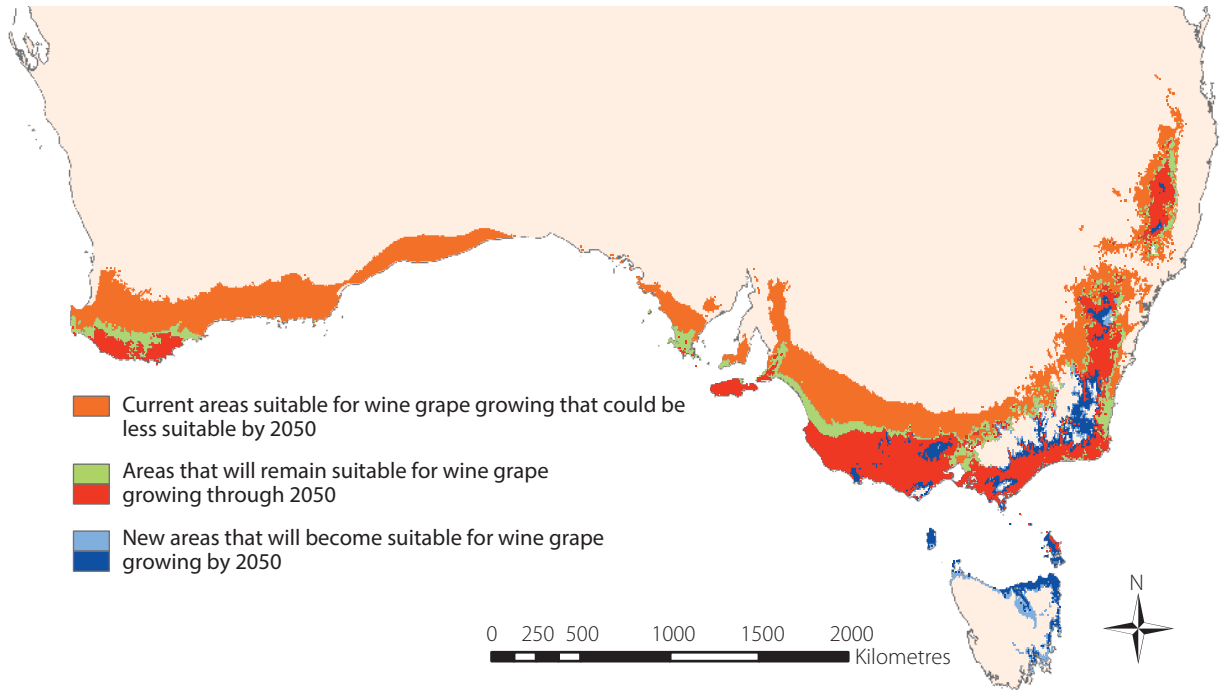

FIGURE 21.4.2 The effect of climate change on wine production

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but cool enough to keep sugar production sufficiently low. Excess sugars make the wine too sweet and result in alcohol levels that are too high. Grapes produced in cooler climates ripen earlier, producing a fresher, more acidic harvest. Each variety has its specific requirements, but generally vines need 1300–1500 hours of sunshine during the growing season and around 690 mm of rain. If the climate is too warm, raisins rather than wine grapes will be made.

It is not surprising that winemakers are concerned about climate change and global warming. Researchers have predicted a two-thirds fall in production in the world's premier wine regions. Australia is facing a dramatic change, as shown in Figure 21.4.2. Some wineries are already shifting to cooler areas like Tasmania, and Western Australian vineyards are introducing water-saving techniques. Other producers are using alternative energy sources, reducing their greenhouse emissions and planting extra trees and shrubs to act as carbon sinks, while some are switching to hotter climate grape varieties or shading the grapes.

Organic wine

Chemists define all wine as organic because wine is based upon carbon compounds. In chemistry, organic materials are those containing carbon (except carbonates, carbon dioxide and carbon monoxide). However, this is not the definition used by the general public. The word 'organic' is often associated with foods that have been grown or produced without pesticides or additives.

Organic wine is produced from grapes that are grown using only products derived from natural sources. The term 'organic wine' means the use of any chemicals in the winemaking process is minimised and each chemical must be certified organic and from a natural source. This means organic wineries also avoid chemical cleaners. Equipment hygiene is maintained through the use of certified organic products or hot water and steam.

Sulfites must be kept to low levels in organic wine. Organic wines are less stable, so they have a shorter shelf life. This is more of a concern with red wines as they are normally cellared for a longer time. People who are allergic to sulfites may avoid them by drinking organic wine.

PRACTICAL ACTIVITY 21.4.1

Sustainability in the wine industry

21.4.1 Sustainable wines

AIM

To evaluate the environmental, social or economic impact of a sustainable practice for the wine industry such as organic wine, green chemistry practices, use of plastic bottles, wine casks or corks

YOU WILL NEED

A computer with Internet access

WHAT TO DO

1. Read the Sustainable wines weblink.
2. Select another winery and search its website for the sustainable practices that they are using.
3. Select one of the sustainability practices to conduct further research. Check with your teacher that your topic is suitable.

»

WHAT DID YOU DISCOVER?

1. Explain what the wineries are doing to increase their sustainability.
2. What are some of the issues the wineries are facing in this task?
3. Are all the wineries solving the problem in the same way?
4. Where are the wineries getting their information from to inform their decisions?
5. Are the consumers responding positively to the changes?
6. Is the practice helping the sustainability, environmental or social impact of the wine industry?

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Define 'atom economy' and state the method for calculating the atom economy of a reaction.

CATEGORY QUESTIONS

2 Explain how using a catalyst can help make a reaction meet the aims of green chemistry.

3 How is atom economy different to percentage yield?

ELABORATION QUESTIONS

4 During the production of oxygen gas by the electrolysis of water, 100 mL of water reacts, producing 65.0 g of oxygen gas.

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

Calculate the atom economy for this reaction.

EVIDENCE QUESTIONS

5 Discuss possible reasons why green chemistry was not implemented when synthesis reactions were first developed.

6 What arguments would you put forward to the chief executives of drug companies to encourage them to implement green chemistry?

END-OF-CHAPTER EXAM

End-of-chapter test

1 Green chemistry aims to:

- **A** design chemical products and processes that work most efficiently.
- **B** use non-renewable energy.
- **C** design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
- **D** design chemical products and processes that maximise profits.

2 Which of the following are among the 12 principles of green chemistry?

- **A** Use catalysts, not stoichiometric reagents
- **B** Design commercially viable products
- **C** Reuse waste
- **D** Use only new solvents

3 Biodiesel is an example of which of the 12 principles of green chemistry?

- **A** Use of catalysis
- **B** Safer solvents
- **C** Use of renewable feedstocks
- **D** Waste prevention

4 Green chemists reduce risk by:

- **A** minimising the use of all chemicals.
- **B** reducing the hazard inherent in a chemical product or process.
- **C** developing recycled products.
- **D** inventing technologies that will clean up toxic sites.

5 Use the 12 principles of green chemistry to critically analyse the Haber process for the industrial production of ammonia, which was discussed in Chapter 20. Could the Haber process be described as a green process? Write an extended response to explain why or why not this is the case.

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22 POLYMERS, PROTEINS AND CARBOHYDRATES

Introduction

The structure and properties of polymers was covered in detail in Chapter 18. As mentioned, polymers are giant molecules, often called macromolecules, which form when many smaller molecules, called monomers, are joined by covalent bonds. The process of linking monomers together is called polymerisation.

The two most common polymerisation reactions are:

1. addition polymerisation, which involves an addition reaction
2. condensation polymerisation, which involves a condensation reaction.

Stimulus questions

How can one polymer be changed or modified to produce substances possessing a wide variety of properties such as strength, density, hardness and biodegradability?

What are the common features of polymerisation reactions that produce important synthetic substances such as polyesters and important biological polymers such as proteins and starch?

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22.1 Describing the production of addition polymers

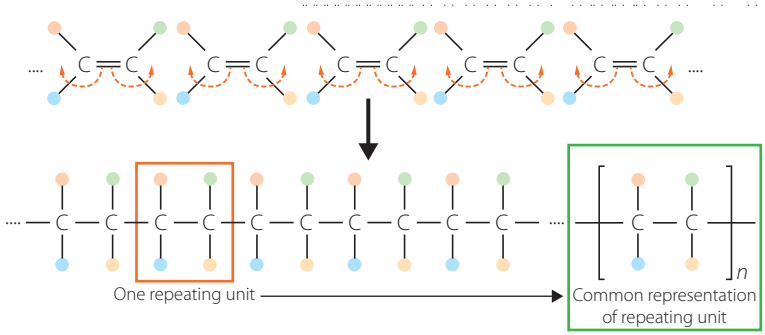
addition polymers polymers formed by adding together molecules without the loss of any atoms

Addition polymers form by adding together molecules without the loss of any atoms. They do this through addition polymerisation, which is a type of addition reaction.

For addition polymerisation to occur, the monomer must have a double bond between two carbon atoms. The breaking of the double bond provides each carbon with an available bond to form bonds between the monomers. The number of monomer units that make up these polymers may range from 100 to more than 100 000. The structure of the monomer determines the structure and properties of the polymer formed.

The general process for the formation of addition polymers is shown in Figure 22.1.1.

FIGURE 22.1.1 A schematic diagram of the formation of an addition polymer from an alkene



Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

Polymers from ethene (ethylene)

One of the most common addition polymerisation reactions occurs in the production of polyethene, which involves the linking of ethene molecules into long chains. Note that while polyethylene is the common name for the polymer produced, the IUPAC preferred name is polyethene. Therefore, the name polyethene will be used when referring to this polymer.

The production of polyethene is represented by the general equation:

$$n(CH_2{=}CH_2) \rightarrow -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

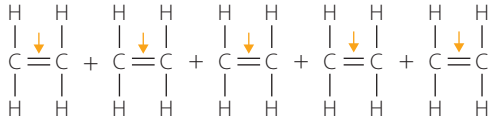
SCIENCE AS A HUMAN ENDEAVOUR

POLYETHENE

Shortly after the discovery of polyethene, World War II began. Within a few years, the production of polyethene increased dramatically as it became a strategic military material. It was used as electrical insulation for high-frequency radar cables. Production spiralled from 8 grams in 1935 to 1441 tonnes in 1944.

During this addition polymerisation reaction, one of the bonds in each of the C=C double bonds is broken, under the influence of a catalyst at high temperature and pressure. This leads to formation of covalent bonds between C atoms on adjacent monomers (ethene molecules) as can be seen below.

In the presence of a catalyst, one of the bonds in each C=C is broken.



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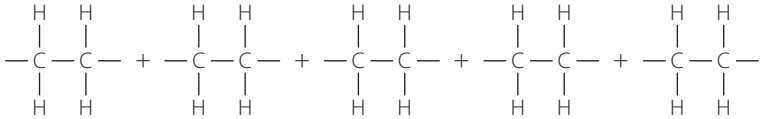
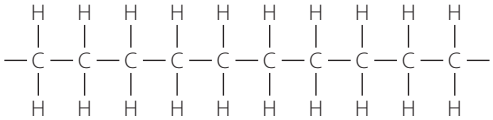
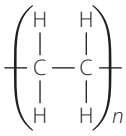
This frees up one electron on each C for further bonding.



New carbon–carbon bonds form between adjacent molecules to give polymer chains.



As can be seen, the polymer is made up of repeating CH_2—CH_2 units, so the structure of the polymer is often written in an abbreviated form $(—CH_2—CH_2—)_n$:



or

where n is the number of monomer units in the molecule.

There are two types of polyethene: low-density polyethene (LDPE) and high-density polyethene (HDPE). They are produced by two different processes. Their different properties are a result of the differences in their structures.

LDPE is produced by a gas phase process using high temperature (300°C), high pressure (1000–3000 atm) and an initiator (to start the reaction). This product has significant chain branching due to some of the hydrogen atoms being replaced by an alkyl group. The branches prevent the polymer chains packing closely together so there is a lot of space in the product and fewer dispersion forces between them. This leads to its low density, low melting point and greater flexibility.

The Ziegler–Natta process for the production of HDPE uses lower pressures (only a few atmospheres) and low temperatures (60°C) and a catalyst that is a mixture of titanium(III) chloride and trialkylaluminium compound (e.g. $(CH_3CH_2)_3Al$). The process forms unbranched polyethene chains that can pack closely together in an orderly way. Because the chains are packed more closely together, this product has a higher density. There is also stronger bonding because there are more dispersion forces between chains, resulting in higher melting point and less flexibility.

HDPE has a more ordered structure so is said to be more crystalline, while LDPE with its more random structure is amorphous (non-crystalline). Figure 22.1.2 shows the difference between the linear chains of HDPE and the branched chains of LDPE.

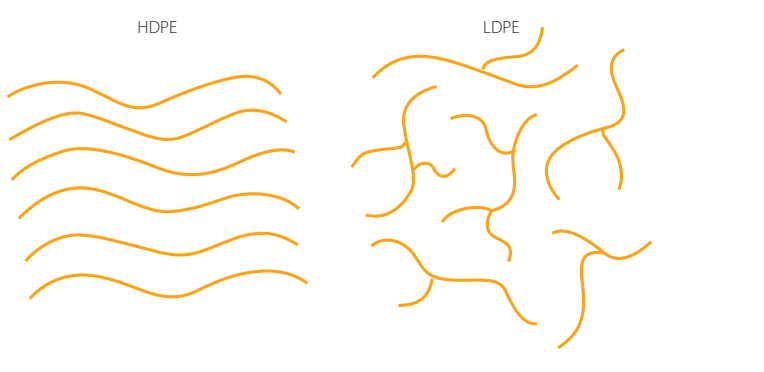


FIGURE 22.1.2 Different arrangements of polymer chains in HDPE and LDPE

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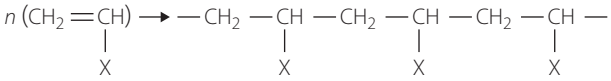
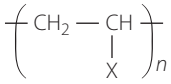
Other addition polymers

As well as being used directly to produce polyethene, ethene is converted into a range of other useful monomers, which are, in turn, used to produce polymers.

The general reaction for the production of a polymer from an alkene was shown in Figure 22.1.1, where each coloured circle represented an H or a substituent group. This can also be represented by the general equation:



where X may be hydrogen or a substituent group. Substituting the hydrogen with different substituent groups, such as a halogen, benzene or alkyl group, produces polymers with different properties. As with polyethene, this can be abbreviated to:



One or more hydrogen atoms of the alkene may be replaced by a different substituent group.

Polytetrafluoroethene (Teflon)

Polytetrafluoroethene (PTFE) is a polymer formed from the monomer tetrafluoroethene, which has the formula $—CF_2═CF_2—$. All the hydrogen atoms have been replaced by fluorine atoms. The structure of the resulting polymer is shown in figure 22.1.3.

Polypropene

Polypropene manufacture uses catalysts, including Ziegler–Natta catalysts, to convert propene to polypropene. The structure of propene and the abbreviated form of the polymer is shown in Figure 22.1.4.

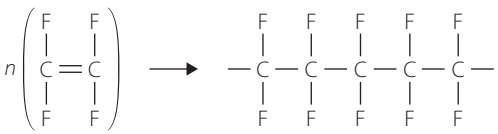


FIGURE 22.1.3 The structure of polytetrafluoroethene

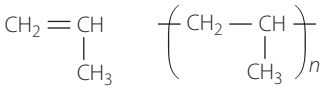


FIGURE 22.1.4 The structure of propene and the abbreviated form of the polymer

TABLE 22.1.1 Summary of three important addition polymers, the monomers they are made from and some of their uses.

POLYMER	NAME AND STRUCTURE OF THE MONOMER	COMMON USES
Polyethene	Ethene (ethylene) $CH_2═CH_2$	LDPE: milk bottles, soft toys, plastic wrap (cling wrap) HDPE: kitchen utensils and containers, more rigid toys, rubbish bins, tougher carry bags
Polypropene	Propene $CH_2═CH—CH_3$	Car bumpers, rope and twine, household goods, moulded chairs, carpets
Polytetrafluoroethene PTFE (Teflon)	Tetrafluoroethene $F_2C═CF_2$	High-grade electrical insulation, non-stick surfaces on cookware, pipe thread sealant

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SECTION REVIEW 22.1

REMEMBERING

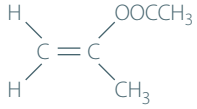
1 **a** Describe what is necessary in a monomer for addition polymerisation to occur.

b Explain the process of addition polymerisation.

2 Name the most common addition monomer and polymer:

APPLYING

3 Perspex is made by addition polymerisation from the monomer:



Draw part of the polymer of Perspex (include at least three monomer units).

4 Given the polymer:

a write down the structural formula of the repeating unit.

b write down the structural formula of the monomer.

22.2 Describing the production of condensation polymers

Addition polymerisation requires that the monomer have a double bond. However, if organic molecules have a functional group at each end, the functional group can undergo a condensation reaction with a functional group on another molecule to form a **condensation polymer**. Condensation polymers are formed when two monomer molecules join together to eliminate a small molecule (often water). The process is called condensation polymerisation. Functional groups such as —NH_2, —OH, —COOH and —COCl are suitable for condensation polymerisation.

condensation polymer when two monomer molecules join together to eliminate a small molecule (often water)

Polyesters and polyamides (nylons) are examples of synthetic condensation polymers whereas polypeptides (proteins) and polysaccharides (cellulose and starch) are examples of natural condensation polymers.

22.2.1 Nylons

Polyesters

Polyesters are condensation polymers in which the monomers are joined by an ester link. An ester and water are formed when a carboxylic acid reacts with an alcohol.

To form a polyester, the monomer molecules need to join at each end, which means they need to have either a carboxylic acid or an alcohol functional group at each end.

Polyesters can be produced from:

- a single monomer that has a hydroxyl (—OH) functional group at one end and a carboxyl (—COOH) functional group at the other
- two different monomers – one monomer with hydroxyl groups at each end (a diol) and one monomer with carboxyl functional groups at each end (a dicarboxylic acid).

The general production of a polyester from a single monomer is shown in Figure 22.2.1. The monomers must be aligned so the hydroxyl and carboxyl acid groups are next to each other.

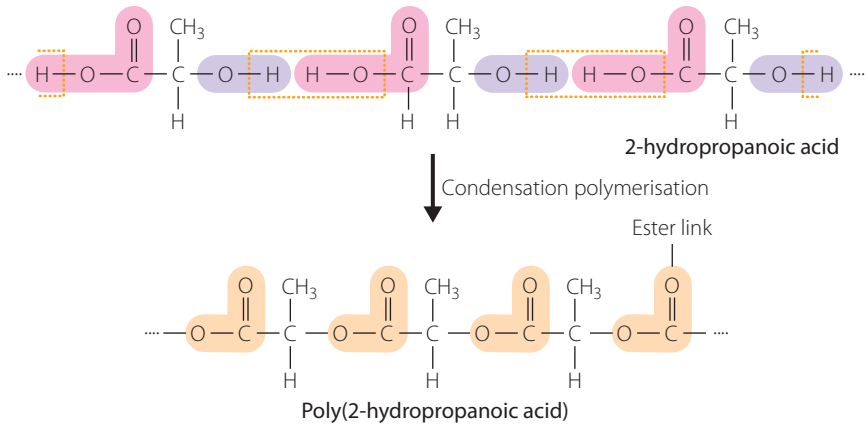


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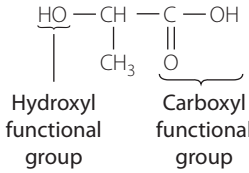
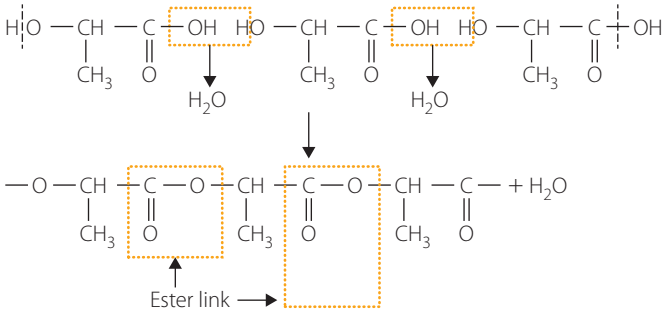
FIGURE 22.2.1 The formation of a polyester from a single monomer

An example of a polyester is poly(lactic acid), which is used to make biodegradable surgical sutures. Lactic acid (2-hydroxypropanoic acid) has a hydroxyl (—OH) functional group at one end and a carboxyl (—COOH) functional group at the other. The structure is:

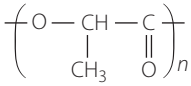


22.2.2 Polyesters and how they are manufactured

The molecules are able to polymerise through an esterification reaction between the carboxyl group of one molecule and the hydroxyl group of another, as shown below.



The general formula for the polymer is:



One disadvantage of a polyester is that it is easily damaged by acids and alkalis. This results in the ester linkages being hydrolysed back to the acid and alcohol monomers. Therefore, polyester fabrics will end up with holes if an acid or alkali is spilled on them.

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Polypeptides (proteins)

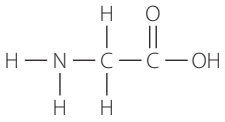
Polypeptides are an important class of naturally occurring condensation polymers. In the case of polypeptides, the monomers are amino acids.

Amino acids contain the amino ($—NH_2$) functional group and the carboxyl (—COOH) functional group. This means amino acids have both acidic and basic properties.

The special structural features common to the 20 amino acid monomers that form proteins are:

- the amino and carboxyl functional groups are attached to the same carbon atom (called the alpha-carbon)
- a hydrogen attached to the alpha-carbon.

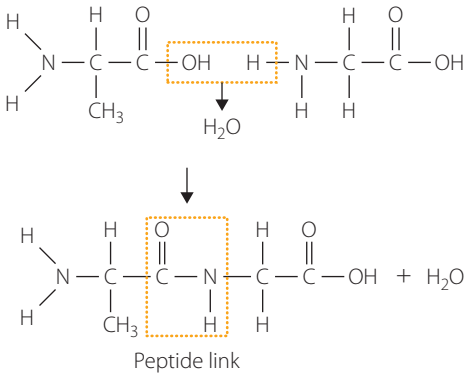
The simplest amino acid is glycine, which has the structure:



Joining amino acids

Amino acids undergo condensation polymerisation to form an amide. The bonds that hold amino acids together are covalent bonds. The link that joins two amino acids together is called a peptide link. The compound formed when two amino acids join together is called a dipeptide and when long chains of amino acid units join, the result is a polypeptide.

For example, when glycine reacts with alanine, the result is the alanylglycine dipeptide:



The resultant dipeptide has functional groups at each end so it can continue to react with other amino acids to produce a polypeptide as shown in Figure 22.2.2.

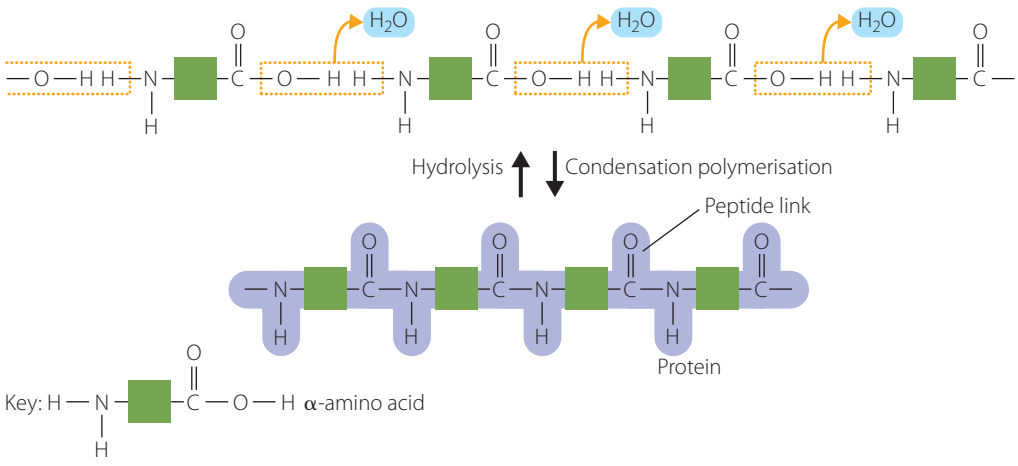


FIGURE 22.2.2 Forming a polypeptide and breaking it down again

Polysaccharides

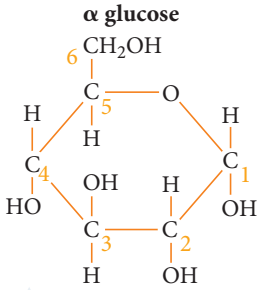


FIGURE 22.2.3 The structure of α-glucose

Polysaccharides are an important class of naturally occurring condensation polymers. In the case of polysaccharides, the monomers are monosaccharides. Common monosaccharides include glucose, galactose and fructose. Glucose is the most important of these in human nutrition because sugar in this form is used by our bodies as an energy source.

The structure of α glucose, an isomer of glucose, is shown in Figure 22.2.3.

Joining monosaccharides

Monosaccharides undergo condensation polymerisation to form polysaccharides. A polysaccharide may contain one type of monomer or different types.

The link that joins two monosaccharides together is called a glycosidic bond. The compound formed when two monosaccharides join together is called a disaccharide and when long chains of monosaccharide units join, the result is a polysaccharide.

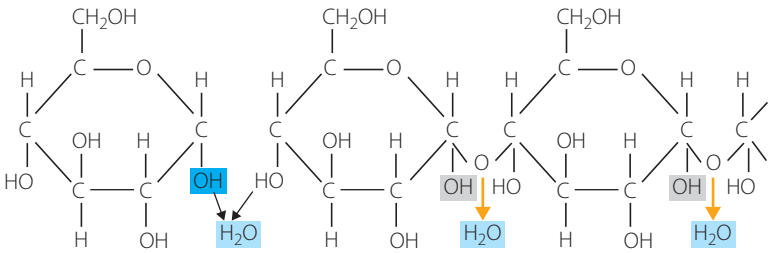


FIGURE 22.2.4 Forming the polysaccharide starch from α-glucose monomers

SECTION REVIEW 22.2

REMEMBERING

1 Name two types of condensation polymers.

2 Explain how condensation polymerisation is different from addition polymerisation.

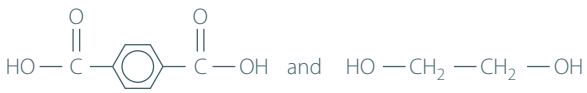
3 Draw the structure of:

- **a** an ester linkage
- **b** a peptide link
- **c** a glycosidic link.

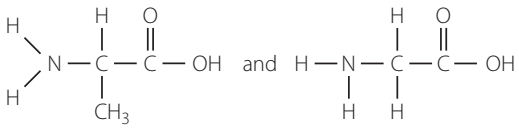
APPLYING

4 Draw three repeat segments showing the structure of the polymers formed when the following react.

a



b

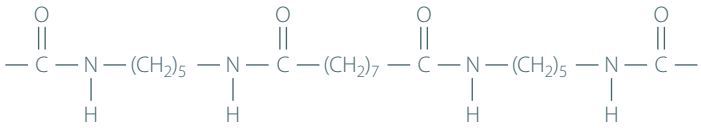


5 For each of the polymers in Question 4:

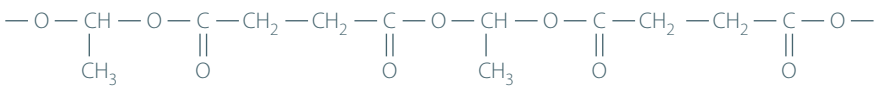
- **a** identify the type of polymer
- **b** circle and name the type of link present
- **c** name the functional group present in the monomer.

6 For each of the polymers i and ii:

i



ii



a identify the type of polymer

b draw the structure of the monomers

c name the monomers.

22.3 Advantages and disadvantages of polymer use

When selecting polymers for particular purposes, it is important to match the properties of the polymer with its intended use. The properties depend on the structure of the polymer molecules and the bonding present.

Important structural features are:

- crystallinity
- branching
- chain length
- side groups
- cross-linking
- stability and biodegradability.

Crystallinity

Molecules of linear polymers such as polyethene can flex and twist. As a result, some molecules will be tangled. The final polymer will have regions that are crystalline and regions that are amorphous (which was observed in the spaghetti cake simulation in Chapter 18).

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FIGURE 22.3.1 Crystalline and amorphous regions in a polymer

In crystalline regions, the polymer chains are closer together, so the intermolecular bonding is stronger. This leads to greater rigidity, and higher softening and melting points. Other properties that arise when the chains are closer are greater density, opaque appearance, and resistance to air, moisture and chemicals. Crystalline regions are non-permeable.

In amorphous regions, the chains are tangled, disordered and have no definite structure. The large gaps between chains means the intermolecular forces are weaker. This leads to more flexibility, and

lower softening and melting points. Other related properties include transparency, permeability to water, air and chemicals and lower density.

The degree of crystallinity in a polymer determines the properties related to that factor. In commercial polymer production the percentage of crystalline and amorphous regions can be controlled. As a result, manufacturers can control many of the properties of the resulting polymer.

Branching

Chains with little or no branching can pack together more closely than chains with a high degree of branching. Therefore, polymers with low chain branching will tend to be more crystalline; they will be denser, less transparent and less flexible than polymers with a high degree of chain branching, which tend to be more amorphous.

The formation of highly branched structures requires more extreme reaction conditions because covalent bonds have to be broken to insert a branch.

Chain length

Chain length is controlled by the conditions and proportions of chemicals used in the polymerisation process. In any batch of polymer, there will be chains of different lengths so the average molecular weight is considered as this reflects the number of monomer units that combine to make one polymer molecule.

For a given type of polymer, the longer the chain length and the smaller the differences in chain length, the higher the melting point and the harder the polymer.

Chain length affects the flow characteristics of the softened polymer, which in turn affects the manufacturing processes. Long chains make the softened polymer more viscous and difficult to extrude, whereas chains that are too short mean the extruded product will sag as it exits the machine. Also, short chains cannot withstand moulding processes that involve blowing the polymer into shape using gases at high temperature.

Side groups

Another way to change the properties of a polymer is to change the side groups that are attached to the carbon backbone. Putting a bigger side group into a linear chain reduces the flexibility of the polymer, making it stiffer. For example, replacing a hydrogen in polyethene with a chlorine atom (PVC) or a benzene ring (polystyrene) restricts the ability of the chain to flop around and causes the material to become stiffer and more rigid.

Cross-linking

cross-linking linear chains linked together to form a more rigid two- or three-dimensional structure

The rigidity and hardness of a polymer can be increased by **cross-linking**. In this process, linear chains are linked together to form a more rigid two- or three-dimensional structure. These cross-links usually form strong covalent or ionic bonds between the polymer chains. The greater the amount of cross-linking, the more strongly the polymer chains are bonded and the more rigid the polymer. Figure 22.3.2 shows an example of cross-linking.

For example, if natural rubber is heated with some sulfur, S—S bonds form between adjacent chains. This makes the material harder and more elastic. This process is called vulcanisation.

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FIGURE 22.3.2 Cross-linking joins chains to each other.

22.3.1 Expanded polystyrene foam

PRACTICAL ACTIVITY 22.3.1

Making a cross-linked polymer

PVA glue is made of long chains of poly(vinyl alcohol), which slide past each other fairly easily, allowing the glue to be poured from the bottle. When borax is mixed with the PVA glue, tetrahydroxyborate ions ($B(OH)_4^-$) form bonds between the polymer molecules of the PVA. The resultant 'slime' is an example of a cross-linked polymer.

AIM

To make slime and test its properties

MATERIALS

- 50 mL of poly(vinyl alcohol)
- 10–15 mL of 4% solution of borax (4 g sodium borate (borax) in 96 mL water)
- distilled water
- disposable plastic cup
- 10 mL measuring cylinder
- wooden paddle pop stick
- gloves
- newspaper

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
Borax and PVA will burn eyes.	Wear a laboratory coat and safety glasses and wash your hands at the end of the experiment. Keep your hands away from your eyes while using the chemicals.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Cover your work area with a few layers of newspaper.
2. Place 50 mL of PVA glue in a plastic cup and add 50 mL of water. Mix thoroughly.
3. Slowly add the borax solution, approximately 5 mL at a time, stirring thoroughly with a wooden paddle pop stick upon each addition. Be careful not to add too much borax or the slime will become too stiff.
4. Remove the slime with the wooden stick and work it with your hands until it is no longer sticky.
5. Test the properties of slime:
   - **a** Take some of the slime in one hand and stretch it slowly. Repeat the stretching exercise rapidly. Does it break apart easier when pulled quickly or slowly?
   - **b** Place the slime in a ball on the table and poke it quickly with your finger. Poke it again slowly. What happens?
   - **c** Form the slime into a ball and see if it bounces.
   - **d** Place a ball of slime on the table and observe it for a few minutes. Does it flow into a puddle or maintain its shape? Does this demonstrate that the slime is a liquid or a solid?
   - **e** Press the slime down on a piece of newspaper. Is the image transferred to the slime?
   - **f** Write on a piece of paper with a permanent marker and then with a water-based marker. Press the slime down on the writing. Is the image transferred to the slime?

»

» g Try to make slime bubbles by wrapping the slime around the end of a straw and blowing gently. An airtight seal must be made between the straw and the slime.

h Place a small amount of slime on a paper towel and set it aside to dry until the following lesson. Note any differences in its appearance and properties.

RESULTS

Record your observations and results of the property tests.

ANALYSIS OF RESULTS

Describe how cross-linking has changed the properties of PVA.

DISCUSSION

22.3.2 Plastics and polymer films

1 a Write the formula for the monomer of PVA.

b Draw a structural diagram of a section of a PVA polymer (including at least four repeating units).

2 Draw a diagram to show how the borax forms cross-links between the polymer chains. Use information in Weblink 22.3.1 to help draw your diagram.

3 How does water affect the elasticity of the polymer?

Stability and biodegradability

Most of the bonds in polymers are strong covalent C—C and C—H bonds, so the polymers are fairly stable. This means that most synthetic polymers, unlike natural polymers, are not biodegradable.

However, PVC has C—Cl bonds, which are weaker than C—H bonds, and are broken by ultraviolet light. The polymer becomes brittle and cracked if it has been in sunlight for some time. Special additives, called stabilisers, are added to the polymer to protect it from degradation.

To increase the biodegradability of synthetic polymers, chemists have copolymerised them with natural polymer segments, such as those in starch. This causes the polymer chain to break down into many smaller segments.

Disadvantages of polymer use

Synthetic polymers, usually referred to as plastics, are fundamental to our lifestyle. They are found in packaging, adhesives, clothes, medical devices and so many other materials that it would be impossible to list them all. These materials have revolutionised sports equipment and been responsible for major advances in electronic technology. The amount of polymers used in the aviation industry has doubled in the last decade because they can be engineered to offer strength and lightness.

From an early age, we have been surrounded by plastic: plastic toys, plastic containers, plastic bags, even non-stick coating on pans, chewing gum and Lycra in clothes. The development of plastics has only occurred in the last 70 years or so and they have only been used on a massive scale over the last 60 years.

Plastics are amazing materials; they come in every shape, size and colour, and with every material property you could think of: strong, flexible, elastic, hard, ductile, transparent, slippery, brittle, to name a few. As chemists develop new plastics, the variety of properties and uses expand dramatically.

However, the widespread distribution and use of plastics has not been without cost. There are two main problems that need to be considered as plastic use continues to escalate. One is what to do with plastic articles after we have finished using them and the other is to find a new source of the raw material of plastic manufacture as the current one runs out.

Recycling plastics: where do they go?

By the 21st century, the volume of plastics on the world market exceeded the total volume of metals. Plastic production worldwide now exceeds 300 million tonnes a year. The amount of plastic manufactured in the first 10 years of this century equals the total produced for the entire last century. Only about 10 per cent of that is recycled. Australia is one of the highest waste producers per person in the world, currently ranked in the top five waste-producing nations.

Australia contributes almost 1.3 million tonnes to plastic production, which is more than 71 kg for every person. Packaging is the largest market for plastics with approximately 376 000 tonnes used per year, accounting for over a third of the consumption of raw plastic materials. Australians use 15 253 tonnes of soft-drink bottles, 30 000 tonnes of milk bottles and 6.9 billion plastic bags every year.

While plastic packaging provides excellent protection for the product and is lightweight compared to metal or cardboard, it is proving to be a major environmental problem. In the past, more than one-third of the plastic consumed in Australia was destined for landfill but today many local councils have recycling facilities for plastic materials.

Six polymeric materials account for 66 per cent of all plastics used, but not all of these can be recycled. Since most plastics are incompatible when mixed together, the different types of plastics need to be separated before they can be recycled. To help identify plastics, manufacturers use a plastics identification code, which is normally stamped on all products.

22.3.3 How plastics are recycled
22.3.4 Plastic identification codes

Recycling is beneficial for the environment in a number of ways. Apart from reducing the amount of landfill, recycling plastic to make new products is more energy efficient and uses only 30 per cent of the energy required to make the original product. Recycling 1 tonne of plastics can save enough energy to run a refrigerator for a month. It takes 125 recycled plastic milk bottles to manufacture a 140-litre wheelie bin.

As well as saving energy, recycling reduces the amount of raw material needed to produce plastics.

Currently, Australians recycle approximately 23 per cent of plastic packaging products. The majority of the remainder goes into landfill. This is creating a major waste management problem. Plastic debris has accumulated in natural habitats from the poles to the equator with substantial quantities in marine environments.

There is also evidence that plastics are fragmenting in the environment and, as a consequence, more organisms will begin to ingest these smaller fragments. There is speculation that this will lead to the transfer of toxic chemicals to wildlife.

22.3.5 Plastic pollution

Polymers: Where do they come from?

Today, much of the raw material for plastics comes from petroleum (crude oil). Crude oil is used mainly as a source of fuel for cars, aeroplanes and trains. However, it has also become an important source of chemicals for making new materials, such as plastics, medicines and fertilisers.

The refining of crude oil by fractional distillation produces an impressive array of products. Crude oil contains a range of hydrocarbons that vary in size and structure, including straight and branched alkanes, alkenes and cyclic hydrocarbons.

The most widely used starting substance for making polymers is ethene. Ethene is obtained from crude oil, either as a by-product of petrol refining or by the deliberate decomposition or cracking of some of the higher boiling point fractions.

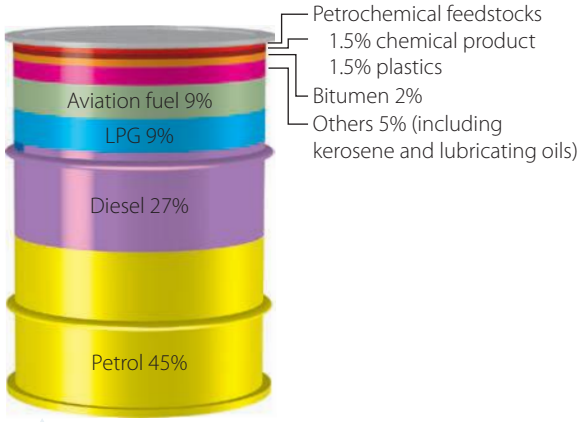


FIGURE 22.3.3 Products made from refining one barrel of crude oil

Health concerns

Most of the polymers in use contain small molecules, either unreacted monomer molecules or additives such as plasticisers or flame retardants deliberately added to give a desired property. These molecules can move through the material and can be released into the air or water supply.

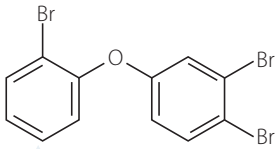


Figure 22.3.4
Tribromodiphenyl ether – one of a class of fire retardant polymer additives causing environmental concern

Recent studies have shown that the class of compounds known as polybrominated diphenyl ethers (PBDEs) which have found widespread use as flame retardant additives in many plastics, may be carcinogenic.

An environmental concern associated with many of the most widely used plastics such as HDPE, LDPE, polypropene and PVC is their degradation over time, producing microscopic particles called microplastics. These particles absorb dangerous substances called persistent organic pollutants (POPs). These pollutant- soaked particles can then be ingested by organisms in the biosphere.

SECTION REVIEW 22.3

REMEMBERING

1 Explain how the percentage of crystalline regions and amorphous regions in a polymer affect its properties.
2 What is cross-linking and how does it change the properties of a polymer?

UNDERSTANDING

3 Explain the relationship between crystallinity and branching.
4 Suggest explanations why:
   a polymers with larger side groups are stiffer.
   b polymers with longer chains form more viscous liquids.

APPLYING

5 Suggest why cross-linked polymers are not recycled.
6 List four properties that would make a polymer suitable for use as a:
   a disposable juice bottle
   b bag in which a roast can be cooked in the oven
   c transparent cover for outdoor light bulbs
   d tubes for a drip in a hospital
   e plastic raincoat.
7 Explain how biodegradable polymers can be produced using natural polymers such as starch.

22.4 Condensation reactions of amino acids

In Section 22.2 the condensation reaction between two amino acids to form dipeptides and, ultimately, polypeptides was introduced. In this section, the condensation reaction between amino acids will be explored in more detail.

As seen in Chapter 18, the general structure of an α amino acid has an amino functional group (—NH_2) and a carboxyl group (—COOH) attached to the same carbon atom, as well as a hydrogen atom and an 'R' group.

Forming the peptide bond

The simplest dipeptide is formed from the simplest amino acid, glycine.

A further condensation reaction can occur to give a tripeptide. For example, using the amino acids alanine, glycine and phenylalanine.

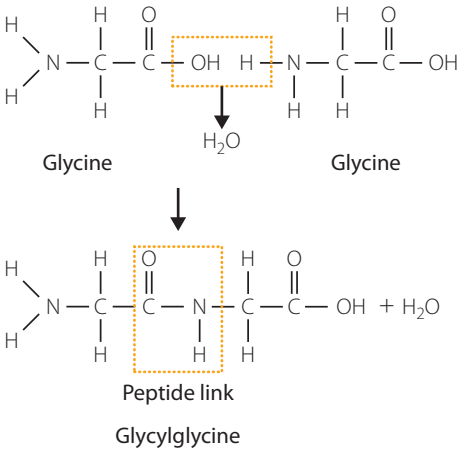


FIGURE 22.4.1
Dipeptide formed from glycine

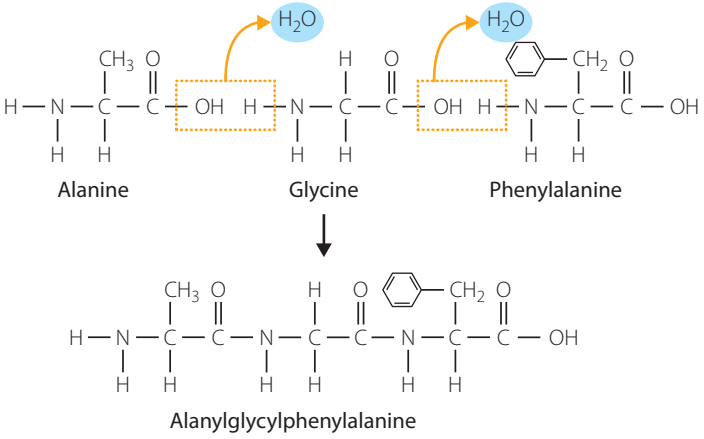


FIGURE 22.4.2
Formation of the tripeptide alanylglycylphenylalanine

The resultant tripeptide has functional groups at each end so it can continue to react with other amino acids to produce a polypeptide as shown in Figure 22.4.2.

Unlike some other polymers, which have a regular repeating unit, polypeptides can have various combinations of amino acids. Biochemists have developed a shorthand way of drawing them. Each of the 20 amino acids that make up the body's proteins has been given a three-letter abbreviation, as can be seen in the examples in Figure 22.4.1. In this example, the tripeptide alanylglycylphenylalanine, can be written as Ala–Gly–Phe. A possible sequence of a peptide with eight amino acids is Lys–Cys–Asp–Cys–Gly–Val–Val–Thr.

When hundreds to thousands of amino acid units join together, the result is a protein. So proteins are giant polypeptides. In the final protein, there is still an amino group at one end and a carboxyl group at the other.

SECTION REVIEW 22.4

REMEMBERING

1 Draw and name the link that occurs between amino acid monomers.

UNDERSTANDING

2 Draw the structural formula of a dipeptide formed between the following amino acids and identify the link between them.

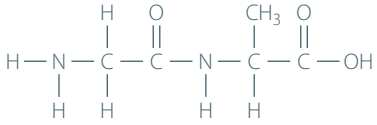
a Alanine and cysteine

b Glycine and serine

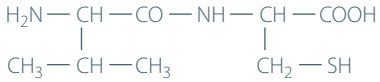
APPLYING

3 Write the equation for the hydrolysis of the dipeptides shown below and name the amino acids formed.

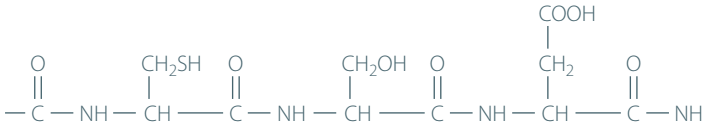
a



b



4 A section of a protein chain is shown.



a How many different amino acids reacted to produce this segment?

b Draw the structure of the amino acids identified in part a.

22.5 Condensation reactions of monosaccharides

The condensation reaction between monosaccharides to form polysaccharides was introduced in Section 22.2. We will now discuss this reaction between monosaccharides in further detail.

Disaccharides

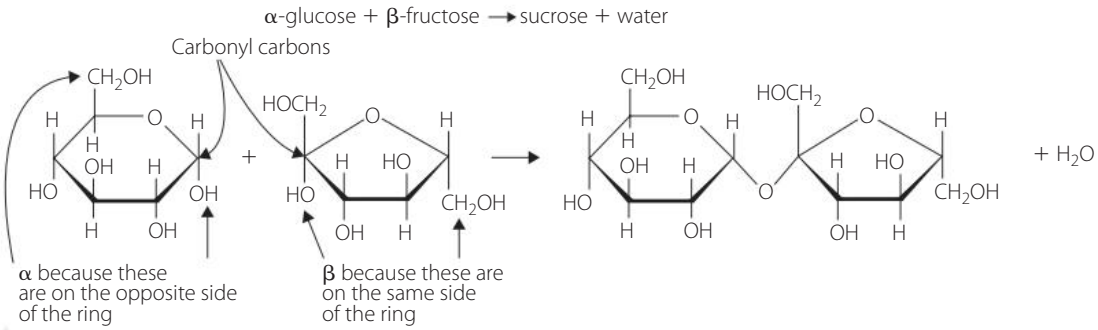
Monosaccharides are the building blocks of other carbohydrates. When two monosaccharides join, they form a disaccharide. Common disaccharides are sucrose from cane sugar, maltose from malt and lactose from milk.

The reaction that occurs to form the disaccharide is a condensation reaction because a water molecule is released. This can be written simply as:

$$2C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$$

While the molecular formula makes the reaction seem simple, when the structural formulas are considered the situation becomes more complicated because there are different isomers and different forms of these isomers.

Sucrose is formed by linking the carbonyl carbons of α-glucose and β-fructose.



Smith et al. 2010 Chemistry in use. Book 2

FIGURE 22.5.1 The formation of sucrose

The link that joins the monosaccharides is called **a glycosidic link**, —C—O—C—.

Maltose is produced when two glucose monomers join and lactose is produced when a glucose monomer and a galactose monomer join.

These three disaccharides have different properties due to their different structures. Maltose and galactose are not as sweet as sucrose while fructose is sweeter than sucrose. Their melting points are: lactose 253°C, sucrose 186°C and maltose 160°C. They have similar densities.

Disaccharides are too large to pass through cell membranes so they need to be broken down to their constituent monomers in the digestive system. This hydrolysis reaction is the reverse of the condensation polymerisation reaction by which they are formed and adds water to give a new —OH group to the fructose ring and 3H to the oxygen on the glucose ring.

PRACTICAL ACTIVITY 22.5.1

Analysing sugar in soft drinks

Recently consumers have become more conscious of the number of kilojoules (or calories) in food and drinks. The kilojoules in soft drinks are due to a sugar. A broad range of drinks is marketed according to their sugar content or lack of sugar; for example, Coke Zero, Pepsi Max.

Sugar also increases the density of a solution. You may have already performed some investigations related to density of solutions if you studied Context 1, 'Wine', on page 5. The density of solutions of unknown sugar concentration can compared with the densities of sugar solutions of known concentration.

AIM

Write an aim for your experiment.

MATERIALS

- 60 g sugar
- six 100 mL beakers
- distilled water
- 10 mL pipette
- pipette filler
- electronic balance
- drinks to test, such as Coca-Cola, Pepsi, diet soft drink, apple juice, sports drink, Lucozade

RISK ASSESSMENT

WHAT ARE THE RISKS IN DOING THIS EXPERIMENT?	HOW CAN YOU MANAGE THESE RISKS TO STAY SAFE?
The samples could become contaminated.	Do not consume any of the drinks being tested.

In your write-up, add any more risks you can think of, as well as ways to manage them.

PROCEDURE

1. Prepare 100 mL of each of five standard sugar solutions of (% weight/weight) 0%, 5%, 10%, 15% and 20%. For example, a 5% solution can be made by dissolving 5 g of sugar in 95 g of water.
2. Weigh an empty beaker.
3. Use the pipette to add exactly 10 mL of the 0% sugar solution to the empty beaker and reweigh it.
4. Record the masses in a data table.
5. Repeat steps 2–4 with each of the prepared solutions. Make sure you rinse the pipette and remove any trapped liquid between each use.
6. Calculate the density of each of the standard solutions.
7. Repeat steps 2–4 with each of the drinks provided. Note: carbonated drinks must be allowed to go flat before performing any measurements.

RESULTS

Draw up a table similar to the following to record your results.

SUGAR SOLUTION OR DRINK	MASS OF EMPTY BEAKER (g)	MASS OF BEAKER WITH SOLUTION (g)	MASS OF SOLUTION (g)	VOLUME OF SOLUTION (mL)	DENSITY (g mL^2)
0%					
5%					
10%					
15%					
20%					

ANALYSIS

1. On a piece of graph paper, plot a graph of density versus sugar content (%) and draw the line of best fit.
2. Use the graph to determine the sugar content of each of the drinks you tested.

DISCUSSION

1. **a** Why did you need the carbonated drinks to go flat before conducting the test?
   b If this had not been done, what effect would it have had on the values obtained?
2. What value did you obtain for the diet drink? What did you expect? Comment on any difference.
3. The sugar found in most drinks is usually fructose; however, you used sucrose to make the standard solutions. Use a chemical data book to find out the densities of fructose and sucrose. Comment on what assumption was made about the densities in this experiment and how this impacted the results.

CONCLUSION

Summarise what you have found.

Polysaccharides

Polysaccharides were covered in Chapter 18. Polysaccharides are all polymers of glucose with different glycosidic links, amount of branching of the polymer chain and degree of polymerisation.

The nature of the glycosidic linkage is different because cellulose consists of long chains of β-glucose joined together, while starch and glycogen consist of α-glucose molecules joined together (Figure 22.5.2).

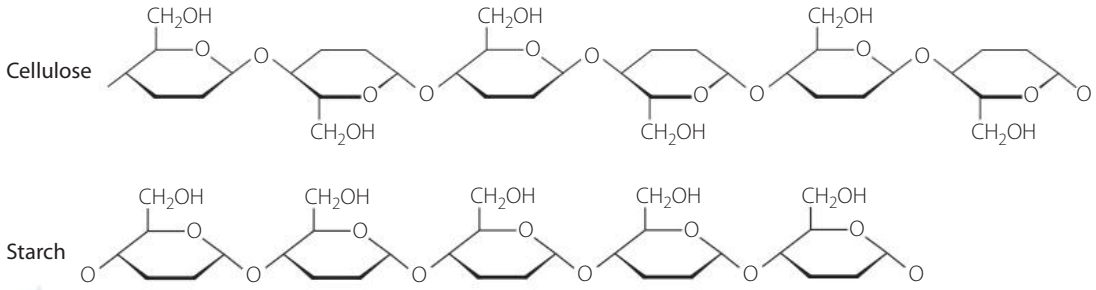


FIGURE 22.5.2 The structures of starch and cellulose

The starch polymer consists of two parts. The smaller part (about 20 per cent), amylose, is a straight-chain polymer that can form spirals due to intrachain hydrogen bonding. Amylopectin, which forms the major part (80 per cent), is a highly branched chain. These chains occur when one glucose molecule condenses with three other glucose molecules instead of the normal two. This part of the molecule cannot form spirals.

Cellulose has unbranched molecules that preferentially form hydrogen bonds with each other to form a strong cross-linked type structure. This cross-linking gives cellulose its strength and rigidity. Unlike starch, cellulose is insoluble in water. Cellulose is a highly crystalline polysaccharide, which accounts for many of its properties.

Glycogen is highly branched with an amorphous structure.

22.5.1 Carbohydrates

SECTION REVIEW 22.5

REMEMBERING

1 Describe the differences between monosaccharides, disaccharides and polysaccharides.
2 Name and draw the structure of the linkage that joins monosaccharide units together.
3 What functional group is characteristic of carbohydrates?

UNDERSTANDING

4 Explain why monosaccharides and disaccharides are soluble in water.
5 **a** Why is the combined mass of the monosaccharides resulting from the hydrolysis of a disaccharide greater than that of the disaccharide?
b Write the equation for the hydrolysis of sucrose.
6 Describe the differences between cellulose, starch and glycogen in terms of their structure, bonding and properties.

ANALYSING

7 Using the empirical formula for starch, $C_6H_{10}O_5$:
a calculate the percentage of oxygen and carbon in one repeating unit
b calculate the molecular weight of a molecule of starch that contained 300 monomer units
c write an equation for the hydrolysis of one unit
d write an equation for the hydrolysis of 50 units
e explain whether or not the equation is accurate and why.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Describe the similarities and differences between addition and condensation polymerisation.

2 Explain how and why the following factors affect the property of a polymer.
- **a** Cross-linking
- **b** Branching
- **c** Side groups

3 A linear polymer is one in which:
- **a** the chains are aligned parallel to each other.
- **b** there is no cross-linking.
- **c** there are many side branches.
- **d** the chains are very short.

4 As the chain length of a polymer increases, the polymer becomes:
- **a** stronger.
- **b** less dense.
- **c** more easily melted.
- **d** more soluble.

5 For a monomer to be able to undergo addition polymerisation, it should contain:
- **a** at least three carbon atoms.
- **b** both hydrogen and oxygen.
- **c** a multiple bond.
- **d** a halogen.

6 When a polymer is formed by condensation polymerisation, the:
- **a** mass of the polymer formed is less than the total mass of reactants.
- **b** polymer must be linear.
- **c** polymer must be cross-linked.
- **d** polymer must be thermoplastic.

7 When sucrose is digested, it yields the two monosaccharides:
- **a** glucose and lactose.
- **b** glucose and maltose.
- **c** glucose and glucose.
- **d** glucose and fructose.

8 Which of the following compounds is an amino acid?
- **a** Ethanoic acid
- **b** Alanine
- **c** Lactose
- **d** DNA

9 Which of the following is *not* a property of most amino acids?
- **a** They are highly soluble in non-polar organic solvents.
- **b** They may be positively and/or negatively charged.
- **c** They may act as both acids and bases.
- **d** They can undergo condensation polymerisation forming polypeptides.

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ELABORATION QUESTIONS

10 What are the similarities and differences between an ester link and a peptide link?

11 Teflon is the name given to the polymer used to coat kitchenware so it is non-stick. It is formed by reacting tetrafluoroethene in the presence of a catalyst. In this process:

- **a** a condensation reaction takes place producing the polymer and water.
- **b** a condensation reaction takes place producing the polymer only.
- **c** an addition reaction takes place producing the polymer and water.
- **d** an addition reaction takes place producing the polymer only.

END-OF-CHAPTER EXAM

End-of-chapter test

1 The monomers for addition polymerisation must be:

A alkanes.

B alkenes.

C alcohols.

D carboxylic acids.

2 The regions in a polymer where the chains are tangled are referred to as:

A knotted.

B amorphous.

C liner.

D crystalline.

3 What two functional groups are needed to form a polyester?

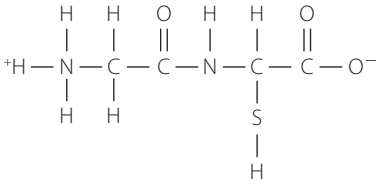
A Alcohol and amine

B Amine and aldehyde

C Alcohol and carboxylic acid

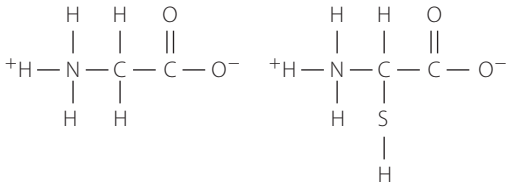
D Amine and carboxylic acid

4 The figure below shows the structure of a small section of a protein.



The amino acids used to form this are:

A



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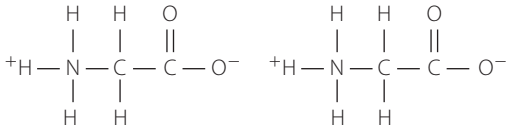

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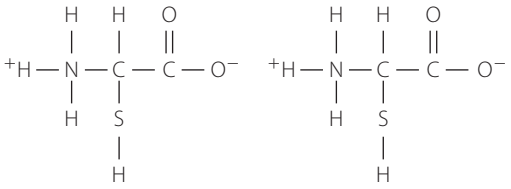

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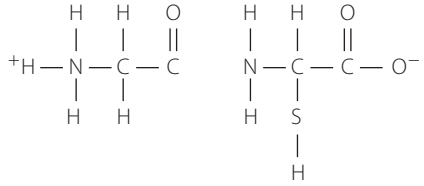

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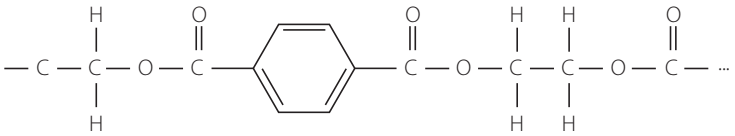
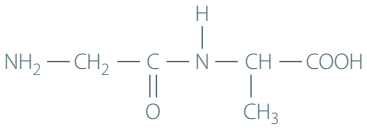
5 PET, also known as terylene or dacron, is a common polymer used in a wide variety of applications from synthetic fabrics to soft-drink bottles. A section of the polymer is shown below.



Draw the structures of two monomers from which this polymer could be made.

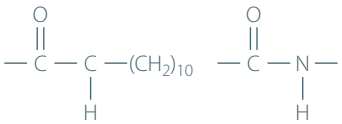
6 Two amino acids glycine (Gly) and alanine (Ala) join to form the dipeptide glycylalanine (Gly–Ala) as shown below.



a Copy the diagram, and circle and name the bond that joins the two amino acids together.

b Write the equation for the reaction by which this dipeptide hydrolyses back to the original amino acids.

7 Consider the following section of a protein chain.



Draw and name the amino acids that reacted to produce this section of the protein.

8 Compare the structures of cellulose and starch, and explain the difference in their properties in terms of their structure and bonding.

23 MOLECULAR MANUFACTURING

Introduction

Molecular manufacturing is an advancing branch of chemistry that uses different chemical techniques and processes to control how a chemical is formed. Chemicals can be joined in specific ways to tailor a product for use in different fields. For example, in medicine, molecular manufacturing can be used to deliver drugs to precise sites within the human body or to perform surgeries on the nanoscale. Researchers are producing smart materials that are more water resistant, scratch-proof, durable or stronger than before. The production of fuel cells, batteries and solar panels is being advanced every day because of the precise construction of materials using these processes.

Stimulus questions

How can plastics be altered to have specific properties such as water and scratch resistance and increased durability with flexibility?

As electronic devices such as mobile phones and computers become more complex, how can their electronics be reduced to a microscopic scale?

Diagnosing and treating diseases such as cancer can involve drastic procedures traumatic to the human body. How can drugs be designed to target specific cancer cells?

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23.1 What is molecular manufacturing?

Molecular manufacturing is the production of molecules, crystals and other chemical structures, that have been designed to have a specific shape or chemical composition. These materials are incorporated into fabrics, batteries, medical devices and many other products. Devices and applications that incorporate these manufactured molecules have many advantages over their conventional versions. For example, manufacturers have created batteries with hundreds of times more life than current battery technology. Molecular manufacturing has also allowed researchers to develop innovative technology such as specialised drug delivery systems that can target disease in the body. This has made treatment more effective and patients suffer fewer side effects.

molecular manufacturing
the production of molecules, crystals and other chemical structures, that have been designed to have a specific shape or chemical composition

Macro vs nano properties

Most molecular manufacturing involves manipulating structures at the nano level. This makes **nanotechnology** very important in molecular manufacturing. Nanotechnology is science, engineering and technology that occur at the nanoscale, around 1–100 nanometres. A **nanometre** (nm) is extremely small, just one-billionth of a metre. Figure 23.1.2 shows how some common objects compare in size. When we look at things on the nano scale, we are talking about objects the size of atoms and molecules.

The following measurements demonstrate how small a nanometre is:

- a gold atom is 0.3 nm in diameter
- a human hair is 100 000 nm thick
- A strand of human DNA is 2 nm in diameter.

nanotechnology
science, engineering and technology that occur at the nanoscale, around 1–100 nanometres

nanometre (nm)
one-billionth of a metre

23.1.1 Size and scale

SCIENCE AS A HUMAN ENDEAVOUR

NANOTECHNOLOGY

Unwittingly, nanotechnology has been used throughout history. The medieval makers of stained-glass windows trapped silver and gold nanoparticles in the glass matrix, which reflected light differently depending on their size. The gold nanoparticles could be red, green or orange depending on their size (50–100 nm). The silver particles could be blue, dark orange or yellow (40–100 nm).

In Italy around 1450–1600, artists created ceramic plates and bowls using copper and silver particles between 5 and 100 nm. Depending on how the light reflects off the different particles, the colour changes, making the object iridescent. Even earlier than this, the Chinese used gold nanoparticles as a dye in their porcelain.

The Lycurgus Cup is a roman cup created around the fourth century. It is made from glass that contains gold and silver nanoparticles. In daylight it appears green. But if light is shone directly through the glass, it appears red.

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FIGURE 23.1.1
A medieval stained-glass window contains nanoparticles that reflect light to create colour

Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

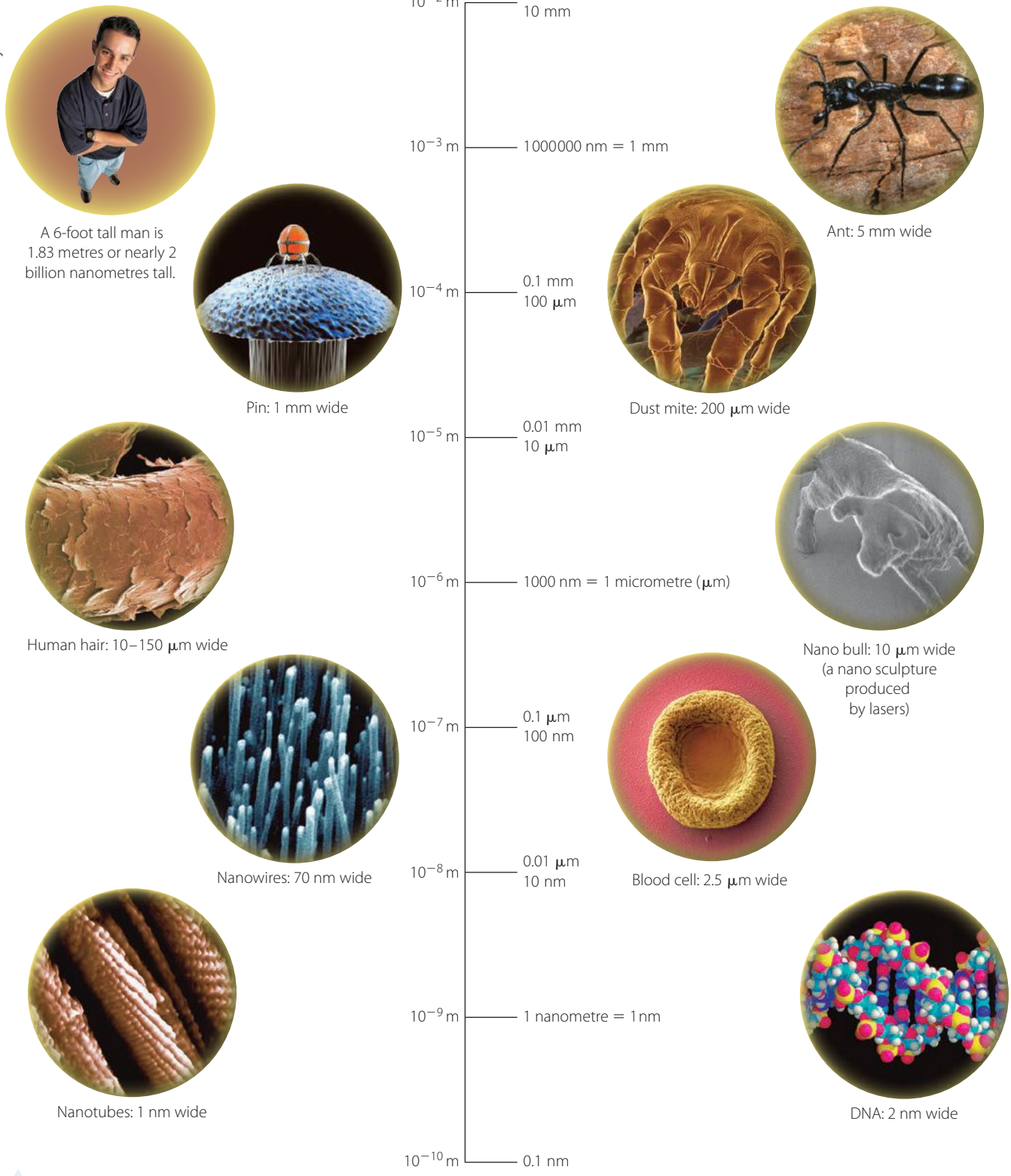

FIGURE 23.1.2 Sizes of some objects

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Nanoparticles behave very differently from the same particles on the macro scale. When particles are between 1 and 100 nm, their properties change compared to the same substance on the macro scale. For example, as a particle becomes smaller, the surface area of the substance becomes much larger and this affects the way it reflects light. This can result in a substance such as gold, which is yellow when the particles are macro sized, being either red or purple when the particles are nano sized.

Other properties that change between the macro and the nano scale are melting point, conductivity, magnetic properties, chemical reactivity and fluorescence, which is the ability of a substance to emit light when it has absorbed energy.

How is molecular manufacturing done?

Molecular manufacturing can be performed in many ways. We will explore three broad methods.

Method 1: The orientation effect

This is also referred to as **mechanosynthesis**. This involves positioning molecules so that the desired functional groups line up, all reactions are efficient and there is less waste and fewer undesired products forming. This occurs naturally in processes such as protein synthesis and DNA replication. Specifically manufactured proteins can be built in the form of a molecular machine called a nanomachine. Nanomachines can manufacture molecules as suggested in Figure 23.1.3.

mechanosynthesis positioning molecules so that the desired functional groups line up

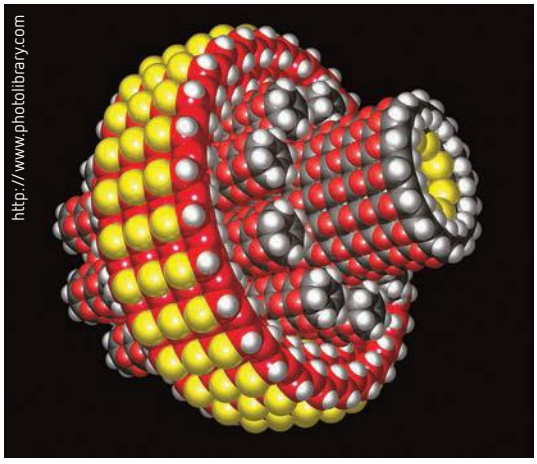

FIGURE 23.1.3 An artist's impression of a nanomachine. This is a molecule created to perform a very specific task such as building a larger molecule like a protein.

Method 2: Manipulation of structures at the atomic or molecular level

This method is done in two ways:

1. The bonding between atoms, ions and molecules can be altered, manipulated or controlled. If the bonds that form can be controlled, then specific properties can be given to the final structure.
2. Substances can be built by adding or substituting specific atoms in a structure, as shown in Figure 23.1.4. This also gives the final structure very specific properties. In this manner, chemicals and materials can be tailored for a specific purpose, as can be seen in Figure 23.1.5.

Method 3: Use of protecting groups

Large molecules often have many reactive sites and/or functional groups. Sometimes a different functional group will react rather than the one that has been targeted and a non-desired product is formed. This is wasteful and leads to a reduced yield of the desired product. These functional groups can be prevented from reacting by adding a protecting group.

FIGURE 23.1.4 Atoms being added individually to a structure to create a very specific final molecule

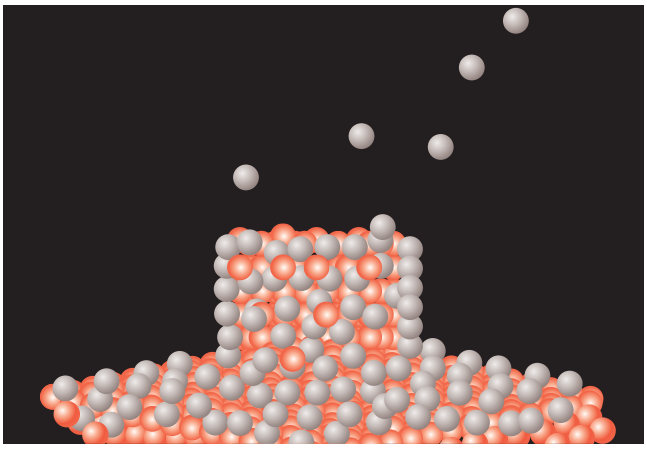

FIGURE 23.1.5 This material is a nanofabric that does not absorb water or other liquids. The properties of the fabric have been changed so that the water beads rather than being absorbed.

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Top-down and bottom-up approaches

top-down approach starting with a larger substance and converting it into a smaller, more useful substance

bottom-up approach building a desired structure from the atomic and molecular scale, by adding atoms individually or by adding molecules together to make a larger, more complex molecule

A **top-down approach** to molecular manufacturing involves starting with a larger substance and converting it into a smaller, more useful substance, or only keeping part of the original substance. This can be done by removing atoms, grinding or crushing the substance or breaking it into smaller parts. This approach often requires vast amounts of energy and materials and creates a lot of waste.

A **bottom-up approach** involves building a desired structure from the atomic and molecular scale, by adding atoms individually or by adding molecules together to make a larger, more complex molecule. This method is much harder because it is done on the atomic scale, but it creates less waste and requires much less energy.

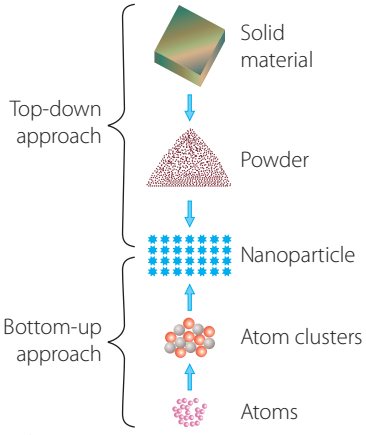

FIGURE 23.1.6 Comparison of the top-down and bottom-up approach to making the same nanoparticle

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Protein synthesis

Molecular manufacturing can involve protein synthesis, developed for use in the medical and pharmaceutical industries. As you know, proteins are found in all living organisms. Proteins can be structural, such as the keratin found in hair and fingernails, or collagen found in tendons and cartilage. Other proteins perform specific jobs inside the body; enzymes perform many tasks, getting rid of waste, breaking down starch or fats, synthesising DNA or taking part in metabolic pathways including respiration or photosynthesis. Other examples of proteins are:

- insulin, a hormone that helps to control glucose metabolism in the body
- haemoglobin, which carries oxygen to the cells
- **antibodies** that help fight disease.

antibodies
proteins that help fight disease

Joining amino acids

As discussed previously, the basic unit of a protein is the amino acid. To form the primary structure of a protein, a strictly defined sequence of amino acids is joined to make a long chain of amino acids called a polypeptide. To form a polypeptide, many amino acid units join together in a specific sequence. A polypeptide chain can be seen in Figure 23.1.7. Each different protein has a unique sequence of amino acids. All molecules of the same protein have the same sequence.

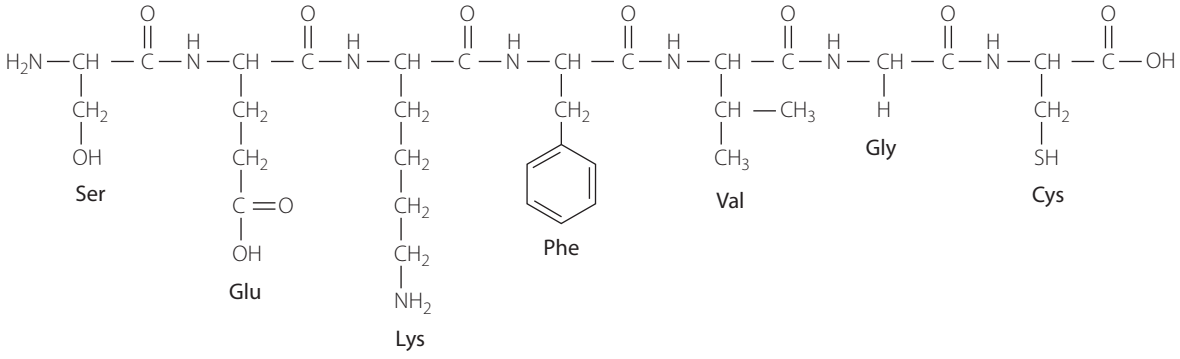

FIGURE 23.1.7 A polypeptide chain made of the amino acids serine, glutamine, lysine, phenylalanine, valine, glycine and cysteine. Each amino acid is represented by its first three letters.

For a protein to form, the two functional groups of the constituent amino acids must line up perfectly. If two amine groups come into contact, then they will not join. Many of the amino acids are quite large and it is unlikely that the correct functional groups would come into contact if they were just randomly floating around.

How do amino acids line up perfectly?

The blueprint for every protein in a living organism is found in the DNA in its cells. Figure 23.1.8 shows the major steps of how protein synthesis occurs in a cell.

A molecule called **messenger RNA** (mRNA) is a copy of the DNA code in the nucleus. It is needed to synthesise the protein. The mRNA leaves the nucleus of the cell and a large ribosome surrounds the mRNA. The ribosome links the amino acids together in the correct sequence as specified by the mRNA. A ribosome has two sections, called subunits. The small subunit reads the mRNA; the larger unit joins the amino acids together to make a polypeptide chain.

The amino acids are carried on the molecule **transfer RNA** (tRNA), which collects a specific amino acid, then lines up with the matching part of the mRNA.

messenger RNA (mRNA)
a copy of the DNA code in the nucleus

transfer RNA (tRNA)
collects a specific amino acid, then lines up with the matching part of the mRNA

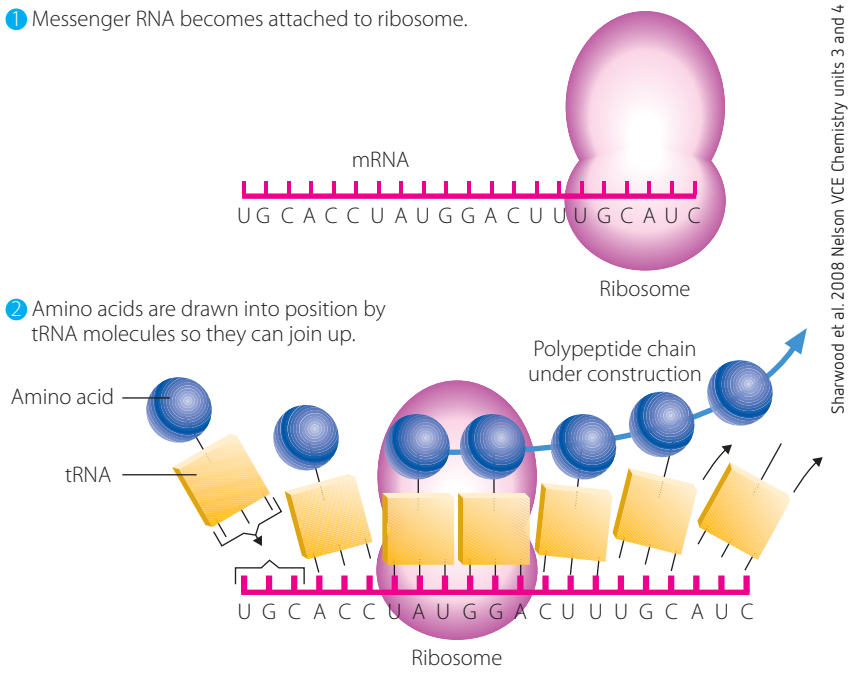

FIGURE 23.1.8 Protein synthesis using a ribosome

The job of the ribosomes is to ensure that each amino acid is in the correct place so that the carboxylic acid and amine functional groups are lined up to create the long polypeptide chain. A ribosome is a naturally occurring molecular machine that makes polypeptide chains.

Artificial protein synthesis

Scientists have the ability to grow proteins in cells, such as bacterial and yeast cells. Genetically modified bacterial and yeast cells have been used to produce diabetes medications, clotting drugs to treat haemophilia and human growth hormone to treat dwarfism. But bacterial and yeast cells cannot produce all the proteins we need.

Artificial peptides and proteins can also be synthesised in the laboratory. The most common method used is solid phase peptide synthesis (SPPS). A resin is used to attach the amino acids so that they are in a specific orientation. Initially, one amino acid is attached to the resin, then each amino acid in the chain is attached in turn, allowing the amide link to form before the next amino acid is added. When the polypeptide chain is complete, it is removed from the resin and allowed to fold into the protein shape. The resin acts like the ribosome in natural protein synthesis.

Artificial protein synthesis also allows incorporating new amino acids that do not occur naturally. Every amino acid has two isomeric forms except for glycine. Remember that isomers have the same molecular formula but a different structure. In this case, the two isomers have a similar structure and are mirror images of one another – stereoisomers. However, if the two isomers are placed over one another, they are not the same, unlike other objects that have a mirror image. This phenomenon is known as **chirality**.

chirality
two isomers that do not have a mirror image; when placed over one another, they are not the same

The best example of chirality is your hands. You have a left and a right hand and if you put one on top of the other with both palms down, they will not line up. If you put your left hand in front of a mirror, you will see a right hand in the mirror. This is a mirror image.

All natural amino acids are called L-amino acids, but they all also have a D form that is their stereoisomer. This is shown in Figure 23.1.9.

In the pharmaceutical industry, the incorporation of D-amino acids is important in producing drugs such as penicillin. The bacteria targeted by penicillin have a cell wall made of a polysaccharide

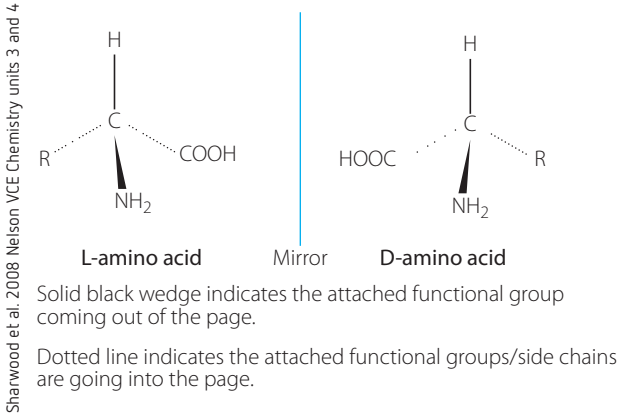

FIGURE 23.1.9 The L and D forms of an amino acid are mirror images (stereoisomers) of one another.

and peptide units. The polypeptide starts with L-alanine and finishes with D-alanine. As the bacteria grow their cell wall, cross-links form between two peptide chains. Penicillin binds in place of the usual D-alanine molecule and causes disruption of these cross-links. As the cross-links do not form, the cell wall breaks down and the bacteria die. If an L-alanine molecule were present in the penicillin, then it would be unable to bind to this site because it is the wrong shape.

Carbon nanotubes

Another form of molecular manufacturing is the creation of **nanotubes** – a tube that is constructed on the nano scale. It can be made from silicon, DNA or other materials, but the most common is carbon. A carbon nanotube is formed from sheets of **graphene**, covalently bonded carbon, with each sheet only one atom thick. The sheets are rolled into long tubes, and can be single-walled, double-walled or have a variety of other shapes.

nanotube
a tube constructed on the nano scale; most commonly made from carbon

graphene
covalently bonded carbon

How nanotubes are built

The best quality nanotubes are created by a method called arc-evaporation. A current is passed between two graphite electrodes, causing the graphite to vaporise. The vaporised graphite settles on the walls of the reaction vessel and on the cathode. The graphite on the cathode forms nanotube structures as the atoms settle and bond to each other.

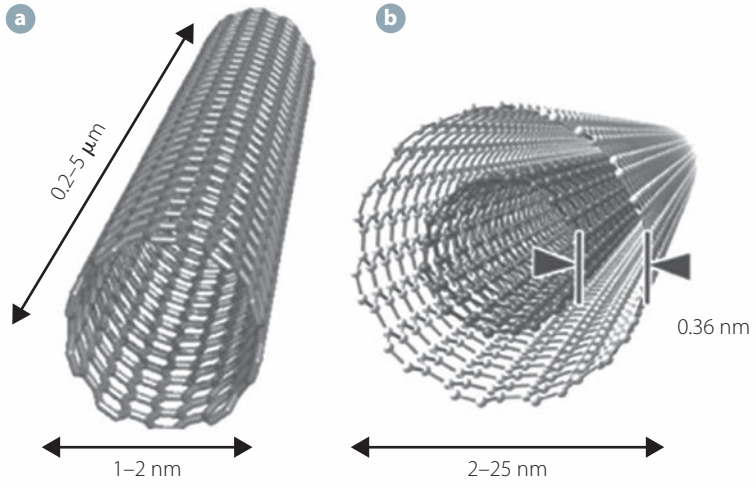

FIGURE 23.1.10 **a** Single-walled and **b** double-walled carbon nanotubes

Another method of producing nanotubes is to pass a carbon-containing gas, such as a hydrocarbon, over a catalyst containing nanoparticles of a metal such as iron, cobalt or nickel. These metal particles cause the hydrocarbon to break down into its component atoms. The carbon atoms then begin to grow into nanotubes.

Both of these methods involve 'growing' the carbon nanotube atom by atom. This is an example of a bottom-up approach to producing nanomaterials.

Properties of carbon nanotubes

Carbon nanotubes are the strongest and stiffest materials yet discovered or made. A single carbon nanotube was tested to have a tensile strength equivalent to a mass of 6422 kilograms on a cable with a cross-sectional area of $1\,mm^2$. As they also have a low density, this makes them ideal for structural purposes. Carbon nanotubes have been used to develop strong but flexible materials that can be implanted into the human body as artificial muscles and bones.

One of the most useful properties of carbon nanotubes is their high electrical conductivity. This makes them useful in batteries and fuel cells to produce electricity. Other properties that can be designed in a particular nanotube include optical properties, such as reflection and transmission of light, and thermal conductivity so they can be used under high-temperature conditions.

Nanorobots

Nanorobots are artificially created proteins designed to perform specific mechanical tasks. Producing nanorobots uses DNA nanotechnology. Using the structure of DNA in cells, where it carries genetic information, scientists have been able to build a range of devices with applications across medicine, engineering and materials production.

The precise, ordered structure of DNA can be used to produce artificial nucleic acid structures for uses outside its normal function as a carrier of genetic information. Scientists have been able to use nucleic acids to build two-and three-dimensional crystal lattices, nanotubes, DNA computers and nanorobots.

Nanorobots, just like robots in industry, have a particular task. A molecular robot can be used to recognise a particular shape so can have applications in medicine where it could recognise diseased cells, viruses or specific bacteria. A molecular robot can be used to carry chemicals to a particular area of the body, again giving it a number of applications in medicine.

SCIENCE AS A HUMAN ENDEAVOUR

MOLECULAR MACHINES

Scientists have created a 'spider' out of DNA that is capable of walking across a surface, towards a target. The spider is a molecular machine designed to respond to the surface it walks across. The surface it is walking across is a highly folded piece of DNA.

The spider has legs that interact chemically with the DNA surface. To take a step, the legs break a DNA strand on the surface, which weakens the interactions between the spider and the surface. The spider then moves forwards to where the interactions between itself and the surface are stronger. The spider is a DNA molecular machine that can sense the environment and respond to it.

Other scientists have developed a DNA machine that can pick up nanoparticles, useful as part of an assembly line to manufacture a larger structure, or in the human body to target toxic substances.

Nicolle R Fuller/Science Photo Library

FIGURE 23.1.11 A DNA spider 'walks' across a DNA molecule towards a target (in red).

Chemical sensors used in medicine

A **biosensor** is a structure that can detect a change in a biological component such as a particular chemical. It can also be used as a measurement device. A **nanosensor** is a sensor that is nanosized. Biosensors can detect when a particular chemical is present in the blood or body. Specific chemicals can indicate when a particular disease is present.

biosensor
a structure that can detect a change in a biological component

nanosensor
a sensor that is nanosized

For example, cancer cells produce specific chemicals that indicate when a tumour is present. Bacteria and viruses do the same. A biosensor can detect these chemicals and indicate if any of these are present. One of the major advantages of a biosensor over conventional tests is that the assessment of the patient and detection of the problem can occur much earlier. This reduces risk as the disease can be treated far earlier than usual.

An example of better monitoring reducing patient risk is shown in the assessment of patients with diabetes mellitus. Sufferers produce ketones as their blood insulin decreases. Propanone (acetone) is one of these ketones and is usually detected in the patient's urine. A nanosensor called a cantilever, seen in Figure 23.1.12, has a particular structure that will bind with the acetone in the air as a patient breathes out. The cantilever structure is covered with molecules that recognise and bond to the ketone molecules produced by a patient with diabetes mellitus.

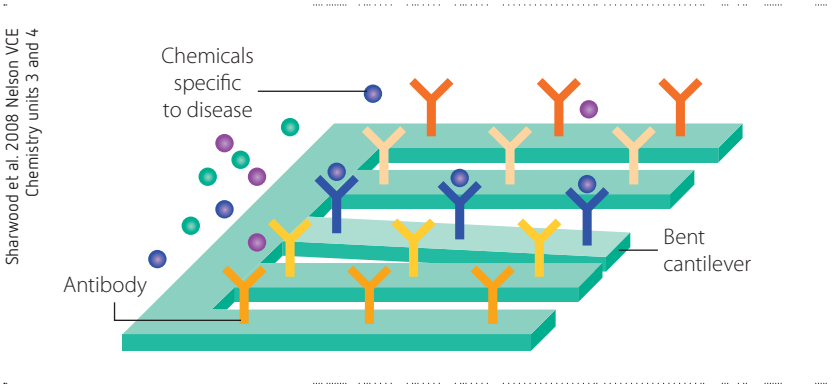

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FIGURE 23.1.12 A bent cantilever due to bonding of particles to the antibodies on the surface

When the cantilever binds to the acetone, the structure changes because of the extra molecules now bound to the surface. As it is a nanosensor, it has useful nanoproperties. As the cantilever changes shape, it generates a small electrical charge that can be measured and used to determine the concentration of acetone present. The more molecules present, the more the cantilever is bent out of shape, and the larger the electrical charge generated. In this way, the amount of molecules present can be measured.

The cantilever itself is manufactured on the atomic level so that it has the specific shape seen in Figure 23.1.12. It appears like a series of diving boards with each 'board' able to move independently. Cantilevers can be made of materials such as silicon, or from polymers. Both structures are manufactured with a specific shape by using methods such as atomic manipulation. In this process, atoms are added together in a particular arrangement to give a final structure that has the required electrical conductivity property needed for sensing.

This cantilever has a number of advantages over conventional detection of ketones. First, the patient only needs to breathe on the sensor rather than provide a urine sample. Second, the cantilever can detect acetone in much smaller amounts than conventional tests. This allows doctors to identify anomalies in blood glucose much earlier, reducing the overall risk to the patient, who can adjust their blood glucose concentration before symptoms appear.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1. What is molecular manufacturing?
2. What is nanotechnology?
3. Describe the difference between a top-down and a bottom-up approach to molecular manufacturing.
4. Explain what is meant by chirality.

ELABORATION QUESTIONS

5. Describe how protein synthesis occurs inside a cell.
6. Describe how artificial protein synthesis is used to grow proteins.
7. Explain the difference between L- and D-amino acid isomers.
8. Explain why carbon nanotubes are useful.
9. Explain why the construction of carbon nanotubes is described as a bottom-up process.

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END-OF-CHAPTER EXAM

End-of-chapter test

1 Molecular manufacturing may occur through:

A a top-down approach where atoms are gradually put together to make a nanoparticle.

B a bottom-down approach where atoms are gradually put together to make a nanoparticle.

C a top-down approach where a larger substance is broken down into smaller parts.

D a bottom-up approach where a larger substance is broken down into smaller parts.

2 The name of the structure that positions amino acids in a cell in the appropriate orientation is:

A golgi apparatus.

B enzyme.

C ribosome.

D mRNA.

3 The name given to ensuring that the particles collide in the correct orientation so that the functional groups lineup is:

A retrosynthesis.

B protecting groups.

C photosynthesis.

D mechanosynthesis.

4 L and D forms of amino acids exhibit chirality because they:

A are mirror images of each other but are not the same when placed over the top of one another.

B are stereoisomers and therefore are different shapes.

C are structural isomers and therefore have the same molecular formula but different structural formula.

D have different R groups attached to the carbon atom.

5 One advantage of artificial protein synthesis is:

A choosing the monosaccharide sequence and therefore the properties of the protein.

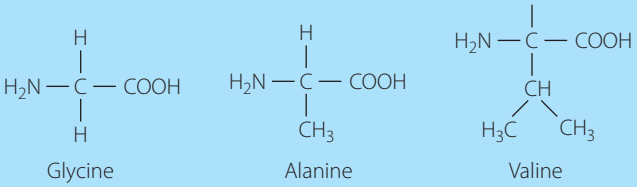
B the incorporation of L forms of amino acids that do not exist naturally.

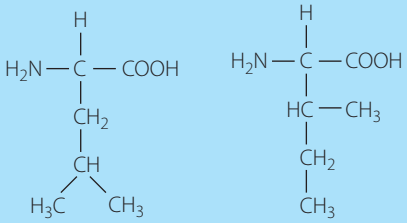
C the amino acids are randomly attached so there is more variety in the proteins produced.

D that it can produce a protein with specific properties.

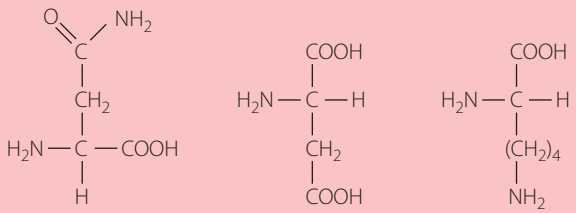
6 Using the amino acids given below, explain why joining glycine and alanine will only result in two different dipeptides while joining valine and aspartic acid will result in three different dipeptides.

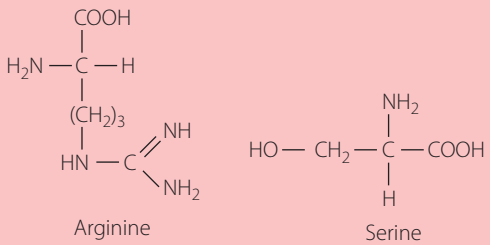
Amino acids with non-polar R groups





Amino acids with polar R groups





7 Top-down and bottom-up approaches are used to create nanoparticles and nanostructures.

a Suggest reasons why a top-down approach uses more energy considering the methods used.

b Suggest drawbacks to using a top-down approach.

8 Suggest a possible negative outcome that could arise from molecules joining in the incorrect orientation.

UNITS 3 AND 4 PRACTICE EXAMINATION

MULTIPLE CHOICE

QUESTION 1

Cholesterol is a steroid with the chemical formula $C_{27}H_{45}OH$. If a sample of cholesterol contains 0.356 g carbon, then the mass of hydrogen present will be:

A 0.012 g.
B 0.12 g.
C 0.05 g.
D 0.52 g.

QUESTION 2

The equation for producing ammonia, NH_3, is given below:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

If the reaction takes place in a sealed container and equilibrium has been established, which of the following would subsequently cause the proportion of ammonia to increase?

A Adding an inert gas
B Increasing the temperature
C Adding a suitable catalyst
D Decreasing the volume of the container

QUESTION 3

The pH of a solution is changed from 14 to 11. This means that the concentration of

A hydroxide ions has decreased by a factor of 3.
B hydrogen ions has decreased by a factor of 1000.
C hydroxide ions has decreased by a factor of 1000.
D hydrogen ions has decreased by a factor of 3.

QUESTION 4

A solution of sodium carbonate was used to measure the concentration of a solution of HCl. An aliquot of the sodium carbonate solution was placed in a conical flask and titrated with the hydrochloric acid from a burette. The correct indicator for this reaction would be one that changes colour when the number of moles of hydrogen ions added

A just exceeds half the number of carbonate ions originally present.
B equals the number of carbonate ions originally present.
C just exceeds the number of carbonate ions originally present.
D just exceeds double the number of carbonate ions originally present.

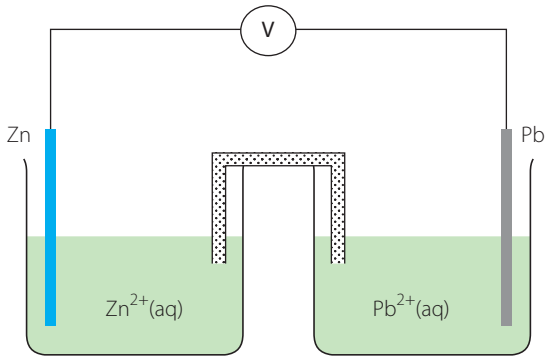
QUESTION 5

In which of the following species does antimony have an oxidation state of +3?

A H_3SbO_4
B Sb_2O_5
C SbO_3
D Sb_4O_6

QUESTION 6

A galvanic cell is set up according to the diagram below:



In this cell, the lead electrode will be:

A the cathode and positively charged.
B the cathode and negatively charged.
C the anode and positively charged.
D the anode and negatively charged.

QUESTION 7

Why is it not possible to plate an object with calcium metal using an aqueous solution of 1 M calcium chloride as the electrolyte?

A Water is a stronger reductant than Cl^-.
B Water is a stronger oxidant than Cl^-.
C Water is a stronger reductant than Ca^{2+}.
D Water is a stronger oxidant than Ca^{2+}.

QUESTION 8

Sodium can be extracted by the electrolysis of sodium chloride. Which of the following would be the best choice for the electrolyte and the anode in a commercial cell?

	Electrolyte	**Anode**
A	Conc. NaCl	Graphite
B	Aqueous NaCl	Graphite
C	Conc. NaCl	Iron
D	Aqueous NaCl	Iron

QUESTION 9

The compound 3-methyl, 2-pentanamine as the semi-structural formula:

A $CH_3CH(CH_3)CH(NH_2)CH_2CH_3$
B $CH_3CH_2CH(CH_3)CH(NH_2)CH_3$
C $CH_3CH(NHCH_3)CH_2CH_2CH_3$
D $CH_3CH(NH_2)CH_2CH(CH_3)CH_3$

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QUESTION 10

A student performs two tests on an organic compound. In the first test, the compound was completely combusted in oxygen, with 3 moles of the compound forming 9 moles of carbon dioxide. In the second test, a few drops of bromine were added to the compound. The compound did not react with the bromine. The formula of the compound could be:

A C_3H_6
B C_3H_8
C C_9H_{18}
D C_9H_{20}

QUESTION 11

Which of the following statements about 1-butene is not correct?

A It has a higher boiling point than propene.
B It undergoes an addition reaction with hydrogen chloride, HCl, resulting in 1-chlorobutane as the major product.
C It undergoes an addition polymerisation reaction.
D It undergoes complete combustion, producing 4 molecules of carbon dioxide and 4 molecules of water.

QUESTION 12

Which two functional groups form the peptide link that is found in proteins?

A $-NH_2$ and $-NH_2$
B –COOH and –OH
C $-NH_2$ and $-NH_2$
D –COOH and $-NH_2$

QUESTION 13

Lactose is a naturally occurring disaccharide formed when a molecule of glucose combines with a molecule of galactose. Glucose and galactose are isomers with the same molecular formula of $C_6H_{12}O_6$. The formula of lactose is most likely to be:

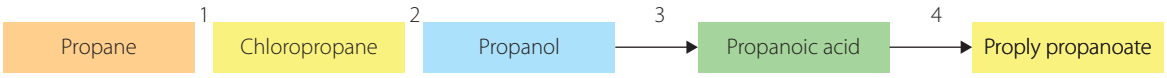
A $C_{12}H_{24}O_{12}$
B $C_{12}H_{22}O_{11}$
C $C_{12}H_{20}O_{10}$
D $C_{10}H_{24}O_{11}$

QUESTION 14

Galvanised iron consists of iron covered with a thin layer of zinc. A piece of galvanised iron has been scratched and is starting to corrode. During this process:

A the zinc acts as the negative electrode and the zinc is oxidised
B the zinc acts as the negative electrode and the iron is oxidised
C the iron acts as the negative electrode and the zinc is oxidised
D the iron acts as the negative electrode and the iron is oxidised

Questions 15 to 18 refer to the flow chart below showing the production of the ester propyl propanoate:



QUESTION 15

Step 3 is best described as:

A substitution.
B esterification.
C condensation.
D oxidation.

QUESTION 16

A substitution reaction occurs in:

A Step 1.
B Step 2.
C Steps 1 and 2.
D Steps 1, 2 and 3.

QUESTION 17

The other reagent required in Step 2 is:

A hydroxide.
B H_2SO_4.
C acidified $KMnO_4$.
D Cl_2/ultraviolet light.

QUESTION 18

In step 4, propanoic acid reacts with:

A propane.
B chloropropane.
C propanol.
D propene.

QUESTION 19

An important step in the production of nitric acid is the conversion of nitrogen monoxide into nitrogen dioxide, shown in the equation $2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta H = -114 \text{ kJ mol}^{-1}$

Which of the following sets of conditions would you expect to provide the best equilibrium yield?

A Temperature: 800°C and pressure: 1 atm
B Temperature: 20°C and pressure: 1 atm
C Temperature: 800°C and pressure: 5 atm
D Temperature: 20°C and pressure: 5 atm

QUESTION 20

The functional group formed when two molecules of glucose form a disaccharide is:

A a carboxylic acid.
B an alcohol.
C an ether.
D an ester.

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SHORT-ANSWER QUESTIONS

QUESTION 1

Dimethyl ether, CH_3OCH_3 can be converted into methanol by adding water, as shown in the following reaction:

$$CH_3OCH_3(g) + H_2O(g) \rightleftharpoons 2CH_3OH(g);\ \Delta H = +24 kJ\,mol^{-1}$$

The equilibrium constant, *K*, for this reaction at 200°C is 0.256.

a Write an expression for *K* for this reaction.

b Calculate the value of the equilibrium constant at 200°C for the following reaction:

$$2CH_3OH(g) \rightleftharpoons CH_3OCH_3(g) + H_2O(g)$$

c Dimethyl ether is pumped into an empty 30.0 L reactor vessel. At equilibrium, the vessel contains 0.283 mol of dimethyl ether at 200°C.

i Calculate the concentration in mol L^{-1} of dimethyl ether at equilibrium.

ii Calculate the amount in moles of methanol present at equilibrium.

iii Calculate the amount in moles of dimethyl ether initially pumped into the reaction vessel.

QUESTION 2

The pH values of 0.10 M solutions of four different acid solutions at 25 °C are shown in the table below:

Acid	pH
A	4.0
B	0.6
C	1.0
D	2.1

a One of the acids in the table must be diprotic. Indicate which one, then explain your reasoning.

b Which acid in the table has the lowest K_a value? Explain why.

c If acids C and D are both diluted by a factor of 10, explain which of these acids would have the greater change in pH value.

d The K_a for selenious acid, H_2SeO_3 is 2.4×10^{-3}. Calculate the concentration of a solution of selenious acid that would have the same pH as acid B.

QUESTION 3

'Causda' is a chemical that can be used to unblock drains and is known to contain caustic soda (sodium hydroxide, NaOH) as the active ingredient. A student wishes to determine the percentage of active ingredient in a sample of Causda, by titrating with 0.2500 M HCl solution.

The student dissolves 2.500 g of Causda in water and makes the solution up to exactly 250.0 mL. 25.00 mL aliquots of this solution were then titrated with the HCl solution using a suitable indicator. The average of the three titres obtained was 18.76 mL.

a Write an equation for the reaction between NaOH and HCl.

b What pieces of laboratory equipment would be required to:

i 'make the solution up' to exactly 250.0 mL

ii measure a 25.00 mL aliquot

iii measure the volume of a titre.

c Deduce the percentage of sodium hydroxide in the sample of Causda, quoting your answer to the appropriate number of significant figures.

QUESTION 4

A chemist carried out reactions between three metals, P, Q and R and solutions of their sulfate salts. The chemist made the following observations during the experiment:

- P dissolved in a solution of Q_2SO_4 forming a sample of Q at the bottom of the container
- R did not react with PSO_4
- Q did not react with $R_2(SO_4)_3$.

a Use the information provided to place the metals in order of increasing reductant strength. Explain your reasoning.

b Metals P, Q and R can be extracted from the commonly occurring ores – PS, Q_2O and R_2S_3. Which metal is likely to be the easiest to extract from its ore and which would be the most difficult?

QUESTION 5

A child's chemistry set contains solutions of Al^{3+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, a dilute acid, Ni^{2+} and pieces of iron, zinc, magnesium and tin.

Answer the questions below and, for each one, include a balanced equation to illustrate your answer.

a Describe an experiment that the child could carry out that would involve reducing Al^{3+} ions to Al metal.

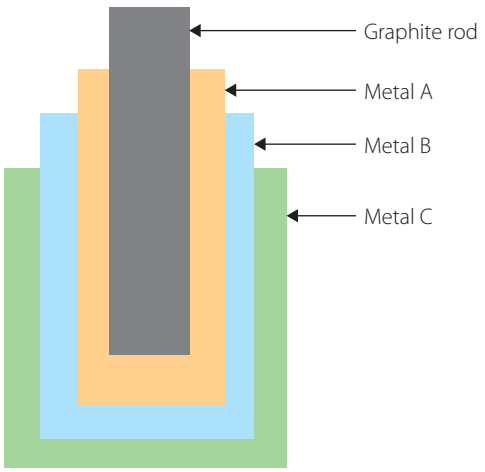
b If a mixture of Ni^{2+} and Zn^{2+} were prepared, how could the child ensure that the Ni^{2+} ions were reduced, without the Zn^{2+} reacting?

c Describe an experiment to show how the child could obtain hydrogen gas.

d If the child constructed a galvanic cell using the materials available, which combinations of metals and solutions in the set would produce the largest voltage?

QUESTION 6

Two graphite rods are placed in an aqueous solution containing 0.05 moles each of $CuCl_2$, AuCl and $FeCl_2$. An electric current is applied through the rods to the solution. At the end of the experiment, all of the metals have been deposited onto one of the rods, forming three successive coatings, as shown in the diagram below:



a Identify the three metals, A, B and C, and explain your answer, with reference to the electrochemical series.

b If the second graphite rod was instead made from copper, explain how this would have affected the results of the experiment.

c If 0.05 moles of sodium chloride were also added to the solution mixture and then electrolysed with the other metals, explain at which point in the sequence the sodium metal would have been deposited and why.

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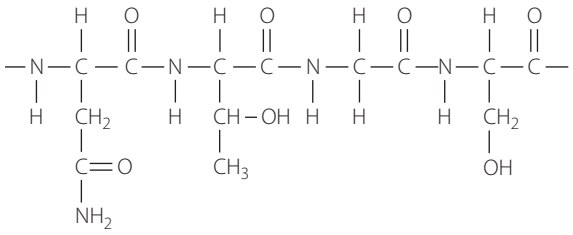
QUESTION 7

The structure of a protein is shown below:



a On the structure above, circle the three peptide bonds that are shown in the fragment.

b Draw the structural formulae of the four amino acids from which this fragment is made, and name the acids.

c What type of reaction would be required to convert the protein into its constituent amino acids? What reagent would help it to do this?

d Large protein molecules are formed from peptide chains being twisted and folded into specific shapes. Identify two interactions that help maintain these complex structures.

e An amino acid commonly found in proteins has the molecular formula $C_3H_7O_3N$. Draw the structure of this molecule and name it.

EXTENDED-RESPONSE QUESTION

QUESTION 8

The Haber process involves manufacturing ammonia from the gases nitrogen and hydrogen in the following reaction:

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$

Describe the procedures to follow when manufacturing ammonia to ensure that:

- the process is carried out economically, in terms of rate of reaction and equilibrium yield
- the process follows the principles of green chemistry; select three of the principles and describe in detail how the process in consistent with them.

ANSWERS

CHAPTER 1 CHEMICAL EQUILIBRIUM SYSTEMS

1.1 SECTION REVIEW

REMEMBERING

1 The forward reaction is the reaction proceeding from left to right as written on the page. The reverse reaction is the opposite of this, proceeding from right to left, as written.

2 A closed system is isolated from any external environment, with no reactants, products or energy able to be gained or lost.

3 No – some reactions, such as baking a cake, are irreversible.

UNDERSTANDING

4 To indicate that the reaction can occur in both directions.

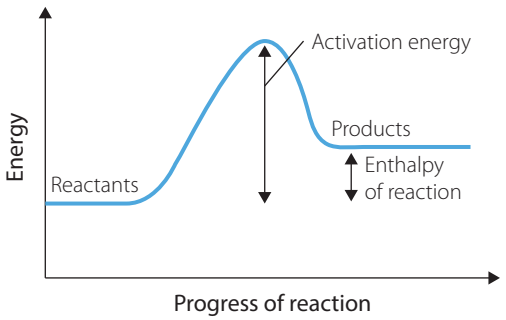
5 The heat energy released during a reaction is equal to the enthalpy difference between the reactants and products. Hence if the reaction is reversed, the energy difference is the same, but simply reversed.

APPLYING

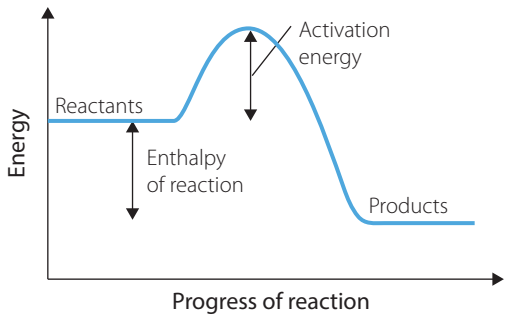
6 a $H_2O \rightarrow H^+ + OH^-$

b $H^+ + OH^- \rightarrow H_2O$

c



d



1.2 SECTION REVIEW

REMEMBERING

1 a Equilibrium: a system in balance

b Dynamic equilibrium: a system in balance but where forward and backward reactions are occurring at the same rate

c Open system: where one or more reactants or products in a reaction can be either added or lost

d Closed system: where the chemicals involved in a reaction are all contained within a fixed space

e Steady state: a system where the properties, such as volume or temperature, do not change

2 a False (in an open system) – an open system can never reach equilibrium as reactants or products are lost and hence the system will continually be adjusting as a consequence.

b True (involves a reversible reaction)

3 a True – at equilibrium, the rate of the forward and reverse reactions will be the same

b False – at equilibrium the concentrations of reactants and products are no longer changing and have reached constant values.

c False – at equilibrium, the properties such as volume and temperature do not change and so are constant.

UNDERSTANDING

4 The process shown in Figure 1.2.1: As the reaction proceeds, the rate of the forward reaction will fall as the reactants are used. Conversely, the rate of the reverse reaction will increase as the products are formed. Eventually, the rates of the two reactions will become equal and equilibrium will have been reached.

The process shown in Figure 1.2.2: Concentration of reactants decreases gradually in a curve until eventually becoming horizontal. Concentration of products increases gradually in a curve until eventually becoming horizontal. The rates of reaction show a similar shape graph, although reach the same value.

1.3 SECTION REVIEW

REMEMBERING

1 Activation energy – the minimum amount of energy required in order for a reaction to occur

2 Activated complex – a transition state, or intermediate formed during a reaction as a precursor to the product, but which has a high energy and so is relatively unstable.

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UNDERSTANDING

3 The reversibility of chemical reactions is dependent on reactions with a lower *activation energy*. They are more likely to be reversible than those with a higher activation energy, because the energy required to reverse the reaction is much lower.

1.4 SECTION REVIEW

UNDERSTANDING

1 A dynamic equilibrium is a system where a forward and reverse reactions are occurring simultaneously but at the same rate, so that there is *no net change in the concentrations* of the reactants and products.

2 Rate of reaction depends on the *concentrations of reactants*. At the beginning of a reaction, the concentration of reactants is highest and then decreases as the reaction proceeds, hence so does the rate of reaction.

APPLYING

3 At equilibrium, the concentrations of reactants and products do not change, so when these values are constant, it can be concluded that equilibrium has been reached.

4 At equilibrium, the rates of the forward and backward reactions are equal.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Equilibrium: a balanced system

b Dynamic equilibrium: a system where the forward and backward reactions are occurring simultaneously, but at the same rate

c Reversible: a reaction where the products can be converted back to the reactants

d Chemical system: the chemicals involved in a reaction

e Surroundings: everything except the chemicals involved in a reaction

f Closed system: a system where the reactants and products cannot leave

g Open system: a system which is not enclosed, so that reactants and products (e.g. gases) can leave as they are formed

h Physical change: a change where no new substance is created

i Chemical change: a change involving the creation of a new substance

j Activation energy: the minimum amount of energy required for a reaction to occur

k Enthalpy: heat energy that is either absorbed or released in the breaking and making of chemical bonds during a reaction

l Activated complex: a species formed at an intermediate stage between the reactants and products

CATEGORY QUESTIONS

2 As the reaction proceeds, the rate of the forward reaction will fall as the reactants are used. Conversely, the rate of the reverse reaction will increase as the products are formed. Eventually, the rates of the two reactions will become equal and equilibrium will have been reached.

3 Concentration of reactants decreases gradually in a curve until eventually becoming horizontal. Concentration of products increases gradually in a curve until eventually becoming horizontal.

4 The rates of reaction show a similar shape graph, however rather than simply becoming constant, the rates for the forward and back reactions become the same when equilibrium is reached.

ELABORATION QUESTIONS

5 An open system can never reach equilibrium because as reactants or products are lost, the system continually adjusts.

6 Reactions with a lower activation energy are more likely to be reversible than those with a higher activation energy, because the energy required to reverse the reaction is much lower.

END-OF-CHAPTER EXAM

1 C

2 B

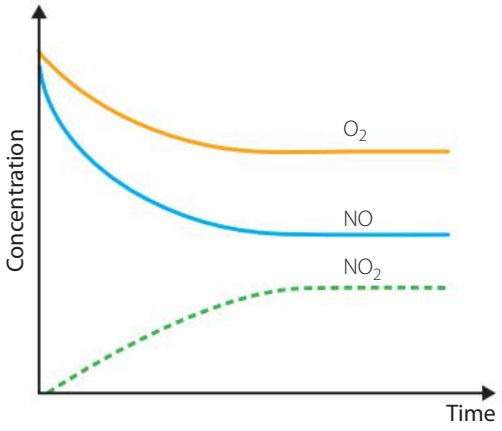
3 B

4 A

5 Your paragraph should contain the following information:

- at equilibrium, the concentrations of reactants will be constant
- the concentrations of reactants might be equal but also might not be equal
- at equilibrium, the rates of the forward and reverse reactions are equal.

6 Concentrations of O_2 and NO decrease and that of NO_2 increases. Rate of decrease of NO is twice that of O_2 as they react in a 2:1 ratio (see graph below).



CHAPTER 2 FACTORS THAT AFFECT EQUILIBRIUM

2.1 SECTION REVIEW

REMEMBERING

1 a endothermic

b exothermic

c endothermic; exothermic

UNDERSTANDING

2 When the temperature is raised, the rate of both forward and reverse reactions increases. However, as the activation energy of an endothermic reaction is greater than that of an exothermic reaction, when the temperature is raised, the effect on the endothermic reaction is greater than on the exothermic reaction. Hence, the position of equilibrium moves in favour of the endothermic reaction.

2.2 SECTION REVIEW

REMEMBERING

1 Concentration is the amount of a substance per unit volume.

2 Collision theory states that a reaction will occur as the result of two reacting particles colliding with a sufficient amount of energy.

UNDERSTANDING

3 Altering the concentration of one reactant increases the rate of one of the reactions without altering the rate of the other reaction. Consequently, the position of equilibrium is altered.

2.3 SECTION REVIEW

REMEMBERING

1 Reaction b will not be affected by a change in total volume, as the number of gaseous particles (and therefore volume) does not change as the reaction occurs.

Reaction a has a change from 3 molecules to 2.

Reaction c has a change from 4 molecules to 2.

UNDERSTANDING

2 Altering the total volume of a gaseous system causes a change in the concentration of the particles. If the number of reactant particles is not equal to the product particles, then the effect of the concentration change is different for the two reactions. Hence the rate of one reaction increases by more than the other, and therefore the position of equilibrium is altered.

3 In both cases, the effect is to reduce the concentration of the particles.

2.4 SECTION REVIEW

REMEMBERING

1 Le Chatelier's principle states that 'a system at equilibrium will act to minimise the effect of any change imposed on it'.

UNDERSTANDING

2 The catalyst alters the rate of both reactions equally and, therefore, does not alter the position of equilibrium.

APPLYING

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

4 a If you add more sodium hypochlorite pellets, the system will act to reduce the concentration of ClO^- by moving the position of equilibrium to the right, forming a greater amount of HClO.

b If you add more sodium hydroxide, this will reduce the amount of H^+ ions, so the system will act to oppose this change and replace the lost H^+ ions by moving the position of equilibrium to the left, favouring the reverse reaction.

c If the temperature of the water increases, the system will act to reduce this increase by shifting to the left and favouring the reverse reaction, which is endothermic.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Endothermic reaction: a reaction that absorbs heat from the surroundings as it occurs, so lowering the temperature.

b Collision theory: a theory stating that a reaction will occur when two particles collide with sufficient energy, thus the rate of a reaction is determined by the rate at which the particles collide.

c Le Chatelier's principle: a principle stating that a system at equilibrium will react to oppose constraints such as concentration of reactants, total pressure or temperature that are made to it by shifting its position to the left or to the right.

d Catalyst: a substance that will increase the rate of a chemical reaction, without being used up in that reaction.

CATEGORY QUESTIONS

2 Particles will only react if they collide with an energy level greater than the threshold activation energy. In an endothermic reaction, particles need to absorb energy from the surroundings, and the activation energy will be greater than for the reverse exothermic reaction. Hence, an exothermic reaction may not be reversible if the activation energy of the reverse endothermic reaction is sufficiently large such that no particles have sufficient energy to react.

3 Changing the total pressure by changing the total volume changes the concentration of all of the particles present. If the number of reactant and product particles is the same, then the effect of changing the total pressure does not affect

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the forward and reverse reactions differently, and so does not affect the position of equilibrium. If, however, the number of reactant and product particles are different and, for example, the overall pressure has been increased, then the system can act to oppose the change imposed and so to reduce the overall concentration of particles by shifting to favour the reaction producing the smaller number of particles.

ELABORATION QUESTIONS

4 The change made is a reduction in total volume, resulting in an increase in the concentration of both N_2O_4 and NO_2. The system acts to oppose this change by shifting to the left, causing NO_2 to be converted to N_2O_4, thus reducing the overall concentration of particles and opposing the effect of the change that was initially made.

5 When the system is at equilibrium, the rates of forward and reverse reactions are occurring at the same rate. Hydronium ions are a reactant in the reverse reaction. Hence, if the concentration of hydronium ions is reduced, the rate of the reverse reaction is reduced and the rate of the forward reaction is unchanged. Therefore, there is a shift in the equilibrium position to the right and the amount of CO_3^{2-} and H_3O^+ ions increase. As the concentration of products increases, the rate of the reverse reaction then increases until it becomes the same as that of the forward reaction and equilibrium is re-established.

6 a Equilibrium shifts to the right and the concentration of NO_2 increases.

b Equilibrium shifts to the left and the concentration of N_2O_4 increases.

c Equilibrium shifts to the right and the concentration of NO_2 increases.

d Equilibrium shifts to the left and the concentration of N_2O_4 increases.

e Equilibrium shifts to the left and the concentration of N_2O_4 increases.

EVIDENCE QUESTIONS

7 Answers will vary according to research.

END-OF-CHAPTER EXAM

1 C

2 B

3 B

4 a If the amount of ammonia is increased, the rate of the reverse reaction will be increased and initially, the rate of the forward reaction will be unchanged. This causes a subsequent increase in the concentration of hydrogen and nitrogen, and eventually the rate of the forward reaction will gradually increase until it is equal to that of the reverse reaction and equilibrium is re-established.

b At equilibrium, the rate of both forward and reverse reactions is the same and, hence, there is no net change in the concentration of reactants and products.

CHAPTER 3 EQUILIBRIUM CONSTANTS

3.1 SECTION REVIEW

1 a Equilibrium expression: the ratio of the concentration of products to reactants used to calculate the equilibrium constant.

b Equilibrium constant: the numerical value of the equilibrium expression when the system is at equilibrium.

c Homogenous system: a system where all the reactants and products are in the same state.

d Heterogeneous expression: a system where some reactants and products are in different states.

2 a $K = \frac{[SO_3]^2}{[SO_2]^2.[O_2]}$

b $K = \frac{[H_2].[CO]}{[H_2O]}$

c $K = [O_2]$

d $K = \frac{[H_3O^+]\ [SO_4^{2-}]}{[HSO_4^-].[O_2]}$

e $K = \frac{[CrO_4^-]^2.[H^+]^2}{[Cr_2O_7]^{2-}.[H_2O]}$

3 a 0.00482

b 4.29×10^{-6}

3.2 SECTION REVIEW

1 If $Q = K_C$, then the system *is at equilibrium.*
If $Q < K_C$, then there are less products and more reactants than at equilibrium. This indicates *that the system will move to the right as it approaches equilibrium.*
If $Q > K_C$, then there are more products and less reactants than at equilibrium. This indicates *that the system will move to the left as it approaches equilibrium.*

3.3 SECTION REVIEW

1 If the equilibrium constant is 1, then the concentrations of reactants and products are equal. If $K < 1$, then there are more reactants than products at equilibrium; if $K > 1$, then there are more products than reactants at equilibrium.

2 Reaction quotient $= 5/(0.5 \times 0.5^2) = 40$. $Q > K$; therefore, the system is not at equilibrium and will move to the left as equilibrium approaches.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 For a reaction $aA + bB \rightleftharpoons cC + dD$ at equilibrium,

$$K_C = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

2 Temperature

CATEGORY QUESTIONS

3 Calculation of reaction quotient is the same as equilibrium constant; however, the two values are equal when the system is at equilibrium.

4 Pure solids and liquids do not vary in their concentration.

5 [reactants]>[products]

ELABORATION QUESTIONS

6 a $K_C = \frac{[HCl]^2}{[H_2]\,[Cl_2]}$

b $K_C = \frac{[SO_4]\,[H_3O]}{[H_2O]\,[HSO_4]}$

7 $RQ = 5/(0.5 \times 0.5^2) = 40$, greater than K, so system is not at equilibrium

a $n(PCl_5) = 0.15$; $n(PCl_3) = 0.25$; $n(Cl_2) = 0.25$

b $[PCl_5] = 0.015$; $[PCl_3] = 0.025$; $[Cl_2] = 0.025$

END-OF-CHAPTER EXAM

1 C

2 A

3 B

4 a 0.035

b Endothermic; *K* increases as temp increases, so the forward reaction is favoured and must therefore be endothermic.

CHAPTER 4 PROPERTIES OF ACIDS AND BASES

4.1 SECTION REVIEW

REMEMBERING

1 a Acid: a substance that can donate a proton (H^+ ion) to a base.

b Base: a substance that accepts a proton from an acid.

c Hydronium ion: the ion that forms when a proton is donated to a water molecule (H_3O^+).

d Monoprotic acid: a substance that can donate one proton to a base.

e Diprotic acid: a substance that can donate two protons to a base.

f Triprotic acid: a substance that can donate three protons to a base.

UNDERSTANDING

2 a $H_2C_2O_4(aq) + H_2O(l) \rightarrow HC_2O_4^-(aq) + H_3O^+(aq)$

$HC_2O_4^-(aq) + H_2O(l) \rightarrow C_2O_4^{2-}(aq) + H_3O^+(aq)$

b $HNO_2(aq) + H_2O(l) \rightarrow NO_2^-(aq) + H_3O^+(l)$

c $CH_3COOH(aq) + H_2O(l) \rightarrow CH_3COO^-(aq) + H_3O^+(aq)$

d $H_3AsO_4 + H_2O(l) \rightarrow H_2AsO_4^-(aq) + H_3O^+(aq)$

$H_2AsO_4^-(aq) + H_2O(l) \rightarrow HAsO_4^{2-} + H_3O^+(aq)$

$HAsO_4^{2-}(aq) + H_2O(aq) \rightarrow AsO_4^{3-}(aq) + H_3O^+(aq)$

APPLYING

3 Potassium hydrogen phthalate is a monoprotic acid. The only H atom it can donate is the one bonded to the oxygen atom.

$C_8H_5KO_4 + H_2O(l) \rightarrow C_8H_4KO_4^-(aq) + H_3O^+(aq)$

4.2 SECTION REVIEW

REMEMBERING

1 a Strong acid: an acid that readily donates a proton to water.

b Weak acid: an acid in which only a small proportion of the molecules will donate their proton.

c Concentrated acid: a solution in which there are is large number of H_3O^+ ions per unit volume of water.

d Dilute acid: a solution in which there is a small number of H_3O^+ ions per unit volume of water.

UNDERSTANDING

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

b $CH_3CH_2CH_2NH_2(l) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + H_3O^+(aq)$

APPLYING

3 Sulfuric acid would have the highest conductivity. It is a strong diprotic acid whereas carbonic acid is weak:

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

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

Carbonic acid is a weak diprotic acid. Very few carbonic acid molecules or hydrogen carbonate ions dissociate to produce H_3O^+ ions:

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

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

Since H_2SO_4 dissociates completely, it produces more ions in solution, resulting in greater electrical conductivity.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Polyprotic: a substance that can donate more than one proton to a base.

b Amphiprotic: a substance that can gain or lose a hydrogen ion to act as an acid or a base.

c Hydrogen salt: a salt formed when only some of the hydrogen atoms in an acid are replaced.

CATEGORY QUESTIONS

2 a Barium hydroxide ($Ba(OH)_2(s)$)

$Ba(OH)_2(s) + 2H_2O(l) \rightarrow Ba^{2+}(aq) + 2OH^-(aq) + 2H_2O(aq)$

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b Benzoic acid ($C_6H_5COOH(l)$)

$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^+(aq) + H_3O^+(aq)$

ELABORATION QUESTIONS

3 a = a concentrated strong acid.
b = a dilute strong acid.
c = a concentrated weak acid.
d = a dilute weak acid.

4 A concentrated strong acid: there is a large number of + ions and there are no un-ionised molecules.
A dilute strong acid: there is a small number of + ions and there are no un-ionised molecules.
A concentrated weak acid: there is a large number of + ions and there are many un-ionised molecules.
A dilute weak acid: there is a small number of + ions and there are many un-ionised molecules.

EVIDENCE QUESTIONS

5 B = H_2SO_4 = strong, diprotic acid = largest conductivity
E = HCl = strong monoprotic acid = large conductivity
D = H_3PO_4 = weak triprotic acid = relatively large number of H_3O^+
A = H_2CO_3 = weak diprotic acid
C = CH_3COOH = weak monoprotic acid

END-OF-CHAPTER EXAM

1 C
2 C
3 D
4 Both are strong acids because they are 100% dissociated. X must be diprotic and Y must be monoprotic. Therefore:
X = H_2SO_4
Y = HCl (or HNO_3)
5 a HCl/NH_3 – high conductivity initially indicating strong acid (HCl). Conductivity decreases gradually to the neutralisation point after which conductivity rises gradually to a low maximum conductivity indicating a weak base (NH_3).
b HCl/KOH – high conductivity initially indicating strong acid (HCl). Conductivity decreases rapidly to the neutralisation point after which the conductivity increases rapidly indicating a strong base (KOH).
c CH_3COOH/KOH – low conductivity initially indicating weak acid (CH_3COOH). Conductivity decreases rapidly to the neutralisation point after which conductivity rises rapidly to a high maximum conductivity indicating a strong base.
d CH_3COOH/NH_3 – low conductivity initially indicating weak acid (CH_3COOH). Conductivity decreases gradually to the neutralisation point after which conductivity rises gradually to a low maximum conductivity indicating a weak base.

CHAPTER 5 PH SCALE

5.1 SECTION REVIEW

REMEMBERING

1 a An ionisation reaction that takes place in pure water or aqueous solution in which a water molecule loses a hydrogen ion to become a hydroxide ion. The hydrogen ion immediately attaches to another water molecule to produce the hydronium ion.
b K_w is the equilibrium constant representing the equilibrium expression that shows water ionising into two ions.

APPLYING

2 a $[H_3O^+] = 1.45$ M, $[OH^-] = \frac{10^{-14}}{1.45} = 6.9 \times 10^{-15}$ M
b $[OH^-] = 0.89$ M, $[H_3O^+] = \frac{10^{-14}}{0.89} = 1.12 \times 10^{-14}$ M
c $[H_3O^+] = 1.5 \times 2 = 3.00$ M, $[OH^-] = \frac{10^{-14}}{3.00} = 3.33 \times 10^{-15}$ M
d $[OH^-] = 2 \times 0.89 = 1.78$ M, $[H_3O^+] = \frac{10^{-14}}{1.78} = 5.62 \times 10^{-15}$ M

5.2 SECTION REVIEW

1 pH = 3
2 pH = 4.9
3 pH = 12.6
4 $[NaOH] = 3.2 \times 10^{-5}$ M
5 pOH = 3
6 pOH = 4.9
7 pH = 1.5
8 8.5 g
9 277 mL

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a pH is a number representing the acidity or alkalinity of a solution on a logarithmic scale that is based on the hydrogen ion concentration.
b pOH is a number representing the acidity or alkalinity of a solution on a logarithmic scale that is based on the hydroxide ion concentration.
c pH scale is a scale that measures the acidity and alkalinity of a solution, based on the concentration of hydrogen ions in a solution.
d pOH scale is a scale that measures the acidity and alkalinity of a solution, based on the concentration of hydroxide ions in a solution.

EVIDENCE QUESTIONS

2 1×10^{-6} M
2×10^{-12} M

3 a Black coffee, pH 5 $[H_3O^+] = 10^{-5}$ M, $[OH^-]$ 10^{-9} M

b Oven cleaner, pH 14 $[H_3O^+] = 10^{-14}$ M, $[OH^-]$ 10^{0} M

c Cola drink, pH 3 $[H_3O^+] = 10^{-3}$ M, $[OH^-]$ 10^{-11} M

d Toothpaste, pH 5.8 $[H_3O^+] = 10^{-8}$ M, $[OH^-]$ 10^{-6} M.

4 a 2

b 12

c 0

d 13

e 2

f 0.64

g 1.76

h –0.10.

ELABORATION QUESTIONS

5 a $n(HCl) = cV = 0.2 \times 50 \times 10^{-3} = 10 \times 10^{-3} = 1 \times 10^{-2}$
$n(NaOH) = cV = 0.1 \times 100 \times 10^{-3} = 1 \times 10^{-2}$
pH = 7 because $[H^+] = [OH^-]$

b $\frac{10^{-6}}{2} = 5 \times 10^{-7} = 0.0000005$ M
pH = 6.3

END-OF-CHAPTER EXAM

1 B

2 A

3 A

4 pOH scale

5 1×10^{-8} M
5×10^{-3} M

6 $n_{HCl} = 1.087 \times 0.025 = 0.027$ mol $= n_{250.00\ mL}$
$n_{25.00\ mL} = 0.027/12.5 = 2.174 \times 10^{-3}$ mol $= n_{100.00\ mL}$
$c_{100.00\ mL} = 2.174 \times 10^{-3}/0.1 = 0.02174$ mol
pH $= -\log_{10} 0.02174 = 1.67$ pOH $= 14 - 1.67 = 12.33$

7 $n\ Ba(OH)_2 = 0.108 \times 0.03895 = 4.2 \times 10^{-3}$ mol,
n $OH^- = 2 \times 4.2 \times 10^{-3} = 8.4 \times 10^{-3}$ mol
$n\ HNO_3 = 0.116 \times 0.04486 = 5.2 \times 10^{-3}$
Excess $= 8.4 \times 10^{-3} - 5.2 \times 10^{-3} = 3.2 \times 10^{-3} = OH^-$
$c\ OH^- = 3.2 \times 10^{-3}/(0.03895 + 0.04486) = 0.038$ M
pOH $= -\log_{10} 0.038 = 1.42$
pH $= 14 - 1.42 =$ *12.58*

8 a 3×10^{12} $H_3O^+(aq)$ in a single drop of water

b 3×10^{19} $H_3O^+(aq)$ in a single drop of 1.0 mol L^{-1} HCl

c 3×10^{5} $H_3O^+(aq)$ in a single drop of 1.0 mol L^{-1} NaOH

CHAPTER 6 BRØNSTED–LOWRY MODEL

6.1 SECTION REVIEW

REMEMBERING

1 The Arrhenius definition:
Acids produce H^+ ions in solution
Bases produce OH^- ions in solution

UNDERSTANDING

2 Yes. A strong acid is one in which most, if not all, of the acid molecules have dissociated into ions. A dilute acid is one in which there are few acid molecules (solute) per volume of water (solvent).

3 According to the Arrhenius theory of acids and bases, the carbonate ion, CO_3^{2-}, should not possess any basic properties because it is unable to produce hydroxide ions OH^- in solution. However, carbonate compounds exhibit basic properties – high pH, reactions with acids and so on. The Brønsted–Lowry definition can explain the basic properties of carbonates by defining a base as a substance that can accept one or more H^+ ions from an acid.

APPLYING

4 a Ammonia solution, $NH_3(aq)$ weak

b Carbonic acid, $H_2CO_3(aq)$ weak

c Nitric acid, $HNO_3(aq)$ strong

d Hydrochloric acid, HCl(aq) strong

e Sodium hydroxide, NaOH(aq) strong

5 a HNO_3/NO_3^- H_2O/H_3O^+

b NH_4^+/NH_3 H_2O/H_3O

c HSO_4^-/SO_4^{2-} O^{2-}/OH^-

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

e $HC_2H_3O_2/C_2H_3O_2^-$

6 a H_2CO_3

b H_2O

c $H_2PO_4^-$

6.2 SECTION REVIEW

APPLYING

1 HCO_3^- is amphiprotic because it can act as an acid or a base.
As an acid: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$
As a base: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

2 HSO_4^- is amphiprotic because it can act as an acid or a base.
As an acid: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$
As a base: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_2SO_4(aq) + OH^-(aq)$

6.3 SECTION REVIEW

REMEMBERING

1 A solution that resists changes in pH when acid or alkali is added to it.

2 A solution of ammonia and ammonium chloride.

UNDERSTANDING

3 b

4 Sodium methanoate, CH_3ONa

APPLYING

5 Basic buffer

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CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Amphiprotic: a substance that can gain or lose a hydrogen ion to act as an acid or a base.

b Buffer solution: a solution of a weak acid and its conjugate base (or vice versa) that can counteract the addition of an acid or a base to maintain a constant pH.

c Acidic buffer: an acidic buffer contains a weak acid and its conjugate base.

d Basic buffer: a basic buffer contains a weak base and its weak conjugate acid.

CATEGORY QUESTIONS

2 An acidic buffer solution would be prepared by dissolving the salt of a weak acid in a solution of the weak acid.
For the H_2CO_3/HCO_3^- buffer system, a known mass of sodium hydrogen carbonate would be dissolved in a carbonic acid solution of known concentration.
A basic buffer solution would be prepared by dissolving the salt of a weak base in a solution of the base.
For the NH_3/NH_4Cl buffer system, a known mass of ammonium chloride would be dissolved in an ammonia solution of known concentration.

3 a This is a solution of a weak base in equilibrium with its conjugate acid. The pH will depend on the relative amounts of these substances but will be about 8–9.

b $CH_3CH_2NH_2(aq) + H_2O(l) \rightarrow CH_3CH_2NH_3^+(aq) + OH^-(aq)$
The Cl^- is a spectator ion and plays no part in the system.

c Initially, pH drops due to H_3O^+ from the HCl. Then, more $CH_3CH_2NH_2$ reacts, producing more OH^- ions which neutralise the excess H_3O^+. The pH returns to close to its original value:
$CH_3CH_2NH_2(aq) + H_2O(l) \rightarrow CH_3CH_2NH_3^+(aq) + OH^-(aq)$
The conjugate acid ($CH_3CH_2NH_3^+$) reacts with the excess OH^- ions. The equilibrium is restored and the pH decreases to close to its original value.
$CH_3CH_2NH_2(aq) + H_2O(l) \leftarrow CH_3CH_2NH_3^+(aq) + OH^-(aq)$

ELABORATION QUESTIONS

4 A buffer is an acid/base system in equilibrium. If a small amount of acid is added, the position of equilibrium can shift, according to Le Chatelier's principle, to counteract the addition of the acid and so remain within a narrow pH range.

5 a 26%

b As $[H_3O^+]$ increases, the second equilibrium shifts to the left. This increases the $HCO_3^-(aq)$ to increase which causes the first equilibrium to shift to the left. This reduces the available $CO_3^{2-}(aq)$ for marine organisms.

END-OF-CHAPTER EXAM

1 C

2 B

3 A Brønsted–Lowry acid

4 First dilution: 25 mL of 1.087 M HCl into a 250.00 mL flask = 1.087/10 = 0.1087 M
Second dilution: 20 mL of 0.1087 M into a 100.00 mL flask = 0.1087/5 = 0.0217 M
$pH = -\log_{10} 0.217 = 0.66$
$pOH = 14 - 0.66 = 13.34$

5 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H2O(l)$
$c(HCl) = 0.2 \text{ mol L}^{-1}$ $V = 40 \text{ mL} = 0.040 \text{ L}$ $n = ?$
$n(HCl) = 0.2 \times 0.040 = 0.008 \text{ mol}$ $n(H_3O^+) = 0.008 \text{ mol}$
$c(NaOH) = 0.1 \text{ mol L}^{-1}$ $V = 20 \text{ mL} = 0.020 \text{ L}$ $n = ?$
$n(NaOH) = 0.10 \times 0.020 = 0.002 \text{ mol}$ $n(OH^-) = 0.002 \text{ mol}$
H_3O^+ is in excess by $0.008 - 0.002 = 0.006 = 6.0 \times 10^{-3}$ mol
$V = 40 \text{ mL} + 20 \text{ mL} = 0.060 \text{ L}$

$$[H_3O^+] = \frac{6.0 \times 10^{-3}}{0.060} = 0.100 \text{ mol L}^{-1}$$

$pH = -\log 0.100 = 1.0$

CHAPTER 7 DISSOCIATION CONSTANTS

7.1 SECTION REVIEW

REMEMBERING

1 The equilibrium expression of a weak acid

2 A strong acid is one that dissociates completely in water. Strong acids include hydrochloric acid (HCl), nitric acid (HNO_3) and sulfuric acid (H_2SO_4).
Weak acids only dissociate in water to a small extent. Weak acids include hydrofluoric acid (HF), ethanoic acid (CH_3COOH) and carbonic acid (H_2CO_3).

APPLYING

3 a $H_2CO_3(aq) + 2H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + 2H_3O^+(aq)$

$$K_a = \frac{[CO_3^{2-}][H_3O^+]^2}{[H_2CO_3]}$$

b $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_6N^+(aq) + OH^-(aq)$

$$K_b = \frac{[C_5H_6N^+]\,[OH^-]}{[C_5H_5N]}$$

c $NH_2OH(aq) + H_2O(l) \rightleftharpoons NH_3OH^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_3OH^+]\,[OH^-]}{[NH_2OH]}$$

d $HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$

$$K_a = \frac{[OCl^-]\,[H_3O^+]}{[HOCl]}$$

7.2 SECTION REVIEW

APPLYING

1 a $4.3 \times 10^{-3} \text{ mol L}^{-1}$

b $4.3 \times 10^{-3} \text{ mol L}^{-1}$

c 4.3 %

2 2.9

3 7.2×10^{-4}

4 2.7

5 a $C_6H_7O_6^-(aq) + H_2O(l) \rightarrow H_6H_8O_6(l) + OH^-(aq)$

b 1.3×10^{-10}

6 a $C_5H_6N^+(aq) + H_2O(l) \rightarrow C_5H_5N(aq) + H_3O^+(aq)$

b 5.9×10^{-6}

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Acid dissociation constant: the equilibrium expression of a weak acid.

b Base dissociation constant: the equilibrium expression of a weak base.

c Percentage ionisation: the percentage of acid or base molecules that have ionised in water.

d Polyprotic acid: a substance that can donate more than one proton to base.

CATEGORY QUESTIONS

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

b $CH_3CH_2CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + OH^-(aq)$

c $HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$

ELABORATION QUESTIONS

3 $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$$

$$4.3 \times 10^{-4} = \frac{[CH_3CH_2NH_3^+][OH^-]}{0.2}$$

$$9.27 \times 10^{-3} = [OH^-]$$

$$[H_3O^+] = \frac{[1.0\ x\ 10^{-14}]}{[9.27\ x\ 10^{-3}]}$$

$= 1.08 \times 10^{-12}$ M

$pH = -\log_{10} 1.08 \times 10^{-12} = 11.97$

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

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

b $$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$$

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$$

c $K_a \times K_b = K_w = 1 \times 10^{-14}$

$4.7 \times 10^{-11} \times K_b = 1 \times 10^{-14}$

$K_b = 2.1 \times 10^{-4}$

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

$pOH = 14 - 11.1 = 2.9$

$2.9 = -\log_{10}[OH^-]$

$[OH^-] = 1.26 \times 10^{-3}$ M

b $[NH_4^+] = [OH^-] = 1.26 \times 10^{-3}$ M

c $$\%\ \text{Ionisation} = \frac{[NH_4^+]}{[NH_3]} \times 100 = \frac{1.26\ x\ 10^{-3}}{0.1} \times 100 = 1.26\ \%$$

END-OF-CHAPTER EXAM

1 C

2 D

3 B

4 $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$

5 $$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$

6 $C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$

$K_a \times K_b = 1 \times 10^{-14} = K_a \times 4.3 \times 10^{-10}$

$K_a = 2.3 \times 10^{-5}$

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

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

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

b $$7.54 \times 10^{-3} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = \frac{[H_2PO_4^-][H_3O^+]}{0.1}$$

$[H_3O^+] = 0.027$ M

$pH = -\log_{10} 0.027 = 1.57$

c The values of K_{a2} and K_{a3} are very small. The values of [H3O$^+$] derived from these values would be insignificantly small and so would have no effect on the pH calculated using K_{a1} only.

8 $C_6H_5OH(aq) + H_2O(l) \rightleftharpoons C_6H_5O^-(aq) + H_3O^+(aq)$

$pH = 5.1 = -\log_{10}[H_3O^+]$

$[H_3O^+] = 7.9 \times 10^{-6}$ M $= [C_6H_5O^-]$

$$\%\ \text{ionisation} = \frac{[C_6H_5^-]}{[C_6H_5OH]} \times 100 = \frac{7.9\ x\ 10^{-6}}{0.5} \times 100 = 7.9 \times 10^{-3}\ \%$$

CHAPTER 8 ACID–BASE INDICATORS

8.1 SECTION REVIEW

REMEMBERING

1 a Indicator: a substance that changes colour in solution depending on whether the solution is acidic or basic.

b Indicator (acid form): the form of the indicator that is able to donate a proton to a base.

c Indicator (basic form): the form of the indicator that is able to accept a proton from an acid.

2 $HIn + H_2O \rightleftharpoons In^- + H_3O^+$

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3 $K_a = \frac{[In^-][H_3O^+]}{[HIn]}$

$K_b = \frac{[HIn]}{[In^-][H_3O^+]}$

UNDERSTANDING

4 a $5 \times 10^{-10} = \frac{[P^-]x\ 10^{-6}}{[HP]}$

$5 \times 10^{-4} = \frac{[P^-]}{[HP]}$

$[HP] \gg [P^-]$

Dominant species is HP

b $5 \times 10^{-10} = \frac{[P^-]x\ 10^{-11}}{[HP]}$

$50 = \frac{[P^-]}{[HP]}$

$[HP] \gg [P^-]$

$[HP] \ll [P^-]$

Dominant species is P^-

8.2 SECTION REVIEW

REMEMBERING

1 Define the following terms:

a pK_a: the negative base-10 logarithm of the acid dissociation constant of a solution.

b pK_b: the negative base-10 logarithm of the base dissociation constant of a solution.

c pK_{ind}: the negative base-10 logarithm of the acid dissociation constant of an indicator solution. Used to give an indication of the pH at which the indicator changes colour.

d Indicator pH range: the range of pH values that an indicator changes colour.

2 a hydrofluoric > methanoic > lactic > ethanoic > hydrocyanic > ammonium ion

b aniline < pyridine < hydroxylamine < hydrazine < ammonia < methylamine

UNDERSTANDING

3 $HClr(aq) + H_2O(l) \rightleftharpoons Clr^-(aq) + H_3O^+(aq)$ $pK_a = 6.2$

a $K_a = \frac{[Clr^-][H_3O^+]}{[HClr]}$

b Colour change occurs when pH of the solution = pK_a

Useful pH range = pH ±1 = 5.2 – 7.2

4 a $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$

b $K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$

c $pK_b = 8.77 = -\log_{10} K_b$

$K_b = 1.7 \times 10^{-9} = \frac{[C_5H_5NH^+][OH^-]}{1.00}$

$[OH^-] = 4.1 \times 10^{-5}$ M

pOH = 4.4

pH = 14 – 4.4 = 9.6

APPLYING

5

INDICATOR	USEFUL PH RANGE	pK_a	K_a
Methyl orange	3.1 – 4.4	3.7	2.0×10^{-4}
Congo red	3.0 – 5.0	4.0	1.0×10^{-4}
Bromocresol green	3.8 – 5.4	4.6	2.5×10^{-5}
Bromothymol blue	6.0 – 7.6	6.8	1.6×10^{-7}
Phenolphthalein	8.2 – 10.0	9.1	7.9×10^{-10}
Thymolphthalein	9.3 – 10.5	9.9	1.3×10^{-10}
Alizarin yellow	10.2 – 12.0	11.1	7.9×10^{-12}
Indigo carmine	11.6 – 13.0	12.3	5.0×10^{-13}

8.3 SECTION REVIEW

UNDERSTANDING

1 pH at end point = pK_a (indicator) = $-\log_{10} 7.9 \times 10^{-5} = 4.1$

APPLYING

2 Bromoacetic acid is the strongest acid ($K_a = 1.25 \times 10^{-3}$), followed by hypochlorous acid ($K_a = 3.0 \times 10^{-8}$) followed by hypoiodous acid ($K_a = 2.3 \times 10^{-11}$).
Solution A:
Red in methyl red. pH 1–3
Yellow in m – cresol purple. pH = 3–7
Yellow in alizarin red s. pH 1–4
pH of solution A = 4
Solution B:
Red in methyl red. pH 1–3
Red in m – cresol purple. pH = 1
Yellow in alizarin red s. pH 1–4
pH of solution B = 1
Solution C:
Yellow in methyl red. pH 5–7
Yellow in m – cresol purple. pH 3–7
Red in alizarin red s. pH 5–6
pH of solution C = 6
Solution A = hypochlorous acid
Solution B = bromoacetic acid
Solution C = hypoiodous acid

3 a Bromocresol green

b Indigo carmine

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Indicator: a substance that changes colour in solution depending on whether the solution is acidic or basic.

b Indicator (acid form): the form of the indicator that is able to donate a proton to a base.

c Indicator (basic form): the form of the indicator that is able to accept a proton from an acid.

d pK_a: the negative base-10 logarithm of the acid dissociation constant of a solution.

e pK_b: the negative base-10 logarithm of the base dissociation constant of a solution.

f pK_{ind}: the negative base-10 logarithm of the acid dissociation constant of an indicator solution. Used to give an indication of the pH at which the indicator changes colour.

CATEGORY QUESTIONS

2 $HIn + H_2O \rightleftharpoons In^- + H_3O^+$

yellow blue

3 $HAly + H_2O \rightleftharpoons Aly^- + H_3O^+$

$$K_a = \frac{[Aly^-][H_3O^+]}{[HAly]}$$

$$K_a = \frac{[HAly]}{[Aly^-][H_3O^+]}$$

ELABORATION QUESTIONS

4 Congo red

5 11.75

EVIDENCE QUESTIONS

6 a Yellow to blue: the base form is yellow, so when equivalence point is reached, the acid form of the indicator is dominant, which is blue.

b Weak acid/strong base

END-OF-CHAPTER EXAM

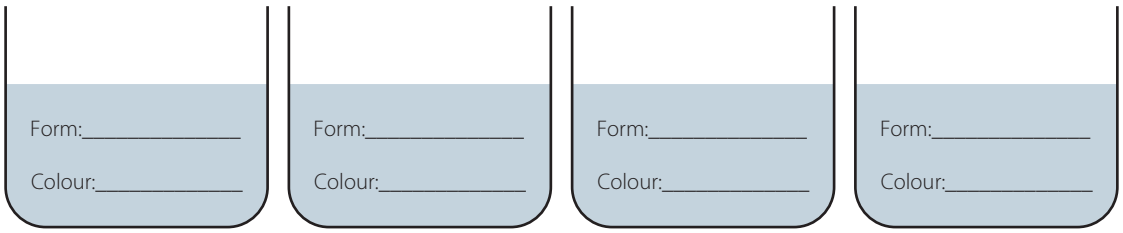
1 C

2 B

3 C

4 D

5



Methanoic acid = pH 3 = yellow = form B (this has the extra two H atoms)

Ammonia = pH 9.5 = purple = form A (this has fewer H atoms)

Propanoic acid = pH 6.3 = mixture of yellow and purple and so will have a mixture of both forms A and B

Water = pH 7 = mostly purple

CHAPTER 9 VOLUMETRIC ANALYSIS

9.1 SECTION REVIEW

REMEMBERING

1 a End point: the pH of an acid–base titration at which the chosen indicator changes colour.

b Equivalence point: the point when the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction.

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UNDERSTANDING

2

ACID	BASE	PRODUCTS	EQUIVALENCE POINT	INDICATOR
Propanoic	**Sodium hydroxide**	Sodium propanoate	5.5	**Methyl red**
Nitric acid	Ammonia	Ammonium nitrate	**4–5**	**Methyl orange**
Hydrochloric	**Potassium hydroxide**	Potassium chloride	**7**	**Phenolp-hthalein**
Acetic	**Ammonia**	Ammonium acetate	None visible	**N/a**

9.2 SECTION REVIEW

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

2 a Molarity of $HCl = 0.5\ \text{mol L}^{-1}$

b Molarity of $Ba(OH)_2 = 0.271\ \text{mol L}^{-1}$

c Concentration of $Ba(OH)_2 = 46.43\ \text{g L}^{-1}$

3 m $(CaCO_3) = 0.2$ g

% $(CaCO_3) = 36.23$

4 m $(NH_4^+) = 0.119$ g

% $(NH_4^+) = 31.7$

9.3 SECTION REVIEW

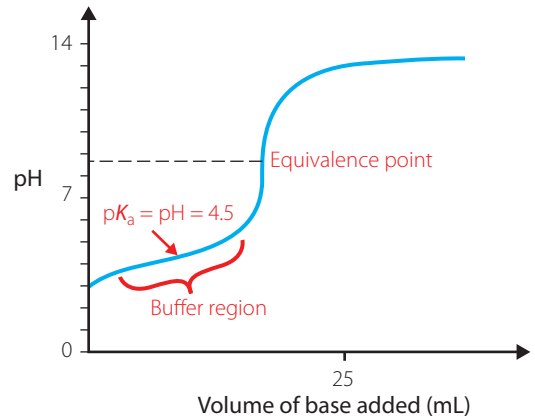
REMEMBERING

1 a Titration curve: a graphical representation of a titration with the x-axis being the volume of titrant added, the y-axis being the pH of the solution.

b Buffer region: the part of a titration curve during which the pH changes little as titrant is added. Occurs when one of the reagents is a weak acid or a base and is the result of a buffer solution being set up.

UNDERSTANDING

2



9.4 SECTION REVIEW

UNDERSTANDING

1 $n CaCO_3 = \dfrac{0.9}{100} = 9.0 \times 10^{-3}$ mol

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

nHCl (reacted with $CaCO_3$) $= 2 \times 9 \times 10^{-3} = 0.018$ mol

nHCl (initial) $= 3.0 \times \dfrac{10.00}{1000} = 0.03$ mol

nHCl (final) = HCl (initial) − HCl (reacted) = 0.03 − 0.018 = 0.012 mol

nNaOH = nHCl (final) = 0.012 mol

$V\text{NaOH} = \dfrac{n}{C} = \dfrac{0.012}{1.25} = 9.6 \times 10^{-3}\ \text{L} = 9.6\ \text{mL}$

CHAPTER REVIEW QUESTIONS

1 a End point: the pH of an acid–base titration at which the chosen indicator changes colour.

b Equivalence point: the point when the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction.

c Titrant: the solution in a burette.

d Analyte: the solution of an unknown concentration that will be analysed.

e Back titration: a method used to determine the mass or concentration of a substance that is not able to be determined directly.

f Titration curve: a graphical representation of a titration with the x-axis being the volume of titrant added, the y-axis being the pH of the solution.

g Buffer region: the part of a titration curve during which the pH changes little as titrant is added. Occurs when one of the reagents is a weak acid or a base and is the result of a buffer solution being set up.

h Primary standard: a solution of accurately known concentration that remains stable under common laboratory conditions for extended periods of time.

2 Sulfuric acid absorbs water from the air.

3 a 1.1725 g

b Answers will vary, but should follow the chapter information.

4 9.4 %

5 $5.5 \times 10^{-5}\ \text{mol L}^{-1}$

END-OF-CHAPTER EXAM

1 B

2 A

3 D

4 B

5 Analyte

6 Back titration

7 $n\ \text{NaOH} = 0.513 \times \dfrac{29.10}{1000} = 0.0149$ mol

Mole ratio tartaric acid: NaOH = 1: 2

n tartaric acid $= 0.0149/2 = 7.45 \times 10^{-3}$ mol,

$\text{M} = m/n = \dfrac{0.956}{7.45\ x\ 10^{-3}} = 128.33$ g

Mole ratio citric acid: NaOH = 1: 3

n tartaric acid $= 0.0149/3 = 4.97 \times 10^{-3}$ mol,

$M = m/n = \dfrac{0.956}{4.97 \times 10^{-3}} = 192.35$ g

Molecular mass of tartaric acid = 150 g mol^{-1}

Molecular mass of citric acid = 192 g mol^{-1}

The substance is citric acid

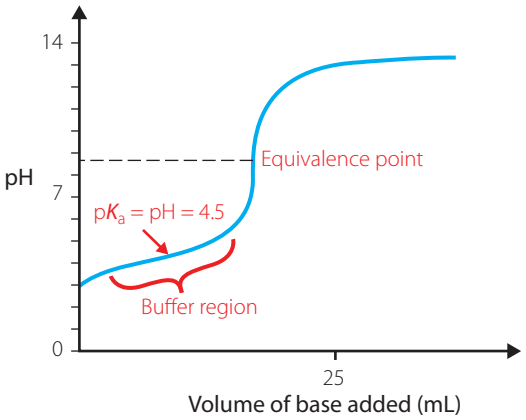
8 $NH_3(aq) + HNO_3(aq) \rightarrow NH_4Cl(aq)$

$n\,HNO_3 = 0.151 \times \dfrac{26.2}{1000} = 3.96 \times 10^{-3} = n NH_3$ in 25.00 mL.

$n\,NH_3$ in 500 mL $= \dfrac{500}{20} \times 3.96 \times 10^{-3} = 0.0792$ mol

$cNH_3 = \dfrac{\frac{0.0792}{20.00}}{1000} = 3.96$ mol L^{-1}

9 a



b $CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3COO^-Na^+(aq) + H_2O(l)$

In the buffer region, the solution consists of a weak acid (CH_3COOH) and its conjugate base (CH_3COO^-):

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

As more NaOH is added the forward reaction is favoured, producing more H_3O^+ which neutralises the OH^-. Although the pH rises, it does so gradually producing the buffer region.

c From the graph, the pH of the equivalence is about 8.5. At this point just enough NaOH has been added to neutralise the H_3O^+. The only species present are H_2O (pH 7), Na^+ ions (no acidic or basic properties) and acetate ions, CH_3COO^-. The acetate ion is the conjugate base of a weak acid and, as such, is a weak base:

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

The acetate ion has a pH of about 8–9

d This is the initial pH of the acetic acid

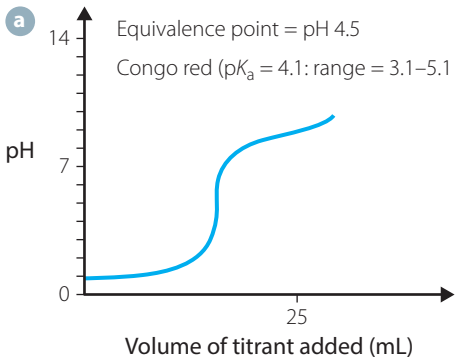
e From the graph, the pH at the mid-point of the buffer region is the pK_a of the acid.

pK_a = 4.5

$K_a = 3.16 \times 10^{-5}$

10

a



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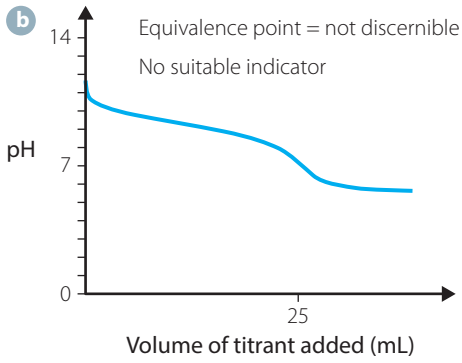

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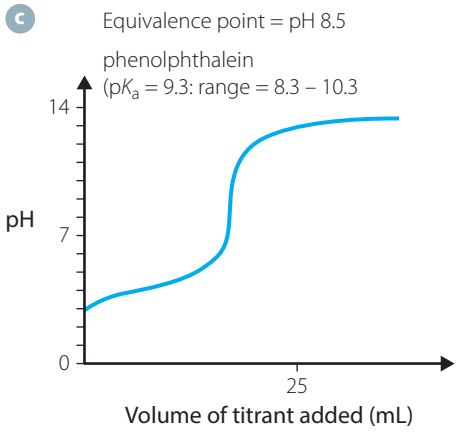

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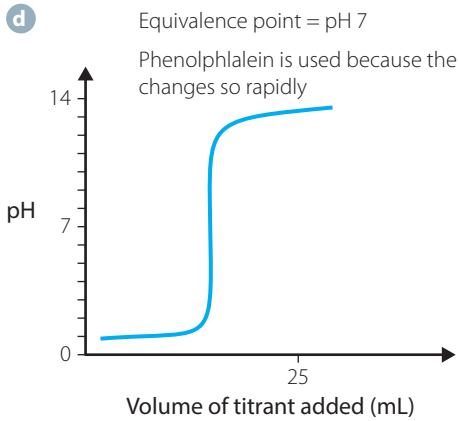

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CHAPTER 10 EQUILIBRIUM, ACIDS AND REDOX REACTIONS

10.1 SECTION REVIEW

REMEMBERING

1 a Loss of electrons

b Gain of electrons

c When an equation has been split into its two components – the oxidation reaction or the reduction reaction.

UNDERSTANDING

2 Oxidation and reduction are complementary processes involving the transfer of electrons. For a substance to lose electrons (oxidation) a substance must be present to gain those electrons (reduction).

3 Aluminium reacts with oxygen in the air to form aluminium oxide, Al_2O_3 which protects the aluminium from any further reaction.

APPLYING

4 a $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ oxidation

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

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

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

5 $2Zn(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Zn^{2+}(aq) + 4OH^-$

ANALYSING

6 a Yes, Zn is higher in the reactivity series than Ag.

b No, Zn is lower in the series than Na.

c Yes, Mg is higher in the reactivity series than Cu.

d Yes, Fe is higher in the reactivity series than Cu.

10.2 SECTION REVIEW

REMEMBERING

1 Number of protons in the nucleus, distance of the valence electrons from the nucleus, number of electron shells between the valence shell and the nucleus.

2 The energy required to remove one electron from an atom or ion of an element in a gaseous state.

UNDERSTANDING

3 a 2.6

b 2.8

4 a Sr loses 2 e^- to gain a full shell, leaving two more protons than electrons.

b Al loses 3 e^- to gain a full shell, leaving three more protons than electrons.

5 Bromine has an atomic number of 35. It therefore has 35 protons, which means it has 35 electrons. It therefore has 35 ionisation energies.

APPLYING

6 Phosphorous electron configuration: 2.8.5. Three electrons are needed for a stable, full outer shell of 2.8.8. The phosphide ion has three extra electrons. Therefore, the formula for the phosphide ion is P^{3-}.

7 Electron configuration of fluorine: 2.7
Electron configuration of bromine: 2.8.8.17
Ionisation energy of fluorine is larger than that of bromine because it requires more energy to remove the outer electron of fluorine because it is more strongly attached to the nucleus. Bromine's outer electron is only weakly attracted because of its distance from the nucleus and the shielding of the nucleus by the extra electron shells.

ANALYSING

8 The second ionisation energy is larger than the first because removing an electron from a positive ion is much more difficult than removing an electron from a neutral atom.

$Ca \rightarrow Ca^+ + e^-$ ionisation energy = 590 kJ mol^{-1}

$Ca^+ \rightarrow Ca^{2+} + e^-$ ionisation energy = 1145 kJ mol^{-1}

9 Ionisation energy of S = 1000 kJ mol^{-1}
Ionisation energy of Mg = 738 kJ mol^{-1}
S contains more protons than Mg, therefore there is a greater attraction of the nucleus for the outer electrons of S than Mg. Therefore, more energy is required to remove an outer electron of S than Mg.

10.3 SECTION REVIEW

APPLYING

1 Ba > Ca > Al > Zn > Fe > Sn > Pb > Cu > Ag > Pt > Au

REFLECTING

2 Answers should mention the phlogiston theory, discovery of oxygen by Joseph Priestly and the work done by Antoine Lavoisier on the weight gains by elements burning in oxygen.

10.4 SECTION REVIEW

UNDERSTANDING

1 a $Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$
$Br_2(l) + 2e^- \rightarrow 2Br^-(s)$
$Mg(s) + Br_2(l) \rightarrow Mg^{2+}(s) + 2Br^-(s)$

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

c $Al(s) \rightarrow Al^{3+}(s) + 3e^-$
$N_2(g) + 6e^- \rightarrow 2N^{3-}(s)$
$2Al(s) + N_2(g) \rightarrow 2AlN(s)$

APPLYING

2 a $NO_2(g) + H_2O(l) \rightarrow NO_3^-(aq) + 2H^+(aq) + e^-$ oxidation

b $2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$ oxidation

c $2H^+(aq) + 2HOCl(aq) + 2e^- \rightarrow Cl_2(g) + 2H_2O(l)$ reduction

d $C_2O_4^{2-}(aq) \rightarrow CO_2(g) + 2e^-$ oxidation

3 a $14H^+(aq) + 3Sn^{2+}(aq) + Cr_2O_7^{2-} \rightarrow 2Cr^{3+}(aq) + 3Sn^{4+}(aq) + 7H_2O(l)$

b $5C_2O_4^{2-}(aq) + 16H^+(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

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

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

e $3Ca(s) + 2P(s) \rightarrow 3Ca^{2+}(s) + 2P^{3-}(s)$

f $2K(s) + F_2(g) \rightarrow 2K^+(s) + 2F^-(s)$

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

h $ClO_3^-(aq) + 2H^+(aq) + e^- \rightarrow ClO_2(g) + H_2O(l)$

10.5 SECTION REVIEW

REMEMBERING

1 a The number of electrons that an atom would have gained or lost to get to its present state; it assumes that each species is completely ionic.

b As above.

UNDERSTANDING

2 $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$
Carbon:
Oxidation state in $C_2H_4 = -2$
Oxidation state in $CO_2 = +4$
This is oxidation.
Oxygen:
Oxidation state in $O_2 = 0$
Oxidation state in CO_2 and $H_2O = -2$
This is reduction.

APPLYING

3 a +5

b −1

c +5

d +6

e +5

4 +6

5 +4

6 −1

7 −1

ANALYSING

8 a $16H^+(aq) + 2MnO_4^-(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$

b $8H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$

10.6 SECTION REVIEW

APPLYING

1 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
$C^{-4} \rightarrow C^{+4} + 8e^-$ oxidation
$2O_2 + 8e^- \rightarrow 2O^{2-} + 2O^{2-}$ reduction

2 $ClO_3^-(s) \rightarrow Cl^-(s) + 1.5O_2(g) + 6e^-$ oxidation
$ClO_3^-(s) + 6e^- \rightarrow Cl^-(s) + 1.5O_2(g)$ reduction

3 $Ca^{2+}(s) \rightarrow Ca^{2+}(s)$ no change
$C^{4+}(s) \rightarrow C^{4+}$ no change
$O^{2-}(s) \rightarrow O^{2-}(g)$ no change
This is not a redox reaction.

ANALYSING

4 a Element V

b Element R

c Element T

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a False – oxidation occurs when a species gains electrons.

b True

c False – magnesium is more reactive than copper and oxidises preferentially in the presence of copper.

d False – a reducing agent loses electrons.

e False – the first ionisation energy is the energy required to remove the outermost loosely held electron from an element in its gaseous state.

f True

CATEGORY QUESTIONS

2 For a species to be oxidised (lose an electron) a species must be present to be reduced (gain that electron).

3 When sodium and potassium react, they do so by losing their outer electron. The outer electron of sodium is more strongly held by the nucleus than potassium and requires more energy to remove – making sodium less reactive.

4 Non-metals react by gaining electrons. Fluorine has a strongly positive nucleus that has very little electron shielding and the outer shell only requires one electron to achieve a stable full outer shell.

5 Once the two outer electrons of calcium have been removed, it is far more difficult to remove an electron from the highly stable full outer shell of the Ca^{2+} ion.

6 Reduction is the gaining of electrons. Chlorine has seven electrons in its outer shell and can easily gain one electron to achieve the stability of a full outer shell. For magnesium to have an electron added to its outer shell that already contains two electrons would require an enormous amount of energy.

7 a Reduction

b Oxidation

c Reduction

d Reduction

e Oxidation

f Reduction

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8 a +6
b −1
c −3
d +4
e +3

ELABORATION QUESTIONS

9 a Redox: Al is oxidised, Fe^{2+} is reduced
b Not redox
c Redox: Fe is oxidised, O_2 is reduced
d Redox: Cd is oxidised, Ni^{3+} is reduced
e Not redox

EVIDENCE QUESTIONS

10 Reducing strength is the ability to be oxidised. A small ionisation energy indicates the element is easily oxidised, which indicates that it is a strong reducing agent.
From the table, reducing strength decreases across a period and increases down a group.
Caesium, Cs (376) is the most reactive metal and so is the strongest reducing agent.
Fluorine, F (1690) is the most reactive non-metal and so is the weakest reducing agent.

END-OF-CHAPTER EXAM

1 A
2 B
3 B
4 C
5 A
6 Reactivity increases down the group.
7 $5Fe^{2+}(aq)$
8 Oxygen and water
9 Carbon:
$C_3H_8 \rightarrow CO_2$
$-2.66 \rightarrow +4$
Oxidation
Oxygen:
$O_2 \rightarrow CO_2$
$0 \rightarrow -2$
Reduction
10 $6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
$H_2O(l) + CH_3CH_2OH(aq) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
$16H^+(aq) + 2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$
11 a Iron nail:
Blue at both ends, pink in the middle
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Blue
$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Pink
Corrosion occurs where the iron has been deformed – at both ends of the nail.
Iron nail wrapped with copper wire:
Blue all along the nail
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Blue
Iron is more reactive than copper. It undergoes more corrosion
Iron nail wrapped with zinc strip
Pink at either end. No blue areas
$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Pink
Zinc is more reactive than iron, so the zinc corrodes instead of the iron.
b White deposit is zinc hydroxide, $Zn(OH)_2$
$Zn(s) \rightarrow Zn^{2+}(s) + 2e^-$

CHAPTER 11 ELECTROCHEMICAL CELLS

11.1 SECTION REVIEW

REMEMBERING

1 a The electrode where oxidation occurs.
b The electrode where reduction occurs.
c A substance that conducts an electric current.

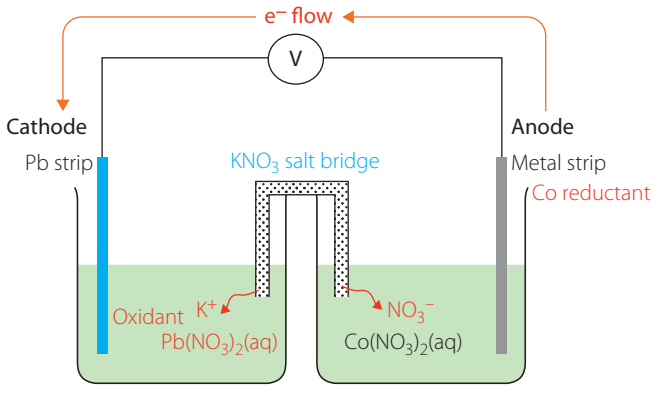
UNDERSTANDING

2

	CELL REACTION	ANODE	CATHODE
Galvanic	spontaneous	−	+
Electrolytic	non-spontaneous	+	−

APPLYING

3



K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > (H) > Cu > Ag > Pt > Au

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a A galvanic cell: a type of electrochemical cell that transforms chemical potential energy to electrical energy in a spontaneous chemical reaction.

b Electrolytic cell: a type of electrochemical cell that transforms electrical energy to chemical potential energy; this is not a spontaneous reaction; it requires the input of electrical energy for the chemical reaction to occur.

c Internal circuit: The internal circuit of an electrochemical cell consists of the strips of metal, solutions and the salt bridge.

d External circuit: The external circuit of an electrochemical cell consists of the connecting wires and the voltmeter or electrical appliance.

CATEGORY QUESTIONS

2

	GALVANIC CELL	ELECTROLYTIC CELL
Reaction spontaneity	Spontaneous	Non-spontaneous
Power source	Chemical reaction	External
Direction of electron flow	Anode → cathode	Anode → cathode
Anode charge	Negative	Positive
Cathode charge	Positive	Negative
Location of oxidation and reduction	Oxidation at anode Reduction at cathode	Oxidation at anode Reduction at cathode
Number of cells and why	Two half – cells to separate the reactants	One cell to contain compound to be electrolysed
Electrode polarity determined by	Determined by the reaction occurring at each electrode	The connection of the electrodes to the power source

ELABORATION QUESTIONS

3 As time passes the reactions in the half-cells approach equilibrium, the reactions slow down and the voltage becomes less.

4 At the cathode, $Cu^{2+}(aq)$ ions are converted to Cu(s) atoms. This electrode contains Cu(s) atoms ONLY.

EVIDENCE QUESTIONS

5 a Cathode = steel, anode = piece of chromium

b Electrolyte = chromium (II) nitrate

c Concentration of the electrolyte

d 1.6 V

END-OF-CHAPTER EXAM

1 B

2 D

3 A

4 D

5 Negative

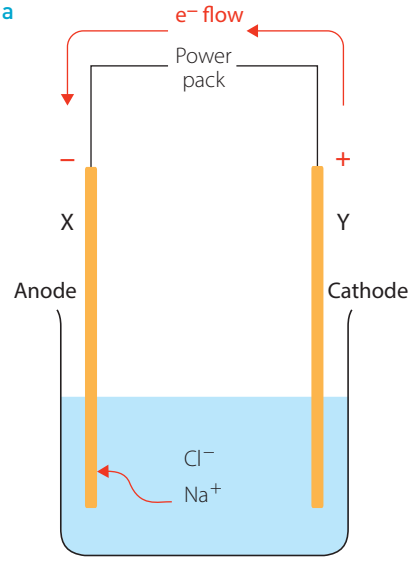
6 External cell

7 Nickel

8 Mercury

9 The salt bridge completes the circuit. Neither K^+, Na^+ or NO_3^- interact chemically with any of the substances in a galvanic cell.

10 a



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

$Na^+(l) + e^- \rightarrow Na(l)$ Reduction

CHAPTER 12 GALVANIC CELLS

12.1 SECTION REVIEW

REMEMBERING

1 A fuel cell is a galvanic cell where a fuel, such as hydrogen or methanol, is oxidised and oxygen is reduced, releasing electrical energy.

2 Chemical potential energy → electrical energy

3 Platinum

UNDERSTANDING

4 During operation of the cell, the copper strip is reduced. The $Cu^{2+}(aq)$ ions are reduced to Cu(s) atoms. Since the $Cu^{2+}(aq)$ ions are responsible for the blue colour, this colour eventually fades.

5 The voltage required by a car can be achieved by using a number of fuel cells stacked together.

6 A fuel cell is a kind of galvanic cell. The reactions occurring are:

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

$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

APPLYING

7 Diagrams should be similar to that in Figure 12.1.1 but with:

a Anode = zinc, cathode = tin

b Anode = Magnesium, cathode = iron.

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12.2 SECTION REVIEW

UNDERSTANDING

1 Cadmium has a more negative standard electrode potential than nickel. It will be oxidised:

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

The cadmium metal will slowly dissolve – its mass will decrease.

2 If the Cd(s) and $Ni^{2+}(aq)$ were mixed, a spontaneous reaction would take place, with electrons transferring instantaneously between the reactions rather than passing through a wire where they can be utilised.

3 All potassium compounds and all compounds containing nitrate ions are soluble. Therefore, whatever the anode and cathode, the potassium nitrate would not interact chemically with anything.

APPLYING

4 During the operation of the cell, the zinc metal of the anode is oxidised to Zn^{2+} ions. Eventually the zinc anode dissolves and no more current flows.

12.3 SECTION REVIEW

REMEMBERING

1 Oxidation: an increase in oxidation state

Reduction: a decrease in oxidation state

2 Cathode

3 It must be soluble and it must form soluble salts when in contact with other solutions.

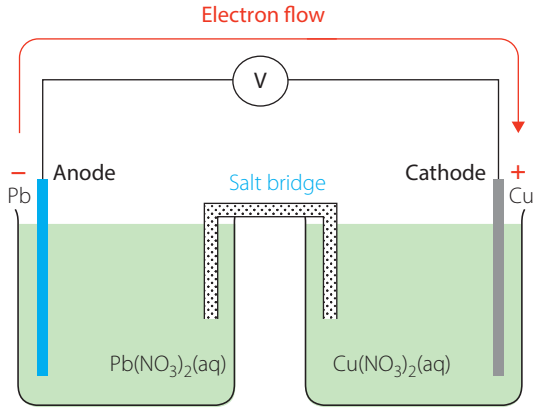
UNDERSTANDING

4 NO_3^-. The reductant is the more easily oxidised metal. As the metal is oxidised, positively charged metal ions move into solution. These are balanced by negatively charged nitrate ions moving into the solution from the salt bridge.

5 Aluminium is a reactive metal that forms an impervious coating of aluminium oxide on exposure to air. This layer must be scraped off or chemically removed.

APPLYING

6 a



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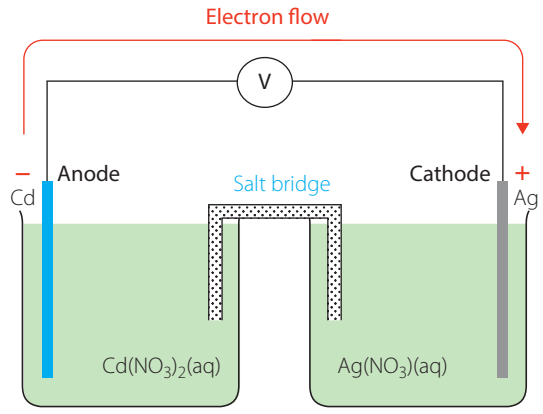
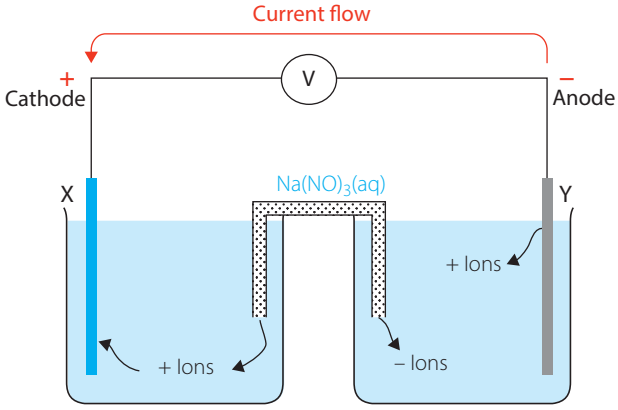


7 $Y(s) \rightarrow Y^{2+}(aq) + 2e^-$ oxidation

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



CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Fuel cell: a galvanic cell where a fuel, such as hydrogen or methanol, is oxidised and oxygen is reduced, releasing electrical energy fuel cell.

b Salt bridge: a link containing electrolyte between the oxidation and reduction half-cells of a galvanic cell.

c Anode: the electrode where reduction occurs.

d Cathode: the electrode where oxidation occurs.

e Oxidation half-cell: the part of a galvanic cell where oxidation occurs.

f Reduction half-cell: the part of a galvanic cell where reduction occurs.

g Oxidation state: the number of electrons that an atom would have gained or lost to get to its present state; it assumes that each species is completely ionic.

CATEGORY QUESTIONS

2 Oxidation half-cell: $Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

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

3 Cd half-cell = anode

Ni half-cell = cathode

ELABORATION QUESTIONS

4 As $Cd^{2+}(aq)$ are produced in the anode half-cell, negative ions from the salt bridge move into the cell to balance the extra positive charge and positive ions flow from the salt bridge into the cathode half-cell to replace the positive ions lost.

5 a Cell voltage produced is directly proportional to the electrolyte concentration.

b More ions means increased likelihood of a reaction taking place.

c Equilibrium has been reached.

d The same

END-OF-CHAPTER EXAM

1 D

2 D

3 D

4 D

5 Oxidant

6 No

7 Catalyst

8 The zinc electrode dissolves. A red-brown coating appears on the copper electrode. The blue colour of the copper nitrate solution slowly fades.

9 Increase the concentration of the solution in contact with the cathode. Decrease the concentration of the solution in contact with the anode. Ensure metal surfaces are free of any coatings.

10 T > Q > l > G

a $T(s) \rightarrow T^{2+}(aq) + 2e^-$ oxidation — anode
$G^{2+}(aq) + 2e^- \rightarrow G(s)$ reduction — cathode

b $Q(s) \rightarrow Q^{2+}(aq) + 2e^-$ oxidation — anode
$L^{2+}(aq) + 2e^- \rightarrow L(s)$ reduction — cathode

c $T(s) \rightarrow T^{2+}(aq) + 2e^-$ oxidation — anode
$L^{2+}(aq) + 2e^- \rightarrow L(s)$ reduction — cathode

d $L(s) \rightarrow L^{2+}(aq) + 2e^-$ oxidation — anode
$G^{2+}(aq) + 2e^- \rightarrow G(s)$ reduction — cathode

CHAPTER 13 STANDARD ELECTRODE POTENTIAL

13.1 SECTION REVIEW

REMEMBERING

1 a A measure of the potential difference of an individual electrode under standard conditions, measured relative to the standard hydrogen electrode.

b A half-cell composed of $H^+(aq)$ ions in contact with $H_2(g)$ under standard conditions.

c A chemical species that causes another species to be oxidised.

d A chemical species that causes another species to be reduced.

2 Standard conditions – 298 K, 1 atmosphere, solution concentrations of 1 mol L^{-1}.

UNDERSTANDING

3 A reference cell enables the potential of all other half-cells to be measured relative to a standard. In this way, the potentials of half-cells can easily be compared.

APPLYING

4 The more negative an $E°$ value is, the stronger is its reducing strength and the less likely it is to be reduced.

Species A = –1.4 V

Species B = +10.70 V

Species B is more likely to be reduced.

5 a H_2O_2 is the oxidising agent
$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

b Cd is the reducing agent
$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

13.2 SECTION REVIEW

REMEMBERING

1 a The difference in electrode potential between the two half-cells that make up a galvanic cell.

b Indicates that a spontaneous reaction will occur between the electrodes of a galvanic cell.

c Indicates that reaction will not occur spontaneously.

2 Step 1: Identify the relevant equations from a suitable table of standard electrode potentials.

Step 2: Determine which metal is being oxidised (anode) and which metal is being reduced (cathode).

Step 3: Use $E°_{cell} = E°_{red} + E°_{ox}$ to determine the cell potential.

UNDERSTANDING

3 When the $E°_{cell}$ is calculated, a positive value will indicate that a spontaneous reaction is occurring.

4 a This is oxidation. The value from the table is reversed, – 0.40 V becomes + 0.40 V

b This is reduction. The value from the table is + 1.09 V

c This is oxidation. The value from the table is reversed, – 2.37 V becomes + 2.37 V

5 The $E°$ values give an indication of the difference in electrical potential energy between the two sides of the equation – this does not change when the quantities in the equation change.

APPLYING

6 $E°_{cell} = E°_{red} + E°_{ox}$
$+1.91 = E°_{red} + (+0.40)$
$+1.51\ V = E°_{red}$
The electrode is the permanganate electrode, which is the cathode

7 a +1.81 V

b –0.80 V

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13.3 SECTION REVIEW

REMEMBERING

1 a The relative stability of reagents in a reaction, dependant on the activation energy.

b Conditions under which a cell operates that are not at 298 K, solutions are not 1 mol L^{-1} and gases are not at 1 atmosphere pressure.

2 Electrodes that are very close to one another in the table. Reactive metals such as aluminium that form impervious oxide coatings on exposure to air.

UNDERSTANDING

3 Using concentrated HCl ensures a greater transfer of electrons from the larger number of Cl^- ions. This ensures a smaller negative value for the oxidation of Cl^- ions leading to a positive cell potential.

APPLYING

4 $H_2O_2(l) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$ oxidation: $E° = -(+0.70) = -0.70$ V

$H_2O_2(l) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ Reduction: $E° = +1.78$ V

$E°_{cell} = E°_{red} + E°_{ox}$

$= +1.78 + (-0.70) = +1.08$ V

A positive value for the cell potential means that this is a spontaneous reaction. If, however the solution is stored in a brown bottle, very little UV light can pass through the brown glass to initiate the reaction.

13.4 SECTION REVIEW

UNDERSTANDING

1 An oxidising agent is more likely to gain electrons than hydrogen. It therefore has a positive standard electrode potential.

2 Fe, Co, Cu, Ag, Hg, O_2, Br_2, Cl_2

EVIDENCE QUESTIONS

2

	$X(NO_3)_2(aq)$	$Q(NO_3)_2(aq)$	$T(NO_3)_2(aq)$	$R(NO_3)_2(aq)$	$M(NO_3)_2(aq)$	$G(NO_3)_2(aq)$
X		✓	✓	✓	✗	✓
Q	✗		✓	✓	✗	✗
T	✗	✗		✓	✗	✗
R	✗	✗	✗		✗	✗
M	✓	✓	✓	✓		✓
G	✗	✓	✓	✓	✗	

$X(s) + Q^{2+}(aq) \rightarrow X^{2+}(aq) + Q(s)$

(others will be similar)

END-OF-CHAPTER EXAM

1 C

2 A

APPLYING

3 a Spontaneous reaction will occur.

b No

CHAPTER REVIEW QUESTIONS

CATEGORY QUESTIONS

1 a $Hg(l) \rightarrow Hg^{2+}(aq) + 2e^-$ oxidation $E° = -(+0.92$ V$)$

$= -0.92$ V

$Zn^{2+} + 2e^- \rightarrow Zn(s)$ reduction $E° = -0.76$ V

$E°_{cell} = E°_{red} + E°_{ox}$

$E°_{cell} = -0.76 + (-0.92)$

$= -1.68$ V

Negative $E°$ indicates reaction will not be spontaneous.

b $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$ oxidation $E° = -(-0.13\text{ V}) = +0.13$ V

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

$E° = +0.96$ V

$E°_{cell} = E°_{red} + E°_{ox}$

$E°_{cell} = +0.13 + (+0.96)$

$= +1.09$ V

Negative $E°$ indicates reaction will be spontaneous.

c $Au(s) \rightarrow Au^{3+}(aq) + 3e^-$ oxidation $E° = -(+1.53) = -1.53$ V

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

$E° = +0.96$ V

$E°_{cell} = E°_{red} + E°_{ox}$

$E°_{cell} = +0.96 + (-1.53)$

$= -0.57$ V

Negative $E°$ indicates reaction will not be spontaneous.

d $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$ oxidation $E° = -0.48$ V

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

reduction $E° = +1.51$ V

$E°_{cell} = E°_{red} + E°_{ox}$

$E°_{cell} = +1.51 + (-0.48)$

$= +1.03$ V

Negative $E°$ indicates reaction will be spontaneous.

3 D

4 B

5 Non-spontaneous

6 Ag

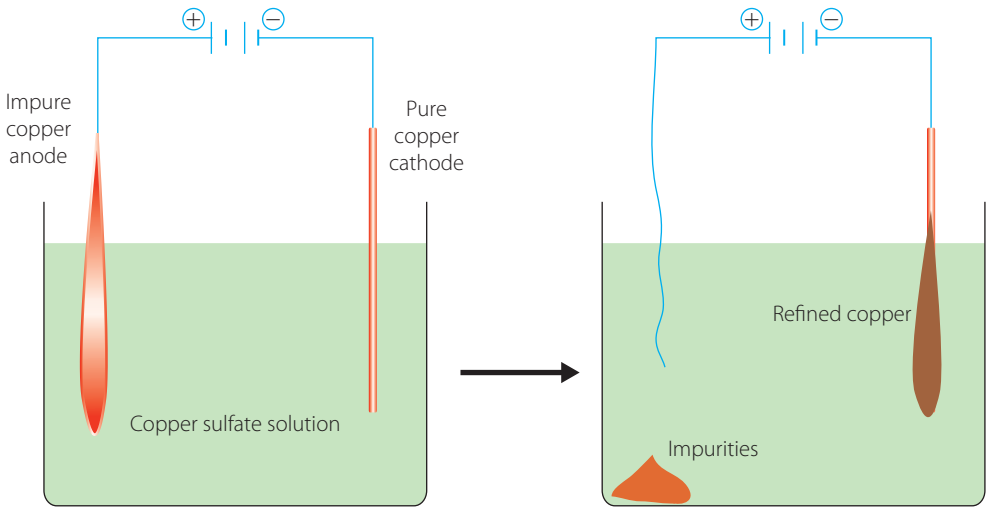
7 HCl could be increased

Temperature could be increased

8 Cell Q–T = +1.5 V
Cell G–Q = +2.0 V
Cell Q–L = +0.50 V
Cell M–Q = + 1.0 V
If Q is set as the reference electrode = 0.0V:–
T = –1.5 V
L = –0.5 V
Q = 0.0 V
M = + 1.0 V
G = + 2.0 V

APPLYING

3



14.2 SECTION REVIEW

REMEMBERING

1 The nature of the electrolyte, the concentration of the electrolyte and the nature of the electrode.

UNDERSTANDING

2 In an aqueous solution the electrolyte is dissolved in water which can, itself, be electrolysed.

3 Polyatomic ions are extremely stable and require very large voltages for them to be oxidised. Water will always be oxidised (producing oxygen at the anode) preferentially to polyatomic ions because it has a less negative charge.

APPLYING

4 a $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

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

c Anode: solution around the anode becomes yellow, some dark coloured crystals sink to the bottom of the beaker.
Cathode: a red-brown solid coats the cathode.

d Add a few drops of starch solution to the area surrounding the anode. If a dark blue colour appears, the anode is surrounded by iodine. Scrape the iron from the electrode, dry and perform magnet test 0.99 V.

CHAPTER 14 ELECTROLYTIC CELLS

14.1 SECTION REVIEW

REMEMBERING

1 a Anode (oxidation): $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
Cathode (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

b Anode (oxidation): $2Br^-(l) \rightarrow Br_2(g) + 2e^-$
Cathode (reduction): $Cu^{2+}(l) + 2e^- \rightarrow Cu(s)$

UNDERSTANDING

2 Inert electrodes do not interfere chemically in the electrolytic process.

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

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

c Anode: colourless, odourless gas produced
Cathode: colourless, odourless gas produced

d Gas produced at anode is O_2. This can be identified by collecting the gas in a test tube and observing if it relights a glowing splint. Gas produced at the cathode is H_2. This can be identified by collecting the gas in a test tube and observing if it goes 'pop' when a lit match is paced in the test tube.

e $E^\circ_{cell} = -0.83 + (-1.23) = -2.06$ V

14.3 SECTION REVIEW

UNDERSTANDING

1 The relative electrode potentials of the ions present and the oxidation and reduction of water.

2 Concentrated: E° values for oxidation of water to give oxygen and oxidation of Cl^- ions to give Cl_2 gas are similar but, due to the increased number of Cl^-ions present, Cl_2 gas is produced.
Dilute: oxygen gas is produced since there are too few Cl^-ions, the water is oxidised preferentially.

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APPLYING

3 Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
$E^\circ = -(+1.23\ V)$
Cathode (reduction) $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^\circ = -0.76\ V$
$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$
$E^\circ_{cell} = -0.76 + (-1.23) = -1.99\ V$

4 Anode = $O_2(g)$
Cathode = $H_2(g)$
Voltage required = 2.06 V
$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 a Electrolysis: the production of a chemical change by the passage of an electric current through an electrolyte.

b Electroplating: the process by which a metal is deposited onto a conductor using an electric current.

c Electrorefining: the refining (purification) of a metal by electrolysis.

ELABORATION QUESTIONS

2 a Very high temperatures are required to melt the zinc bromide. The zinc bromide must be heated in a heat-proof ceramic or nickel crucible.

At the high temperatures required for the experiment, the bromine produced will be bromine gas, which is highly toxic. The experiment must be carried out in a fume cupboard.

b Anode: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$ $E^\circ = -(+1.09\ V) = -1.09\ V$
Cathode: $Zn^{2+}(l) + 2e^- \rightarrow Zn(s)$ $E^\circ = -0.76\ V$
$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$
$E^\circ_{cell} = -0.76 + (-1.09) = -1.85\ V$

EVIDENCE QUESTIONS

3 Anode = $O_2(g)$
Cathode = Cu(s)
Voltage required = 0.89 V
$2CuSO_4(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 2H_2SO_4(aq)$

4 Initially, Cl_2 gas is produced because of the large number of Cl^- ions present. Over time, as Cl^- ions are converted into Cl_2 molecules and disappear, the solution becomes more dilute and water is preferentially oxidised, producing oxygen.

END-OF-CHAPTER EXAM

1 C

2 C

3 C

4 B

5 The reaction is non-spontaneous.

6 Copper metal

7 a The galvanic cell powers the electrolytic cell.

The electrolysis of $CuSO_4$:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^\circ = +0.34\ V$
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^\circ = -(+1.23) = -1.23\ V$
$E^\circ_{cell} = +0.34 + (-1.23) = -0.89\ V$
The galvanic cell must produce at least 0.89 V
$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$
$+0.89 = +0.80 + E^\circ_{ox}$
$-(+0.09) = E^\circ_{ox}$
The metal closest to −0.09 V in the table is Pb = Metal B
Solution A is a soluble lead compound = $Pb(NO_3)_2(aq)$

b Oxidation occurs at electrode B – this produces electrons. Electrode D is, therefore the negative electrode of the electrolytic cell. This is where reduction occurs:
Electrode D (reduction) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Electrode C (oxidation) $H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Electrode C = oxygen gas
Electrode D = copper metal

c Ag electrode = cathode = reduction $Ag^+(aq) + 2e^- \rightarrow Ag(s)$
B electrode = anode = oxidation $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$
C electrode = anode = oxidation $H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
D electrode = cathode = reduction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

d Appropriate half-equations are shown in 7c, above.

8 a Oxygen: relights a glowing splint
Hydrogen: 'pop' test

b Both electrodes involve the oxidation and reduction of water. The electrode with the pink solution in it is the anode because it involves the oxidation of water.
Anode = oxidation $H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode = reduction $H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c H_2O exists in the ratio 2 atoms of hydrogen to 1 atom of oxygen. There is more hydrogen to be liberated than oxygen.

CHAPTER 15 STRUCTURE OF ORGANIC COMPOUNDS

15.1 SECTION REVIEW

REMEMBERING

1 A group of atoms than determines the chemical reactivity of a molecule.

UNDERSTANDING

2 a Hydroxyl

b Carboxyl

c Amine

d Ester

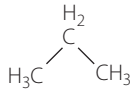
e Ketone

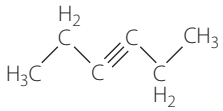
f Aldehyde

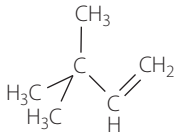
g Amide

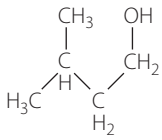
15.2 SECTION REVIEW

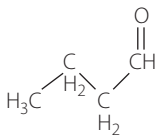
UNDERSTANDING

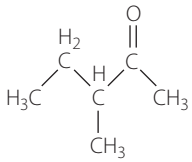
1 a 

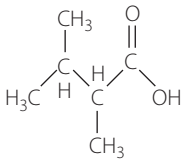
b 

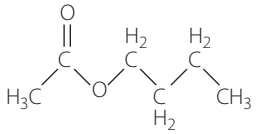
c 

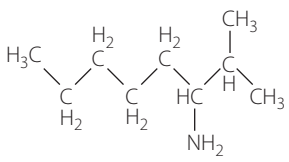
d 

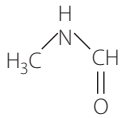
e 

f 

g 

h 

i 

j 

2 a 2,2-dimethylbutane

b 3-methyl, 1-butene

c 2-butanol

d 2-methylbutanal

e Pentanoic acid

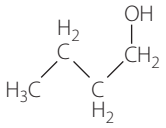
f Propyl pentanoate

g 1-hexanol

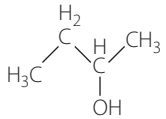
h 3-methyl, 2-butanamine

i N-propyl propanamide

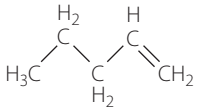
15.3 SECTION REVIEW

1 

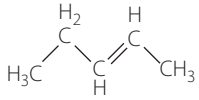
1 butanol



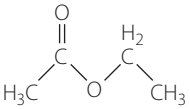
2 butanol

2 

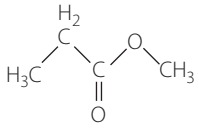
1-pentene



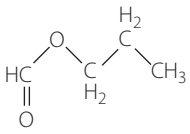
2-pentene

3 

Ethyl ethanoate



Methyl propanoate

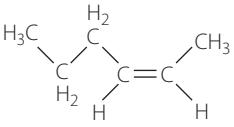


Propyl methanoate

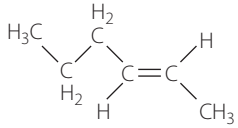
15.4 SECTION REVIEW

UNDERSTANDING

1 Structural isomers have different chemical bonds – the atoms are arranged in a different order. Stereo-isomers have the same structural formula but a different arrangement of atoms in space, around a C═C.

2 

Cis 2-pentene



Trans 2-pentene

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Functional groups determine reactivity of classes of molecules and, therefore, their use.

2 Aldehyde carbonyl occurs on the end of a chain; ketone in the middle of a chain.

3 Amide is the product of condensation between an amine and a carboxylic acid.

CATEGORY QUESTIONS

4 c is an alkane ($C_nH_{(2n+2)}$); b is an alkene (C_nH_{2n}); a is an alkyne ($C_nH_{(2n-2)}$)

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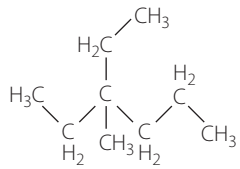
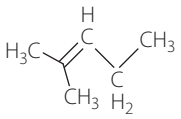
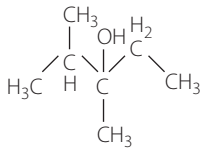
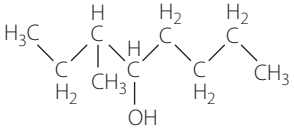
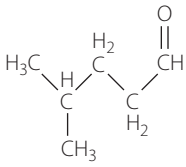
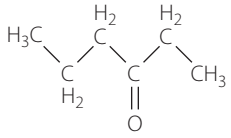
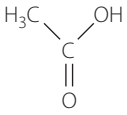
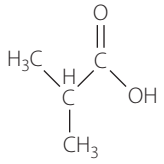
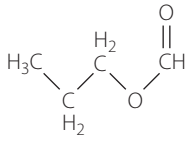
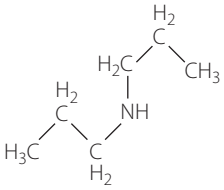
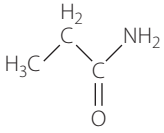
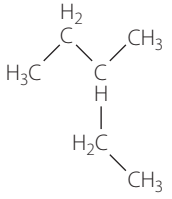
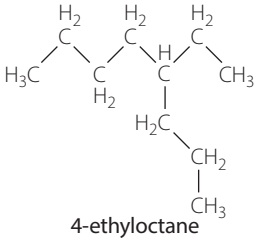
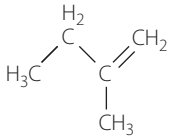
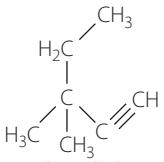
5

a 	b 	c 
d 	e 	f 
g 	h 	i 
j 	k 	

6 a Pentyne
b Butane
c 3-methylpentane
d 3-methyl-2-butanol
e 2-pentanone
f Propyl ethanoate
g Ethanamide

7 Pair a

8

a  3-methylpentane	b  4-ethyloctane
c  2-methyl-1-butene	d  3,3-dimethyl-1-pentyne

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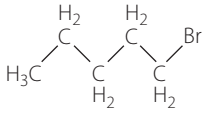	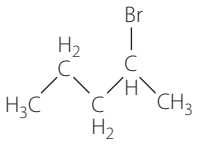	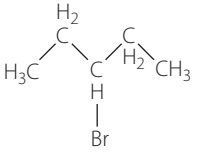
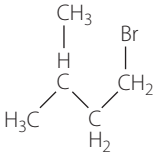	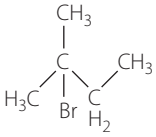	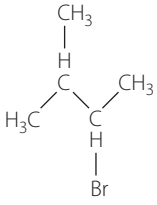
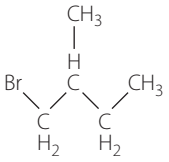	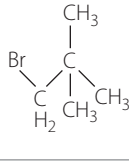	

END-OF-CHAPTER EXAM

1 D
2 C
3 D

CHAPTER 16 PHYSICAL PROPERTIES AND TRENDS OF ORGANIC MOLECULES

16.1 SECTION REVIEW

REMEMBERING

1 Dispersion forces (or Van der Waals forces), dipole–dipole attraction, hydrogen bonding

UNDERSTANDING

2 Carboxylic acids and alcohols have an O—H bond and amines have an N—H bond, which have a high polarity, and therefore result in hydrogen bonding interactions, significantly stronger than dipole–dipole attractions.

16.2 SECTION REVIEW

UNDERSTANDING

1 As the molecular size increases, the surface area contact between molecules increases and, hence, the strength of the dispersion forces between the molecules are increasingly strong.

2 Straight-chain isomers have a greater surface area per size ratio compared to branched chain isomers; hence, the potential for dispersion forces to occur is much greater.

3 Alcohols and carboxylic acids both have O—H bonds, therefore, hydrogen bonding occurs between them that does not occur between the non-polar alkane molecules.
Carboxylic acids have an additional C═O bond compared to alcohols and, therefore, have additional hydrogen bonding, hence higher boiling points.

16.3 SECTION REVIEW

UNDERSTANDING

1 The greater the molecular size, the greater the proportion of the molecule that is hydrophobic and non-polar. Hence, the greater the molecular size, the less soluble it becomes.

2 Propanoic acid, propanol, chloropropane, propane

16.4 SECTION REVIEW

UNDERSTANDING

1 Amines and amides both possess an N–H bond and, therefore, show hydrogen bonding between molecules. They have a higher boiling point than esters of comparable size, which do not have shown hydrogen bonding. Similarly, amines and amides will also demonstrate greater solubility in water than the corresponding ester, because of their ability to form hydrogen bonds with water. As with all organic molecules, the boiling point of these molecules increases with molecular size, because of the increased surface area for dispersion forces to occur between them. The solubility of all these molecules will similarly decrease with molecular size, due to the increased proportion of the molecule that is hydrophobic.

CHAPTER REVIEW QUESTIONS

REMEMBERING

1 a Alcohols have an O—H bond and so can form hydrogen bonds with water.

b The hydrophobic, non-polar proportion of the molecule increases as the size increases and, hence, they become less soluble.

2 The carboxyl group is highly polar and therefore promotes solubility in the molecule. As the molecular size increases, the proportion of the molecule that is hydrophobic increases and so the solubility decreases.

3 Esters have no O—H bond and are therefore not as polar as carboxylic acids or alcohols that do.

4 Amines and amides have N—H bonds that are polar and therefore form hydrogen bonds with water.

UNDERSTANDING

5 The single, double and triple bonds that exist in alkanes, alkenes and alkynes respectively, affect the chemical properties of the molecules as double and triple bonds can take part in addition reactions, while single bonds cannot. These bonds are all non-polar and so do not affect the physical properties of the molecules significantly.

6 Smaller aldehydes and ketones have a greater proportion of the molecule that is polar and therefore are more likely to be soluble in water.

7 The bonding between carboxylic acids is stronger than between alcohols because of the greater polarity of the carboxyl groups and therefore the greater intensity of the hydrogen bonding.

END-OF-CHAPTER EXAM

1 B

2 C

3 A

4 Carboxylic acid molecules have both non-polar and polar sections. Therefore, they can form attractive interactions with non-polar molecules such as oils and dirt and with polar water molecules. Hence, they can solubilise previously insoluble molecules.

CHAPTER 17 ORGANIC REACTIONS AND REACTION PATHWAYS

17.1 SECTION REVIEW

REMEMBERING

1 a A substitution reaction, initiated by ultraviolet light, where a hydrogen atom in an organic molecule is replaced by a halogen atom.

b A reaction where an organic molecule is reacted in oxygen to form carbon dioxide and water.

2 Complete combustion involves the formation of carbon dioxide and water. When there is less oxygen available,

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carbon monoxide or carbon are formed with water, in place of carbon dioxide.

UNDERSTANDING

3 $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$

4 $C_5H_{12}(l) + 3O_2(g) \rightarrow 5C(s) + 6H_2O(g)$

5 $C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$

Possible products could include 1-chloropentane $CH_2ClCH_2CH_2CH_2CH_3$; 2-chloropropane $CH_3CHClCH_2CH_2CH_3$; 3-chloropropane $CH_3CH_2CHClCH_2CH_3$; 1-chloro, 2-methylbutane $CH_2ClCH(CH_3)CH_2CH_3$.

APPLYING

6 $C_8H_{18}(l) + 25/2O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$

Octane requires a greater amount of oxygen per mole to completely combust than pentane. As there is a limited amount of oxygen in air, it is more likely that there will be incomplete combustion, forming carbon with a sooty flame.

ANALYSING

7 Free radical substitution is not an easily controlled reaction and can produce a wide variety of randomly substituted products in an explosive fashion. Hence, it is difficult to use in a systemic synthetic process.

17.2 SECTION REVIEW

REMEMBERING

1 a An addition reaction is a reaction where two molecules combine to form a larger molecule.

b Alkene molecules add to each other to form a long unsaturated polymer chain.

2 Alkenes have a C=C- double bond, which can undergo addition reactions, whereas alkanes do not.

UNDERSTANDING

3 a $CH_2{=}CHCH_3 + Br_2 \rightarrow CH_2BrCHBrCH_3$

b $CH_2{=}C(CH_3)CH_3 + H_2O \rightarrow CHOHCH(CH_3)CH_3$

c $CH_2{=}CHCH_2CH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_3$

d $CH_3CH{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_2CH_3$

APPLYING

4 Possible products are 2-methyl, 1-propanol and 2-methyl, 2-propanol (preferred product).

17.3 SECTION REVIEW

REMEMBERING

1 An alkyne is a hydrocarbon with a carbon–carbon triple bond.

2 They both have double or triple carbon–carbon bonds.

UNDERSTANDING

3 a $CHCCH_3 + Br_2 \rightarrow CHBr{=}CBrCH_3$

b $CHCH + H_2O \rightarrow CH_2{=}CHOH$

c $CHCCH_2CH_3\ 2H_2 \rightarrow CH_3CH_2CH_2CH_3$

d $CH_3CCCH_3 + HBr \rightarrow CH_3CH{=}CBrCH_3$

ANALYSING

4 Ethyne is a gas and burns with a highly exothermic reaction. It is also a small molecule and therefore does not require a large excess of oxygen in order to undergo complete combustion.

17.4 SECTION REVIEW

REMEMBERING

1 An electronegative atom in a molecule such as a halogen atom is replaced by another atom or group called a nucleophile, such as OH^-.

2 Where two molecules are formed from one molecule. It usually involves the formation of a C=C double bond.

3 A bond where there is a significant difference in electronegativity between the two atoms and, hence, a permanent dipole exists.

4 Either substitution or elimination can occur when a haloalkane is reacted with hydroxide ions. If the hydroxide is dilute and aqueous then substitution will occur. If it is concentrated, dissolved in alcohol and heated, then elimination will be preferred.

UNDERSTANDING

5 a $CH_3CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2OH + NaBr$

b $CH_3CH_2CHClCH_3 + NH_3 \rightarrow CH_3CH_2CHNH_2CH_3 + HCl$

c $CH_3CH_2I + KCN \rightarrow CH_3CH_2CN + KI$

d $CH_3CI(CH_3)CH_2Br \rightarrow CH_3C(CH_3){=}CH_2$

APPLYING

6 The products formed will be 2-propanol and propene. Hot, concentrated, ethanolic sodium hydroxide will result in elimination, forming propene and cold, dilute, aqueous sodium hydroxide will result in substitution, forming 2-propanol.

17.5 SECTION REVIEW

REMEMBERING

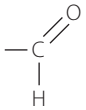
1 Primary alcohols: C—OH group joined to one other carbon atom, e.g. 1-propanol

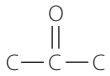
Secondary alcohols: C—OH group joined to two other carbon atoms, e.g. 2-butanol

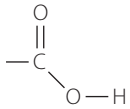
Tertiary alcohols: C—OH group joined to three other carbon atoms, e.g. 2-methyl, 2-propanol

2 Acidified potassium manganate (VII) ($KMnO_4$) or acidified potassium dichromate (VI) ($K_2Cr_2O_7$) –

3 a —O–H

b 

c 

d 

UNDERSTANDING

4 a $CH_3CH_2CH_2OH + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CHO(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

b $5CH_3CH(OH)CH_2CH_3(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3CO\,CH_2CH_3 + 2Mn^{2+}(aq) + 8H_2O(l)$

c No reaction

d $5CH_3CH_2CHO(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3CH_2COOH(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

e $2CH_3OH + 2Na \rightarrow 2\,CH_3ONa(aq) + H_2(g)$

APPLYING

5 Aldehydes take part in redox reactions with chemicals such as potassium dichromate and act as reducing agents.

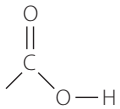
6 The ethanol in the wine can be oxidised aerobically by microorganisms on exposure to the oxygen in the air and form ethanoic acid.

17.6 SECTION REVIEW

REMEMBERING

1 They possess only one carboxyl group, which can ionise and form a hydrogen ion (proton) when added to water.

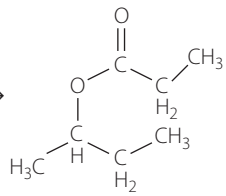
2 A reaction where two molecules are joined to form a larger molecule, with the loss of a water molecule as a by-product.

3 

UNDERSTANDING

4 a $2CH_3COOH + 2\,Na \rightarrow 2CH_3COONa + H_2$ (products: sodium ethanoate and hydrogen)

b $CH_3CH_2CH_2CH_2OH + CH_3COOH \rightarrow CH_3CH_2CH_2CH_2OOCCH_3 + H_2O$ (products: butyl ethanoate and water

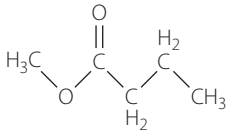
c $CH_3CH_2CHOHCH_3 + CH_3COOH \rightarrow$ 

$+ H_2O$ (products: 2-butyl propanoate and water)

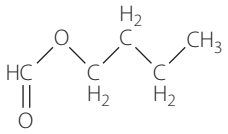
d $CH_3CH_2CH_2OOCCH_3 \rightarrow CH_3CH_2CH_2OH + CH_3COOH$ (products: 1-propanol and ethanoic acid)

e $CH_3OOCCH_2CH_2CH_3 \rightarrow CH_3OH + CH_3CH_2CH_2COONa$ (products: methanol and sodium butanoate)

APPLYING

5 

Methyl butanoate



Butyl methanoate

Methyl butanoate is formed from the condensation reaction between methanol and butanoic acid.
Butyl methanoate is formed from the condensation reaction between butanol and methanoic acid.

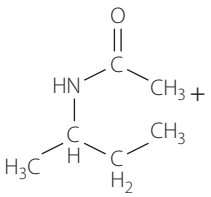
17.7 SECTION REVIEW

REMEMBERING

1 Amine molecules contain the amino functional group (—NH_2); amide molecules contain the amide functional group, which is a linkage between two alkyl chains (—CONH—).

UNDERSTANDING

2 a $CH_3CH_2NH_2 + HNO_3 \rightarrow CH_3CH_2NH_3^+\,NO_3^-$ (product: ethyl ammonium nitrate)

b $CH_3CHNH_2CH_2CH_3 + CH_3COOH \rightarrow$ 

H_2O (products: N-2-butyl ethanamide and water).

3 CH_3CH_2NHCOH (heat with NaOH) $\rightarrow CH_3CH_2NH_2 +$ HCOOH

APPLYING

4 Yes, the presence of the NH group would still enable amides to react with acids. However, the presence of the CO group would mean that they were less basic than amines.

17.8 SECTION REVIEW

ANALYSING

1 The hydrocarbon does not possess a C=C bond.

2 Add sodium carbonate powder. The propanoic acid will effervesce, the propanol will not.

3 1-butanol

4 The greater polarity of the functional group leads to stronger intermolecular interactions and therefore a higher boiling point.

APPLYING

5 Test 1: Add bromine water to each of the six compounds; if decolourised, then the compound must be 1-butene.
Test 2: Add sodium bicarbonate to each of the five remaining compounds; if effervescence occurs, the compound must be butanoic acid.
Test 3: Add red litmus paper to each of the four remaining compounds; if it turns blue, it must be butanamine.

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Test 4: Add granules of calcium chloride to each of the three remaining compounds and then add a small piece of sodium. If bubbles of gas occur, the sample is 1-butanol.
Test 5: Add NaOH to each of the remaining compounds and gently heat the solution. If ammonia is produced, the sample is N-ethylethanamide.
The remaining compound, which will also be the only gas present, is butane.

6 a bubbles of gas would appear

b $2CH_3CH_2CO_2H(aq) + Na_2CO_3(s) \rightarrow CH_3CH_2CO_2Na(aq) + CO_2(g) + H_2O(l)$

17.9 SECTION REVIEW

APPLYING

1 i Chloromethane reacted with aqueous NaOH to form methanol

ii Methanol reacted with acidified potassium dichromate solution to form methanoic acid

iii Methanoic acid reacted with 2-butanol with a H_2SO_4 catalyst to form the ester 2-butylmethanoate

2 i Take half the chloropropane and react it with aqueous NaOH to form 1-propanol.

ii React the 1-propanol with acidified potassium dichromate to form propanoic acid.

iii Take the remaining chloropropane and react it with KCN to form butane nitrile.

iv React the butane nitrile with H_2 and a nickel catalyst to form 1-butanamine.

v React the 1-butanamine with the propanoic acid with a catalyst of c.H_2SO_4 to form N-butyl propanamide.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Primary alcohols, e.g. 1-butanol

Secondary alcohols, e.g. 2-butanol

Tertiary alcohols, e.g. 2-methyl, 2-butanol

CATEGORY QUESTIONS

2 Unsaturated compounds contain C═C double bonds. Saturated compounds do not.

3 Substitution involves replacing 1 atom of a molecule with another from outside the molecule; Addition involves combining two molecules to form one larger molecule.

4 Esterification is the condensation reaction that occurs between an alcohol and a carboxylic acid to form an ester and water. Hydrolysis is the reverse of this, with an ester molecule being converted into the carboxylic acid and alcohol.

ELABORATION QUESTIONS

5 a $HCCCH_2CH_2CH_3 + 7O_2 \rightarrow 5CO_2 + 4H_2O$

b $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

c $CH_3CHCHCH_3 + H_2O \rightarrow CH_3CH_2CHOHCH_3$

d $HCCH + 2Br_2 \rightarrow CHBr_2CHBr_2$

6 a $CH_3CH_2CHOHCH_2CH_3 \rightarrow CH_3CH{=}CHCH_2CH_3 + H_2O$ (products are 2-pentene and water)

b $HC{=}CHCH_3 + H_2O \rightarrow CH_2CHOHCH_3$ (product is 2-propanol)

c $CH_3CH_2CHOHCH_3 + 13/2\ O_2 \rightarrow 4CO_2 + 5H_2O$ (products are carbon dioxide and water)

d $2CH_3CH_2CH_2CH_2CH_2CH_2OH + Na \rightarrow 2CH_3CH_2CH_2CH_2CH_2CH_2ONa + H_2$ (products are sodium hexoxide and hydrogen)

7 a Butanone

b Methanoic acid

c 2-methyl, 2-hexanol

8 a $CH_3CH_2OH(l) + MnO_4^-(aq) + 8H^+(aq) \rightarrow CH_3CH_2CHO(aq) + Mn^{2+}(aq) + 4H_2O(l)$

b $CH_3CH_2CH_2CHOHCH_3(l) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow CH_3CH_2CH_2COCH_3 + 2Cr^{3+}(aq) + 7H_2O(l)$

9 a Bubbles of carbon dioxide would be evolved

b $2CH_3CH_2COOH(l) + Na_2CO_3(aq) \rightarrow 2CH_3CH_2COONa(aq) + CO_2(g) + H_2O(l)$

10 a $CH_3CH_2CH_2COOH(l) + NaOH(aq) \rightarrow CH_3CH_2CH_2COONa(aq) + H_2O(l)$

b $2HCOOH(l) + 2Na(s) \rightarrow 2HCOONa(aq) + H_2(g)$

11 a $CH_3CH_2CH_2OH(l) + CH_3COOH(l) \rightarrow CH_3COOCH_2CH_2CH_3(l)$ (propyl ethanoate) $+ H_2O(l)$

b $CH_3CH_2CH_2CH_2CH_2OH(l) + CH_3CH_2CH_2COOH(l) \rightarrow CH_3CH_2COOCH_2CH_2CH_2CH_3(l)$ (pentyl butanoate) $+ H_2O(l)$

12 a $CH_3CH_2CH_2NH_2(l) + HCl(aq) \rightarrow CH_3CH_2CH_2NH_3Cl(aq)$

b $2HCOOH(l) + (NH_4)_2CO_3(aq) \rightarrow 2HCOONH_4(aq) + CO_2(g) + H_2O(l)$

c $HCOOH(l) + CH_3CH_2CH_2CH_2NH_2(l) \rightarrow CH_3CH_2CH_2CH_2NHOCH(l) + H_2O(l)$

13 $CH_3CH_2COOCH_2CH_2CH_2CH_3(l) + H_2O(l) \rightarrow CH_3CH_2COOH(l) + HOCH_2CH_2CH_2CH_2CH_3(l)$

EVIDENCE QUESTIONS

14 Hydrocarbon would be saturated with no C═C bond.

15 Add some sodium carbonate solution. The propanoic acid would emit bubbles of carbon dioxide.

16 1-butanol

17 Add UI solution to both chemicals (assuming equal concentrations) – the amine would have the higher, more alkaline pH.

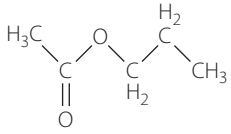
END-OF-CHAPTER EXAM

1 B

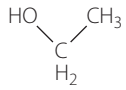
2 B

3 B

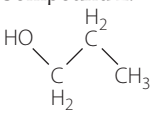
4 a Propyl ethanoate



b Compound K:



c Compound L:



Reagent X: NaOH

CHAPTER 18 ORGANIC MATERIALS: STRUCTURE AND FUNCTION

18.1 SECTION REVIEW

REMEMBERING

1 a Polymer: a large molecule made from many thousands of repeating units.

b Monomer: an individual unit of a polymer.

c Addition polymerisation: the process by which unsaturated monomers link together to form a saturated polymer, losing their double bonds.

d Condensation polymerisation: a reaction where a water molecule is formed as a by-product in the production of a polymer.

e Co-polymer: a polymer made from more than one monomer.

f Primary structure: the sequence of monomers in a co-polymer chain.

g Secondary structure: minor features of the shape of a polymer chain, caused by intermolecular interactions between side chains.

h Tertiary structure: the overall shape of a single polymer chain.

i Quaternary structure: the shape of two or more polymer chains aggregated together, held by intermolecular interactions.

j Biodegradable: a substance that will decay naturally as a result of enzyme produced by living bacteria.

k Tensile strength: the resistance of a substance to being pulled or stretched.

l Cross-links: covalent bonds that exist between polymer chains, holding them together firmly.

m Density: the mass per unit volume.

n Branching: where a polymer chain is not a single straight-chain, but has offshoots.

o Side groups: the different functional groups that can exist in a polymer chain, but that are not part of the main chain.

UNDERSTANDING

2 a The tensile strength of a polymer is affected by the extent of cross-linking between the polymer chains. The greater the cross-linking that occurs, the stronger the polymer will be.

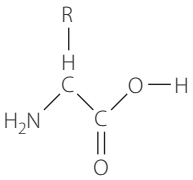
b The density of a polymer is affected by how closely together the chains pack. This is affected by the structure of the chains and in particular the size and frequency of side groups and of branching to the polymer chains.

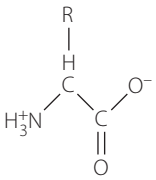
REFLECTING

3 Natural polymers are formed as the result of enzyme action inside a living organism. Hence in nature, the enzymes exist to be able to degrade these polymers also, usually as part of a digestive process. As synthetic polymers are not the result of enzyme action, the appropriate enzymes to degrade them do not exist in nature.

18.2 SECTION REVIEW

REMEMBERING

1 a 

b 

2 They are amino acids with:

a non-polar R groups

b polar R groups capable of forming ions

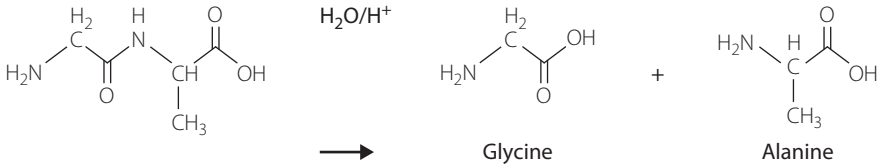
c polar R groups that generally do not form ions.

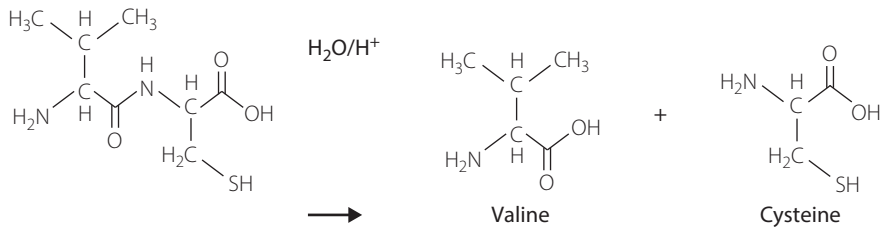
3 Primary structure: sequence of amino acids in peptide chains. Secondary structure: coils and pleats in the peptide chains caused by H–bonding between non-consecutive amino acids. Tertiary Structure: specific arrangement of overall peptide chain, held together by H–bonding and other intermolecular interactions.

UNDERSTANDING

4 Covalent bond; H–bonding; dipole–dipole interactions; dispersion forces

5 A peptide link is an amide link (—NHCO—) that occurs between amino acid molecules in a protein.

6 a 

b 

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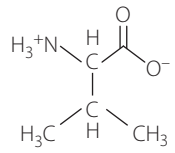
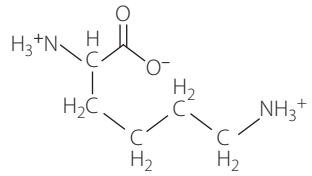
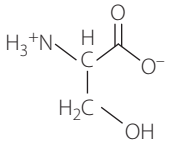
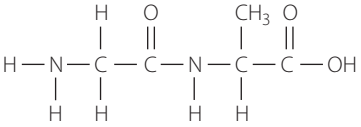
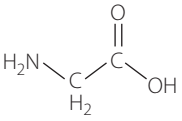
7 a 

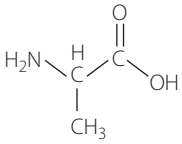
b 

c 

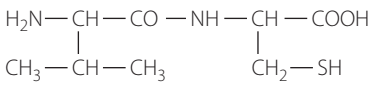
8 a 

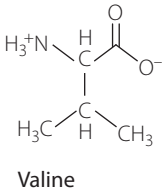


Glycine

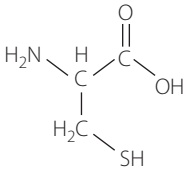


Alanine

b 

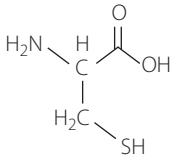


Valine

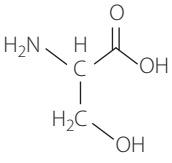


Cysteine

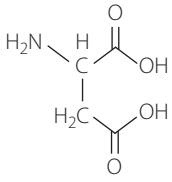
9 a There are three amino acids in the chain.

b 

Cysteine



Serine



Aspartic acid

c Nylon is a co-polymer, made from reacting a di-acid with a di-amine, whereas a peptide chain is made from amino acid monomer units which have both an amino and a carboxyl group.

REFLECTING

10 The secondary and tertiary structures would be permanently changed and the intermolecular attractions would be much weaker, as there would only be dispersion forces acting between the non-polar groups.

18.3 SECTION REVIEW

REMEMBERING

1 a Enzyme: a biological catalyst.

b Active site: the area of the enzyme where it interacts directly with the substrate molecule.

c Substrate: the molecule which is taking part in the reaction which the enzyme is catalysing.

d Denature: the permanent change than can occur to the structure of protein molecules when heated, or exposed to solutions of high acidity or alkalinity.

e Co-enzymes: molecules that assist the operation of enzymes.

2 Temperature, pH, concentration of reactants, presence of an enzyme are all factors affecting the rate of a biological reaction.

UNDERSTANDING

3 Enzymes have a much more specific shape than non-biological catalysts and can therefore bond much more efficiently to complex molecules and cause specific reactions to occur much more successfully.

APPLYING

4 Initially, an increase in temperature causes an increase in the rate of a reaction. However, when the temperature reaches a threshold level, the enzyme can denature and its structure will permanently change. This renders it unable to bind to its original substrate and therefore its activity decreases.

18.4 SECTION REVIEW

REMEMBERING

1 Monosaccharides are molecules of the simple sugars glucose, galactose and fructose. Disaccharides are larger molecules each formed from two monosaccharide molecules. Polysaccharides are long chain polymer molecules formed from many thousands of repeating monosaccharide molecules.

2 A glycosidic link —C—O—C— joins the monomer units together.

3 Carbohydrates all possess the carbonyl functional group, either as an aldehyde or a ketone form.

UNDERSTANDING

4 Monosaccharides and disaccharides are soluble in water due to the presence of the polar O—H bonds which can form hydrogen bonds with water.

5 A water molecule is forms as a by-product when a glycosidic link is formed. Hence, the combined mass of the monosaccharide molecules is greater than the mass of the disaccharide molecule because of the mass of the water.

6 $C_{12}H_{22}O_{11} + H_2O \rightarrow 2\,C_6H_{12}O_6$

7 Starch consists of long chains of α-glucose monomers, either in straight-chain (amylose) or branched chain (amylopectin) form. It is found in plants and used to store energy.
Cellulose consists of long chains of β-glucose monomers. It is used to form the cell walls and structural components of plants. As it is made from β-glucose, animals cannot easily digest it. Glycogen consists of long, highly branched chains of α-glucose molecules. It is formed in animals and used as short-term energy storage.

ANALYSING

8 a % O = 49.3%; % C = 44.4%

b Molecular weight = 48600 g

c $C_{12}H_{22}O_{11} + H_2O \rightarrow 2\ C_6H_{12}O_6$

d $50\{C_6H_{10}O_5\} + 49H_2O \rightarrow 50\ C_6H_{12}O_6$

e This does not take into account the extent of branching that may occur in amylopectin, for example.

18.5 SECTION REVIEW

REMEMBERING

1 Both fats and oils are triglyceride esters and lipids. However, fats are solid at room temperature and oils are liquid at room temperature.

2 Oils generally have more unsaturation in their carbon chains whereas fats tend to be more saturated, without C═C double bonds.

3 A fatty acid is a carboxyl group at the end of a long alkyl chain, which may have one or more unsaturated carbons.

APPLYING

4 The non-polar alkyl chain in a soap can form positive intermolecular interactions with the dirt, and the polar carboxyl group positively interacts with the water molecules, hence the dirt can be solubilised and so washed away.

5 A detergent acts in the same way as a soap except that the sulfonate polar group does not form insoluble precipitates with calcium ions found naturally in water. Hence detergents don't form a scum and are more easily washed away.

18.6 SECTION REVIEW

REMEMBERING

1 a A crystalline polymer is one where the molecules align in a regular repeating 'crystalline' arrangement. In an amorphous polymer, the molecules have no regular arrangement.

b Crystalline polymers have higher melting points and are harder and more brittle than amorphous polymers.

2 A co-polymer is a polymer with more than one different monomer.

APPLYING

3 The three forms of polypropene are atactic, syntactic and isotactic
Isotactic: polymer chains pack well together, so it is hard, strong and stress resistant.
Atactic: more amorphous arrangement of polymer chains, so less packing, less tensile strength and softer.
Syntactic: intermediate properties compared to the other two forms, but useful because it is tough yet flexible.

4 Density is the mass per unit volume. HDPE has a higher density than LDPE because the polymer chains pack more closely together with fewer gaps between them, due to the lack of branching in the polymer chains.

ANALYSING

5 PVC has cross-links between its polymer chains. Hence its structure is much harder to break than that of polystyrene, which has no cross-links.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1
- Polymer: a large molecule made from many thousands of repeating units.
- Monomer: an individual unit of a polymer.
- Addition: a reaction where alkenes lose their double bonds to form a saturated molecule.
- Condensation: a reaction where a water molecule is formed as a by-product.
- Co-polymer: a polymer made from more than one monomer.
- Biodegradable: a substance that will decay naturally as a result of enzyme produced by living bacteria.
- Tensile strength: the resistance of a substance to being pulled or stretched.
- Density: the mass per unit volume.
- Polyamide: a polymer held together by amide bonds – formed between the amino group of one monomer and a carboxyl group of the next monomer.
- Alpha amino acid: an amino acid with one carbon atom separating the amino and carboxyl groups.
- Zwitterion: the form of an amino acid where the amino group is protonated at the same time as the carboxyl group is deprotonated, so that there is no net charge.
- Iso-electric point: the pH value at which the amino acid is in the zwitterion form.
- Enzyme: a biological catalyst.
- Aldose: a sugar containing an aldehyde group.
- Ketose: a sugar containing a ketone group.
- Polysaccharide: a carbohydrate molecule made from many monosaccharide units.
- Crystalline: having a regular, ordered arrangement of atoms.
- Amorphous: without a clearly defined shape or form.
- Detergent: a water-soluble agent that makes dirt and oils soluble yet, unlike a soap, does not form a scum in hard water.

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- Plastic: a synthetic organic polymer that can be shaped and moulded by heat and pressure.
- Thermoplastic: a plastic that can easily be reshaped or remoulded.
- Thermosetting: a polymer with a significant amount of cross-links between its chains that cannot easily be remoulded.
- Vulcanisation: the process of adding sulfur to rubber, so that the sulfur forms cross-links between the chains, thus producing a harder and more elastic substance.
- Isotactic: a polymer where the side-chain functional groups are regularly arranged on the same side of the chain.
- Atactic: a polymer where the side-chain functional groups are randomly arranged on the polymer chain.
- Syntactic: a polymer where the side-chain functional groups alternate above and below the chain.

CATEGORY QUESTIONS

2 LDPE consists of a series of highly branched polyethene chains, which therefore do not pack well together. Consequently, there are gaps within the structure, and the density is low. HDPE involves molecules with little branching, which therefore pack tightly together and are denser than LDPE.

3 A lipid consists of a triglyceride ester – a molecule of glycerol with ester linkages to 3 fatty acid molecules. Fatty acids are molecules with a carboxyl group at one end, joined to a long chain alkyl group. Fats have saturated carbon chains and oils have a greater proportion of unsaturated C═C bonds.

ELABORATION QUESTIONS

4 Enzymes work by bonding with a substrate molecule to a section on the enzyme molecule called an active site. In order for this to be effective and to catalyse enzyme reactions, the shape of the enzyme molecule is essential, in order for it to fit the molecule effectively. The intermolecular forces that hold the polypeptide chains together determine the tertiary and quaternary structure are critical to determining the shape and, therefore, the effectiveness of the enzyme.

5 The key variations involving polymer structure include the amount of branching of polymer chains and also the extent to which cross-links between the chains hold them together. The greater the amount of branching, the more amorphous the polymer structure will be and therefore the less dense, less rigid and more flexible the polymer will be.
The greater the amount of cross-links present, the more rigid and hard the polymer will be.

END-OF-CHAPTER EXAM

1 A

2 B

3 C

4 C

5 Key points include the following information.
- Proteins have amino acid monomer units, polysaccharides have monosaccharides.
- Proteins have amide linkages, polysaccharides have glycosidic links.
- Proteins are co-polymers, being formed from a number of different possible amino acids, whereas polysaccharides are only formed from one monomer – a form of glucose.
- As such, polysaccharides are more uniform and crystalline in structure, due to the less variability that can exist in terms of the intermolecular forces that can exist between chains.
- Proteins would be much more affected by temperature and pH than polysaccharides.
- Students should compare and contrast the structure and properties of starch, cellulose and glycogen with that of proteins.

CHAPTER 19 ANALYTICAL TECHNIQUES

19.1 SECTION REVIEW

REMEMBERING

1 a Adsorb: sticking to the surface.

b Fraction: one of the substances being separated from a mixture by chromatography.

c Buffer solution: a solution than maintains a constant pH when small amount of acid and base are added.

d Ion exchange resin: a polymer that acts as a stationary phase by attracting ions present in a solution.

e Retention time: the length of time taken for a particular fraction to move through a column.

2 The sample is introduced to the top of a column filled with a closely packed stationary phase to which the components can adsorb. A liquid mobile phase is added on top of the sample so that it soaks down through the column. The mobile phase carries the sample with it. Different components of the sample adsorb to the stationary phase to different extents, and therefore travel at different speeds through the column. The different components can, therefore, be differentiated according to their retention time – the time they take to pass through the column

UNDERSTANDING

3 In order to use ion exchange chromatography, the protein may need to be ionised by altering the pH. This may cause the protein structure to denature and hence alter the properties of the protein significantly.

4 Retention time is inversely proportional to the size of the molecules. Larger molecules do not elute through any of the pores in the stationary phase and therefore pass through the column more quickly than smaller molecules, which, trapped by the pores, make slower progress.

APPLYING

5 Proteins have the ability to adsorb to different stationary phases, due to the range of different intermolecular interactions that can occur between the side groups. In addition, the charges on proteins can also alter if the pH is changed, which provides additional opportunity for chromatography to occur.

19.2 SECTION REVIEW

REMEMBERING

1
- Electrophoresis: the process of separating large charged molecules by placing them in an electric field and observing their subsequent migration through a medium such as a gel.
- Migration: the movement of the charged molecules through the gel.
- Electric field: a region of influence around a charged particle where a force is exerted on other charged objects.
- Isoelectric point: the pH level at which an amino acid exists in its uncharged form and therefore is insoluble.

UNDERSTANDING

2 The electric field exerts a force on charged particles within it and, hence, is required to cause the molecules to migrate through the gel.

3 Different protein molecules have different sizes and, therefore, migrate at different speeds through the gel.

4 The buffer solutions provide a pH gradient across the gel, so that as the proteins reach their isoelectric point, they become neutral molecules and therefore insoluble and visible.

REFLECTING

5 Similarities: both techniques involve the separation of a mixture of molecules according to their migration through a stationary phase.

19.3 SECTION REVIEW

REMEMBERING

1 a Radical: an atom or molecule with an unpaired high energy electron.

b Ionisation: the removal of an electron from a molecule to create a positive ion.

c Molecular ion: a complete molecule with one electron removed.

d Mass/charge ratio: the relative mass of a fragment divided by its charge.

e Base peak: the highest peak in a mass spectrum which represents the most abundant fragment. The intensities of other peaks are calculated relative to this one.

2 Use Figure 19.3.1 as a guide.

3 The parent molecular ion – the entire molecule with one electron removed.

4 If the molecule contains an atom that has more than one abundant isotope.

UNDERSTANDING

5 Because the detector plate is negatively charged, a burst of current only occurs when it is struck by a positive cation at the end of the mass spectrometer.

6 The different fragments produced and revealed on the mass spectrum can be analysed and can provide information about the structure of the molecule that they have originate from.

APPLYING

7 a $m/z = 15$: CH_3^+; $m/z = 29$: $CH_3CH_2^+$; $m/z = 29$: $CH_3CH_2^+$; $m/z = 45$: $CH_3CH_2O^+$; $m/z = 46$: $CH_3CH_2OH^+$

b The peak at $m/z = 31$ ($—CH_2OH^+$) is the most commonly produced fragment as it is the base peak. Hence the C—C bond is the most commonly broken bond during fragmentation.

8 $m/z = 43$: $C_3H_7^+$

$m/z = 57$: $C_4H_9^+$

$m/z = 71$: $C_5H_{11}^+$

ANALYSING

9 a Both isomers have the same mass, so would both have a parent ion with an m/z ratio of 86.

b Both base peaks represent fragments generated by breaking the C—C bond adjacent to the C═O group. Hence in molecule A, this fragment is $C_4H_7O^+$ and in molecule B it is $C_3H_5O^+$

c A fragment of $m/z = 29$ would indicate a $C_2H_5^+$ ion can be formed. If this does not exist, the molecule must be A.

10 Mass spectrometry provides a method of detecting and analysing large, complex molecules; for example, in drug analysis or of complex chemicals such as hormones or steroids. Hence it has application in a wide variety of medical fields.

19.4 SECTION REVIEW

REMEMBERING

1 X-rays

2 pH, ionic strength, nature of the precipitant, temperature and presence of cofactors or counter ion are all factors that can affect the quality of crystals of bio-molecules in particular.

UNDERSTANDING

3 Crystals are formed by cooling supersaturated solutions of the substance.

4 Primary advantage: provides the most accurate representation of the structure of molecules.
Primary disadvantage: requires high-quality crystalline samples that involve much preparation.

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5 Because of its complex protein structure it is much more difficult to prepare a high-quality sample of a ribosome that is very susceptible to changes in temperature and pH.

APPLYING

6 Not necessarily – protein structure is affected by temperature and pH, hence the changes that occur during preparation can cause changes.

7 Primarily the analysis of complex bio-macromolecules such as proteins, DNA and viruses.

ANALYSING

8 a, b and f – irregular arrays

19.5 SECTION REVIEW

REMEMBERING

1 IR light is of the correct energy to cause the atoms in molecules to vibrate about their covalent bonds.

2 Because different bonds absorb specific frequencies of IR energy as they vibrate.

3 The fingerprint region is the area of a spectrum with a wavenumber less than 1500 cm^{-1}, where there is a range of absorptions that cannot be attributed to any specific bond, but which provides a pattern unique to that specific molecule, a 'fingerprint' that can be matched to previous images stored in a library.

UNDERSTANDING

4 Would show a peak at 3300 cm^{-1}: 1-propanol, 2-propanol, ethanol, ethanoic acid, methanoic (formic) acid, butanoic acid, 1-methylamine.

APPLYING

5 a X and Y would be methanol and ethanoic acid. Hence, in order to distinguish them, the ethanoic acid would have a strong absorption at approx. 1700 cm^{-1}, which the methanol would not show.

b The methyl ethanoate would have no O—H absorption at approx. 3300 cm^{-1}, but would have a C═O absorption at 1700 cm^{-1}.

c It is difficult to use IR spectroscopy to determine purity; however, the best way is to compare the spectrum produced to a library spectrum of pure methyl ethanoate. The presence of any additional absorptions would suggest that the sample is not pure.

6 a Ethene would have a short but sharp absorption at approximately 1660 cm^{-1}, due to the presence of the C═C bond. This would not be present in ethane.

b The IR spectra of these molecules would be very similar, and could only be distinguished by comparing the spectra to library samples of pure compounds.

c Again, the IR spectra of these molecules would be very similar, and could only be distinguished by comparing the spectra to library samples of pure compounds. However, the iodomethane should have an absorption due to the C—I bond at 500 cm^{-1}, which would not be present on the 2-chloropropane spectrum. However, this falls within the fingerprint region where it is difficult to observe specific absorptions.

d Propanoic acid will show an absorption at 1750 cm^{-1}, due to the presence of the C═O bond, which propanol will not show. In addition, the —OH absorption in propanoic acid will be at a value of approximately 3000 cm^{-1}, whereas that in propanol will be at approximately 3500 cm^{-1}.

ANALYSING

7 Looking at the non-fingerprint region (wavenumbers greater than 1500 cm^{-1}), both spectra have absorptions at 3000 cm^{-1} and at 1500 cm^{-1}, due to the presence of C—H, and C—C bonds. However, the first spectrum has an additional absorption at approx. 1620 cm^{-1}, which indicates the presence of a C═C bond, and, hence, must be the spectrum of hexane.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 IR spectroscopy can identify the presence or absence of specific bonds and so distinguish between these molecules.

2 Mass spectrometry would easily determine the molecular mass and hence be able to distinguish between a series of carboxylic acids.

3 The ability of X-ray crystallography to provide detailed information about the structure of complex molecules has great applications for the ability to use and reproduce their structures and so has very significant applications for science.

4 Mass spectrometry

5 Because it reflects the Relative Atomic Mass – the average mass of an atom, given the presence of the different isotopes.

6 Primarily intermolecular forces – dispersion, dipole–dipole forces and hydrogen bonding with some ionic and covalent interaction between chains.

7 A peak at 35 with a smaller peak at 37 representing an atom of chlorine. Also, the parent ion would have an additional peak with a m/z ratio 2 greater than the original.

CATEGORY QUESTIONS

8 Normally, both techniques are used in conjunction. The IR reveals the presence of specific functional groups and mass spectrometry reveals the molar mass and therefore gives an idea of the molecular size and the length of the carbon chain.

9

TECHNIQUE	IS TECHNIQUE SUITABLE?	EVIDENCE THAT WOULD BE PRESENT	HOW THIS TECHNIQUE COULD DETERMINE IF SAMPLE WAS PURE
IR spectroscopy	Yes	Presence of absorptions due to bonds	Comparison of spectrum with library sample
X-ray crystallography	No		
Mass spectrometry	No		
HPLC/GC	Yes	Bands due to each different molecule present	Only one band would be present in the chromatogram

ELABORATION QUESTIONS

10 a C_3H_7Cl

b Parent ion has m/z = 78. so molecular formula is also C_3H_7Cl.

c Due to the presence of the additional chlorine-37 isotope, an additional parent ion is at m/z = 80.

d Students should draw 1-chloropropane and 2-chloropropane

e 43: $CH_3CHCH_3^+$ 63: $CH_3CH^{35}Cl^+$ 65: $CH_3CH^{37}Cl^+$

f 2-chloropropane is the most likely isomer because of the presence of the CH_3CHCl fragment.

11 The IR spectra of different samples can be matched and will quickly reveal whether two samples are the identical compounds or not. It would be an advantage to take samples over time as IR analysis would quickly reveal whether or not there are any changes to the composition of the samples.

12 Alcohols will usually fragment at the C—COH bond.

1-propanol would be expected to produce a peak at 29 *m/z* due to $CH_3CH_2^+$ and a peak at 21 *m/z* due to CH_2OH^+.

2-propanol would be expected to produce a peak at 15 *m/z* due to CH_3^+ and a peak at 45 *m/z* due to CH_3CHOH^+.

13 a

C	H	O
48.63	8.18	43.19
48.63/12	8.18/1	43.19/16
4.05	8.18	2.7
1.5	3.03	1
3	6	2

Empirical formula: $C_3H_6O_2$

b i The parent peak is 74 so the molar mass is 74. The molecular formula is $C_3H_6O_2$.

ii The peak with a *m/z* value of 45 could be due to $COOH^+$.

The peak with a *m/z* value of 29 could be due to $CH_3CH_2^+$ or CHO^+

c i Carboxylic acids have an OH group. The OH stretch is a broad trough at around 2500–3100 cm^{-1} that is not present.

ii C—H band at 3000 cm^{-1}

C—C band at 1100 cm^{-1}

C═O band at about 1700 cm^{-1}

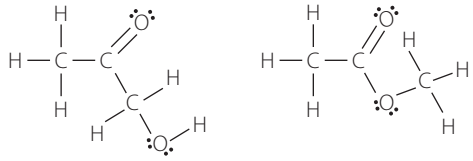
d $CHOOCH_2CH_3$ ethyl methanoate; flavourings: esters

e There are three H environments. One peak with a relative intensity of 3 due to CH_3 probably around 1 ppm, one peak relative intensity of 2 due to the O—CH_2, and one peak with a relative intensity of 1 due to H—COO.

f Ethanol and methanoic acid; esterification or condensation

$HCOOH + CH_3CH_2OH \rightarrow HCOOCH_2CH_3$

g



EVIDENCE QUESTIONS

14 1,2-ethanediol; molar mass 62: consistent as peak at *m/z* of 62. Symmetrical molecule: CH_2OH^+ fragment peak at *m/z* 31 consistent. Other peaks could be due to further fragmentations.

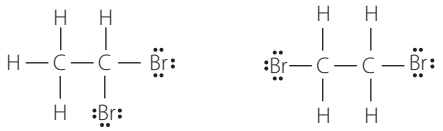
15 Run the sample of salicylic acid in an IR spectrometer. Compare the fingerprint region with a pure sample. If the sample of aspirin was pure, then the fingerprint region would only show the same bands.

If salicylic acid was present in the aspirin, then the broad OH trough would still be present in the IR spectrum of the sample.

UV–vis would be able to determine the purity of the sample. A set of standards could be run with a predetermined amount of salicylic acid and a calibration curve could be developed.

The shifts are small, so this is a ^1H NMR spectra. The molecule has two Br – which may account for the shifts being higher than in Table 15.6. There are two environments, one at a shift near 6 ppm with a relative intensity of 1. This is a quartet that indicates three protons in the neighbouring carbon. The peak at 2.5 is a doublet with a relative intensity of 3. This indicates a singlet proton in the neighbouring carbons.

The two possible isomers for $C_2H_4Br_2$ are:



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16 a Ethanol: CH_3CH_2OH, broad OH band 3300 cm^{-1} no C═O band

b Ethyl ethanoate: $CH_3COOCH_2CH_3$, NO OH band, C═O and C—O bands

c Ethanoic acid CH_3COOH, broad OH band at 3300 cm^{-1} C═O band 1700 cm^{-1}

d Ethyl ethanoate: $CH_3COOCH_2CH_3$, molar mass 88

e Ethanol: CH_3CH_2OH, molar mass 46

f Ethanoic acid: CH_3COOH, molar mass 60

END-OF-CHAPTER EXAM

1 C

2 C

3 A

4 D

5 a $C_6H_{13}NO_2$

b Amides

c Clear differences in the wavenumber values of the peaks in the two infra-red spectra, indicating that the bonds present in the molecules are different.

CHAPTER 20 SYNTHESIS REACTIONS

20.1 SECTION REVIEW

REMEMBERING

1 a Synthesis: to create a product artificially rather than find it occurring naturally.

b Reaction pathway: a series of reactions leading to a specific outcome or product.

c Intermediates: species formed during a reaction pathway as precursors to the desired product.

APPLYING

2 Answers should include a discussion of purity and maximisation of yield of aspirin.

20.2 SECTION REVIEW

REMEMBERING

1 Rate of reaction determines how quickly the product is produced, whereas the yield relates to the position of equilibrium and the percentage of reactant molecules that are converted to products.

2 To the right

UNDERSTANDING

3 100%

4 Removing the product prevents the system from reaching equilibrium and encourages the reactant molecules to continue reacting.

APPLYING

5 46.74%

6 100%

7 a $Cl_2(g) + H_2(g) \rightarrow 2HCl(g)$

b High temperature and high pressure

c Lower temperature

d Hydrogen gas

20.3 SECTION REVIEW

REMEMBERING

1 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ – catalyst of iron/iron oxide; temp = 450°C; pressure of 200 atm

2 $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ – temp 400–450°C; pressure of 1–2 atm; catalyst of vanadium (v) oxide

UNDERSTANDING

3 Reaction is exothermic, so as the temperature increases, the system acts to oppose the change and reduce the temperature by favouring the endothermic reverse reaction.

4 Reaction involves a reduction in volume. As the pressure is increased, the concentration of all particles increases. Hence, the system acts to oppose this change by favouring the forward reaction and reducing the number of particles.

5 It is important that the reactants are introduced to the reactant vessel in the correct molar ratio to ensure that neither is in excess and so avoid wastage.

6 Catalysts enable the reactions to occur at a higher rate at lower temperatures, which saves costs and also prevents the issues of reducing yield.

APPLYING

7 Temperature; pressure; catalyst; recycling of unreacted products; reacting ratio of products; recycling of heat evolved

20.4 SECTION REVIEW

REMEMBERING

1 A biofuel is a material that can be combusted to release energy, but can be produced from living matter.

2 Because they are renewable and, hence, there is an infinite supply.

3 A fuel cell is a galvanic cell that converts the energy from a chemical reaction into electricity, but with a continuous supply of reactants.

4 Chemical energy into electrical energy

5 A substance that lowers the activation energy of a reaction without itself being used up in the reaction.

6 Platinum, rhodium and nickel

UNDERSTANDING

7 Fermentation of glucose and hydration of ethene

8 No. Ethene comes from crude oil, which is a fossil fuel, and so ethanol produced by this method cannot be regarded as a biofuel.

9 Oxidation: $C_6H_{12}O_6 \rightarrow 6CO_2 + 24e^- + 24H^+$

Reduction: $6O_2 + 24e^- + 24H^+ \rightarrow 12H_2O$

10 See Figure 20.4.2

11 By connecting a number of fuel cells in series

12 A fuel cell involves a combustion reaction – the reaction of a fuel with oxygen. This is a redox reaction and the oxidation and reduction half reactions are carried out at separate electrodes, thus generating a voltage.

REFLECTING

13 Answers will vary but should take into account sustainability, renewability and efficiency as a fuel.

14 Answers will vary; usage of fuel cells to replace fossil fuels – issues are storage of the fuels required, e.g. hydrogen.

15 Answers will vary but should take into account sustainability and impact of fuels and waste compared to that of other alternatives.

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1
- Haber process: the industrial production of ammonia.
- Contact process: industrial production of sulfuric acid.
- Biofuels: fuels produced from living material.
- The use of catalysts to break larger molecules in crude oil up into smaller ones.
- Transesterification: the process of producing methyl esters from triglyceride esters.
- Fuel cell: a galvanic cell that generates electricity from a chemical reaction, but where there is a continuous supply of fuel and also removal of products.

2 To form new molecules for specific purposes

CATEGORY QUESTIONS

3 A catalyst enables a high rate of reaction to be achieved at a lower temperature. As the temperature is low, the yield of ammonia is higher.

4 Bioethanol, from the fermentation of glucose; biodiesel from the transesterification of triglyceride esters.

ELABORATION QUESTIONS

5 To ensure a high yield of product, care must be taken to manipulate the equilibrium conditions so that the forward reaction is favoured as much as possible.

6 If the temperature is decreased, the forward reaction will be favoured and, hence, the yield of $Ca(OH)_2$ will be increased.

7 73.13%

EVIDENCE QUESTIONS

8 Ethene is obtained from crude oil, a fossil fuel; hence, obtained by this method cannot be considered a biofuel.

END-OF-CHAPTER EXAM

1 A

2 A

3 B

4 a Raw materials: methane, carbon monoxide, water, oxygen
Waste products: carbon dioxide

b To provide a high concentration of oxygen

c After Reactor 1: CO, H_2, CH_4 CO_2 and H_2O
After Reactor 2: CO, H_2, CO_2
After methanol reactor: CH_3OH, H_2O, H_2

d Water is recycled in the steam generator, unreacted H_2 is reacted after the methanol reactor.

e High energy: Reactors 1 and 2 require high energy to sustain high temperatures; Methanol reactor requires energy to sustain high pressure.

f Energy can be recycled from the methanol reactor and Reactor 2, where the heat generated from the exothermic reactors can be used to heat the other reactors.

g Catalysts are used to maintain a higher rate at a lower temperature to save costs and also enable a higher yield.

h There is a decrease in volume as the reaction occurs; hence, a high yield is favoured by high pressure.

CHAPTER 21 GREEN CHEMISTRY

21.1-3 SECTION REVIEW

REMEMBERING

1 Green chemistry is the area of chemistry that seeks to reduce the impact of chemistry and chemical processes on the environment.

2
- Prevent pollution
- Treat chemicals to make them safe prior to disposal
- Dispose of untreated chemicals safe

UNDERSTANDING

3 An example: *Maximise atom economy* – atom economy refers to the amount of reagent atoms that are present in the desired product. By maximising the number of atoms used that are in the desired product, there are fewer atoms left over at the end of the process. This reduces waste.

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APPLYING

4 45.8%

REFLECTING

5 Responses including reference to sustainability and environmental impact, particularly impact of chemical processes and pollution

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Atom economy is the % conversion of the reactants into the desired product

$$Atom\ economy = \frac{mass\ of\ atoms\ in\ desired\ product}{mass\ of\ atoms\ in\ the\ reactants} \times 100$$

CATEGORY QUESTIONS

2 Catalysts enable less energy expenditure on temperature or pressure to obtain a high rate of reaction.

3 Percentage yield refers to the conversion of the limiting reagent into the desired product. Atom economy acknowledges the waste products and unused reactants.

ELABORATION QUESTIONS

4 88.9%

EVIDENCE QUESTIONS

5 Society was not as attuned to environmental issues; subsequent pollution incidents have made clear the economic cost of leaks and contamination.

6 Economic savings with less waste; less material risk to the company both in terms of reputation and also potential costs if there is environmental contamination.

END-OF-CHAPTER EXAM

1 C

2 C

3 C

4 B

5 Responses will vary

CHAPTER 22 POLYMERS, PROTEINS AND CARBOHYDRATES

22.1 SECTION REVIEW

REMEMBERING

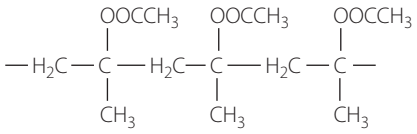
1 a The monomer must have a double bond.

b One of the bonds in each of the —C═C— double bonds is broken under the influence of a catalyst at high temperature and pressure. This leads to the formation of covalent bonds between adjacent monomers, eventually forming long chains of monomers bonded together, an addition polymer.

2 Ethene, polyethene

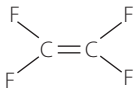
APPLYING

3



4 a

b



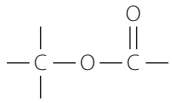
22.2 SECTION REVIEW

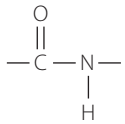
REMEMBERING

1 Natural and synthetic

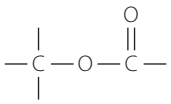
2 Condensation polymerisation is when two monomers join together to eliminate a molecule of water. This type of polymerisation occurs when monomer units have functional groups (reactive sites) at both ends of the molecule.

3 a An ester linkage

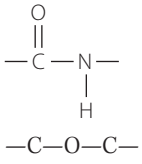




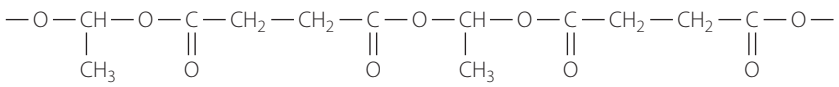
b A peptide link

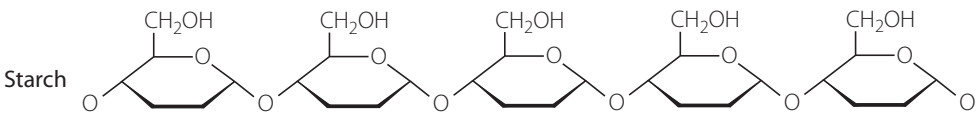


c A glycosidic link



APPLYING

4 a 

b 

5 Polymer i:

a Polyester

b Ester link

c Hydroxyl and carboxyl functional groups

Polymer ii:

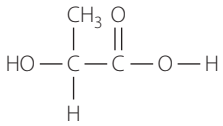
a Polyamide

b Peptide link

c Hydroxyl and amine functional groups

6 Polymer i:

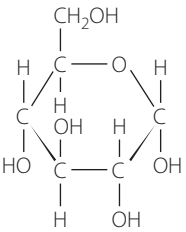
a polyester

b 

c lactic acid

Polymer ii:

a polysaccharide

b 

c glucose

22.3 SECTION REVIEW

REMEMBERING

1 Crystalline regions in a polymer have higher softening and melting points, are more dense, have greater rigidity and are non-permeable.
Amorphous regions have lower softening and melting points, are less dense and are permeable to air, water and other chemicals.

2 Cross-linking is a process whereby linear polymer chains are linked together by covalent or ionic bonds to form rigid two- or three-dimensional structures. Cross-linking can make the polymer more rigid, harder or more elastic.

UNDERSTANDING

3 Crystalline polymers are composed of linear polymer chains that have little or no branching.

4 a Large side groups restrict the ability of polymer chains to move around, making the polymer stiffer.

b Long chains have more dispersion forces between chains and so, when liquid, the chains will still have strong forces between them, making the polymer more viscous.

APPLYING

5 Cross-linking imparts a great degree of strength and rigidity to a polymer. It also ensures a high melting point to the polymer, making recycling too expensive.

6 a Soft, flexible, impermeable, low melting point

b Soft, flexible, impermeable, high melting point

c Tough, rigid, transparent, high melting point

d Tough, tensile strength, impermeable, high melting point

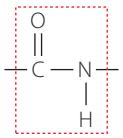
e Soft, flexible, impermeable, high melting point

7 Natural polymers can be used as co-polymers with synthetic polymers such as PVC. The starch within the co-polymer can degrade, breaking down the polymer into many smaller segments.

22.4 SECTION REVIEW

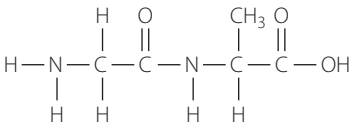
REMEMBERING

1 Peptide link

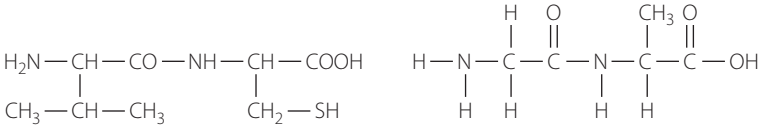


UNDERSTANDING

2 a Alanine and cysteine – peptide link



b Glycine and serine – peptide link



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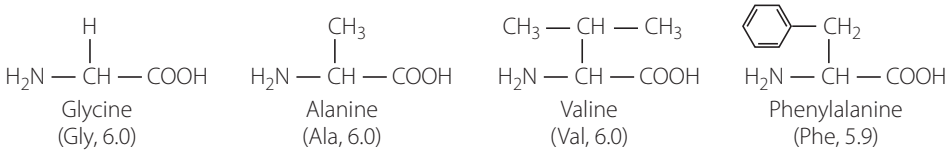
APPLYING

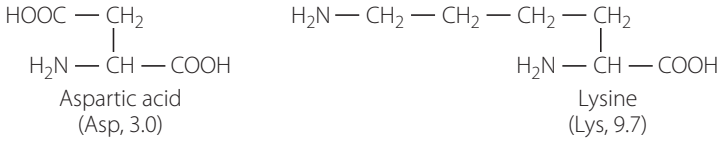
3 a GlyAla → glycine + alanine

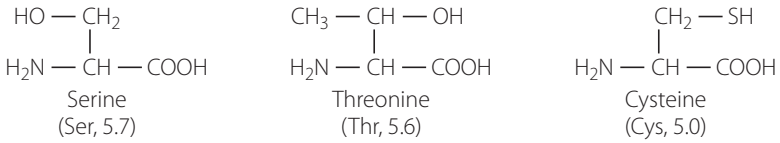
b ValCys → valine + cysteine

4 a Three: cysteine, aspartic acid and serine

b







22.5 SECTION REVIEW

REMEMBERING

1 Monosaccharides: white crystalline, sweet – tasting, soluble in water, one monomer unit
Disaccharides: white crystalline, sweet – tasting, soluble in water, two monomer units
Polysaccharides: many different forms, generally insoluble in water, many monomer units

2 Glycosidic link: —C—O—C—

3 The —OH functional group

UNDERSTANDING

4 They both contain —OH groups, which can form hydrogen bonds with water molecules

5 a When a disaccharide undergoes hydrolysis, a water molecule is added. This is incorporated into the resulting monosaccharides

b $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$

6 Cellulose: contains long unbranched chains of β-glucose that form hydrogen bonds with each other forming a strong cross-linked structure.
Starch: contains α-glucose molecules joined together. Starch contains two main parts, the amylose part (20% of the whole) is a straight-chain polymer that forms spirals because of the hydrogen bonds within the chain. The major part of glucose is amylopectin – a highly branched polymer chain.
Glycogen: Highly branched with an amorphous structure

ANALYSING

7 a $C_6H_{10}O_5 = 162.16 \text{ g mol}^{-1}$
$O = 49.33\%$
$C = 44.44\%$

b $C_6H_{10}O_5 = 162.16 \text{ g mol}^{-1}$
300 monomer units $= 300 \times 162.16 = 48648 \text{ g mol}^{-1}$

c $C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$

d $(C_6H_{10}O_5)_{50} + 4H_2O \rightarrow 50C_6H_{12}O_6$

e This may not be an accurate representation of the reaction:
Total mass of reactants $= (162.16 \times 50) + (4 \times 18) = 8180$ g
Total mass of products $= 180.18 \times 50 = 9009$

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 Both result in the production of polymers. Addition polymerisation requires the monomer to have a C═C double bond. Condensation polymerisation requires the monomer to have a functional group at each end.

2 a Affects rigidity and hardness

b Produces more amorphous structures that are less dense, flexible and transparent

c Affect the rigidity, strength and density

3 a

4 a

5 c

6 a

7 d

8 b

9 a

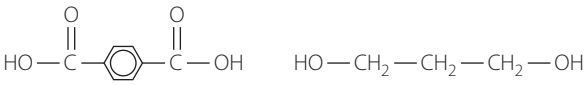
ELABORATION QUESTIONS

10 Both linkages join monomer units together. An ester link is a bond between a hydroxyl group (—OH) of one monosaccharide and a carboxyl group (—COOH) of an adjoining monosaccharide. A peptide link is a bond between the carbon atom of one alpha amino acid and a nitrogen atom of another amino acid along a peptide or protein chain.

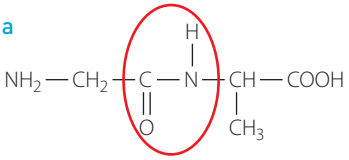
11 d

END-OF-CHAPTER EXAM

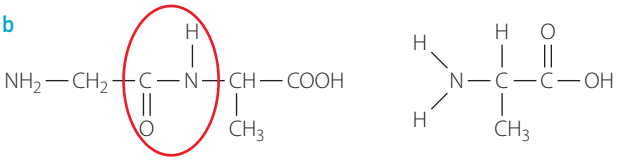
1 B
2 B
3 C
4 A
5



6 a



b



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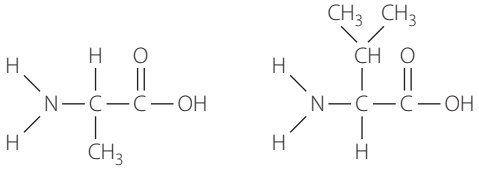


Alanine Valine

8 Cellulose:

- should have a diagram of β-glucose
- should have a diagram showing two β-glucose monomers joined by a glycosidic bond
- should have a diagram of the hydrogen bonding between chains to show cross-linking.

Starch:

- should have a diagram of α-glucose
- should have a diagram showing two α-glucose monomers joined by a glycosidic bond
- should have diagrams of amylose and amylopectin showing their respective spiral
- amorphous structures.

CHAPTER 23 MOLECULAR MANUFACTURING

CHAPTER REVIEW QUESTIONS

DETAIL QUESTIONS

1 The production of chemicals with specific shapes or chemical composition.

2 The science and engineering that occurs on the nanoscale, around 1–100 nm.

3 A top-down approach to molecular manufacturing involves starting with a larger substance and converting it into a smaller, more useful substance, or only keeping part of the original substance. This usually requires large amounts of energy and materials and produces large amounts of waste.

A bottom-up approach involves building a desired structure from the atomic and molecular scale, by adding atoms individually or by adding molecules together to make a larger, more complex molecule. This requires less energy and material and produces less waste.

4 A phenomenon where isomers have a non-superimposable mirror image.

ELABORATION QUESTIONS

5 mRNA leaves the nucleus and a large ribosome surrounds the mRNA. The ribosome links the amino acids together in the correct sequence, as specified by the mRNA. A ribosome has two sections, called subunits. The small subunit reads the mRNA; the larger unit joins the amino acids together to make a polypeptide chain.

6 The most common method used is solid-phase peptide synthesis (SPPS). A resin is used to attach the amino acids so that they are in a specific orientation. Initially, one amino acid is attached to the resin, then each amino acid in the chain is attached in turn, allowing the amide link to form before the next amino acid is added. When the polypeptide chain is complete, it is removed from the resin and allowed to fold into the protein shape. The resin acts like the ribosome in natural protein synthesis.

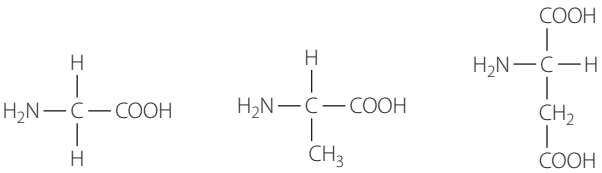
7 L and D isomers are non-superimposable mirror images of one another.

8 They are very strong, flexible, have low density, are good electrical conductors and can have useful reflection and transmission of light properties.

9 Carbon nanotubes are grown atom by atom, by passing a current between two graphite electrodes, causing the graphite to vaporise. The vaporised graphite settles on the walls of the reaction vessel and on a cathode. The graphite on the cathode forms nanotube structures as the atoms settle and bond to each other.

END-OF-CHAPTER EXAM

1 A
2 C
3 D
4 A
5 B
6



Glycine Alanine Aspartic acid

Aspartic acid has three sites that can form bonds with other amino acids, the H_2N – group and the two – COOH groups

7 a A top-down approach may involve grinding, crushing and removing material. This requires large amounts of energy.

b Top-down approaches use large amounts of energy and produce large amounts of waste.

8 Inefficient processes, producing large amounts of waste. Unintentional or unforeseen products that could be toxic.

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UNITS 3 AND 4 PRACTICE EXAM ANSWERS

MULTIPLE CHOICE

1 C	8 C	15 D
2 D	9 B	16 C
3 C	10 B	17 A
4 D	11 B	18 C
5 D	12 D	19 D
6 A	13 B	20 C
7 C	14 A	

SHORT-ANSWER QUESTIONS

QUESTION 1

a $K = \dfrac{[CH_3OH]^2}{[CH_3OCH_3]\cdot[H_2O]}$

b $K = 1/0.256 = 3.91$

c i $c(\text{dimethyl ether}) = 0.283/30 = 9.43 \times 10^{-3}\ \text{mol L}^{-1}$

ii $c(H_2O)$ will be equal to that of dimethyl ether, so

$c(\text{methanol})\ \sqrt{(0.256 \times (9.43 \times 10^{-3})^2)}\ \ 4.77 \times 10^{-3}\ \text{mol L}^{-1}$

so, $n(\text{methanol}) = 4.77 \times 10^{-3} \times 30$

$= 0.143$ moles

iii In the reaction, n(dimethylether) reacted = n(methanol) formed/2

so, n(dimethylether) reacted = $0.143/2 = 0.0715$ moles

Therefore n(dimethylether) at start = $0.283 + 0.0715$

$= 0.354$ moles

QUESTION 2

a B is diprotic. For a 0.1 M solution of a monoprotic acid, assuming complete dissociation, the pH would be 1. Therefore, if the pH of a solution is less than 1, it must have more than 1 proton that can dissociate.

b A has the lowest K_a value. It has the highest pH and, therefore, must have the least amount of proton dissociation taking place.

c The change would be greater for acid C than for acid D. Acid C is a strong acid with complete dissociation. Hence, a 10-fold dilution would result in a pH increase of 1. However, D is a weaker acid than C and, therefore, is only partially ionised. On dilution, there would be an additional increase in ionisation, as the position of equilibrium would move to the right when water is added, as it is a reactant in the dissociation, thus reducing the amount by which the $[H^+]$ decreases. Therefore, the change in pH would be less than 1.

d pH of B is 0.6, therefore, $[H^+] = 10 - 0.6 = 0.251$ M

$K_a = [H^+]^2/[HA] = 2.4 \times 10^{-3}$.

Therefore, $[HA] = 0.251^2/2.4 \times 10^{-3} = 26.25$ M

QUESTION 3

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

b i volumetric flask

ii pipette

iii burette

c $n(HCl)$ in titre $= 0.01876 \times 0.2500 = 4.69 \times 10^{-3}$ moles

$n(NaOH)$ in aliquot = $n(HCl)$ in titre $= 4.69 \times 10^{-3}$ moles

$c(NaOH) = 4.69 \times 10^{-3}/.02500 = 0.1876$ M

mass of NaOH in 1 L solution $= 0.1876 \times 40 = 7.504$ g

mass of NaOH in 250 mL $= 0.250 \times 7.504 = 1.876$ g

% NaOH in Causda $= 1.876/2.500 \times 100 = 75.04\%$ (4 sig figs)

QUESTION 4

a Lowest to highest reductant strength: Q < R < P.

P displaces Q, therefore, it is a stronger reductant; R does not displace P, so is a weaker reductant; Q did not displace R so is a weaker reductant.

b P is likely to be the most difficult to extract from its ore, and Q the easiest. The greater the reductant strength, the less likely it will be that sufficient quantities of a stronger reductant will be available to commercially extract it from its ore. It may be that electrolysis is the preferred method.

QUESTION 5

a Add Mg metal – the only sufficiently strong reductant to reduce Al^{3+}:

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

b Add Fe metal – a stronger reductant than Ni, but not as strong as Zn:

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

$Fe(s) + Zn^{2+}(aq) \rightarrow$ no reaction

c Any of the metals except copper could be used to react with the acid to obtain hydrogen:

e.g. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

d the largest voltage would be between half-cells involving the strongest and weakest reductant – in this case, it would be magnesium and copper.

QUESTION 6

a Metal A is gold, Metal B is copper and Metal C is iron. The electrochemical series shows that the order of oxidant strength in increasing order is Fe^{2+}, Cu^{2+}, Au^+. Therefore, Au^+ will be reduced first and deposited as Au metal and the Fe^{2+} deposited last, forming the outer layer.

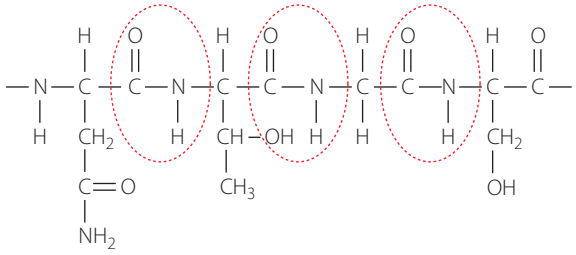
b If the anode in the cell was made from copper, then this would become oxidised and subsequently deposited on the cathode after all the gold had been deposited. Hence the second layer on the cathode would be considerably

thicker. It is unlikely that any iron would be deposited on the cathode, as once the anode has been completely oxidised, it would be completely eroded and, therefore, the circuit would be broken.

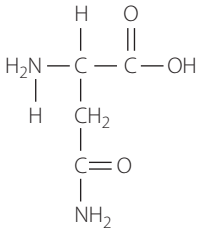
c No sodium metal would be deposited on the cathode, as the electrolyte is an aqueous solution. As water is a stronger oxidant than Na^+ ions, it would be reduced in preference. so that bubbles of H_2 gas would be observed after all of the iron had been deposited. The Na^+ ions would remain in solution.

QUESTION 7

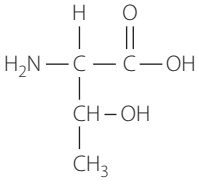
a



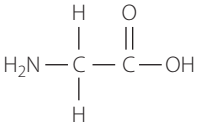
b



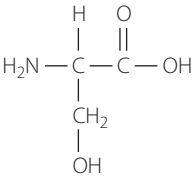
Asparagine



Threonine



Glycine

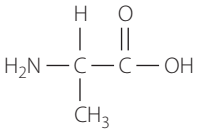


Serine

c Hydrolysis reaction – either sulphuric acid or sodium hydroxide would be the reagents.

d Any two from: hydrogen bonds, dipole–dipole interactions, ionic interactions, covalent bonds (disulphide bridges) or dispersion forces

e Alanine



Alanine

EXTENDED-RESPONSE QUESTION

QUESTION 8

Discussion should include but not be limited to a full description of the Haber process. This should include:

- conditions such as reaction temperature, pressure and catalyst
- justifying and explaining the fact that the temperature and pressures adopted are compromise values, balancing equilibrium yield and rate
- other economic savings, including the use of heat exchangers and recycling unreacted gases
- the three principles of green chemistry should be selected and the process justified in terms of them.

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GLOSSARY

A

acid dissociation equilibrium constant the equilibrium expression of a weak acid $K_a = \frac{H_3O^+[F^-]}{HF}$

accuracy dependent on the measuring instrument that is used; a mass balance that measures to .001 g is a more accurate instrument than a mass balance that measures to .1 g

activated complex a transition or intermediate state formed during a reaction as a precursor to the product, but which has a high energy and so is relatively unstable

activation energy (E_a) the minimum amount of energy required in order for a reaction to occur

active site the area of the enzyme where it interacts directly with the substrate molecule

addition polymerisation formation of polymer chains by the addition reaction of unsaturated monomers

addition polymers form by adding together molecules without the loss of any atoms

addition reaction unsaturated molecules combining with another molecule to become saturated

adsorb sticking to the surface

aldose a sugar containing an aldehyde group

alpha-amino acid an amino acid with one carbon atom separating the amino and carboxyl groups

alpha-carbon the carbon atom in an amino acid that separates the amino and carboxyl groups

α-Helix or **alpha helix** a structure of natural proteins where the carbonyl (C═O) of one amino acid is hydrogen bonded to the amino H (N—H) of an amino acid that is four down the chain, pulling it into a helical structure, like a curled ribbon

amino acid an organic compound containing a carboxyl and an amino group

amorphous without a clearly defined shape or form

amphiprotic a substance that can gain or lose a hydrogen ion to act as an acid or a base

analyte the solution of an unknown concentration that will be analysed

angles of incidence the angle a beam of radiation makes with a line perpendicular to the surface

anion exchange resin a polymer that acts as a stationary phase by attracting anions present in a solution

anode the electrode where reduction occurs

antibodies proteins that help fight disease

atactic a polymer where the side-chain functional groups are randomly arranged on the polymer chain

atom economy the efficiency of a chemical reaction. The greatest efficiency is where the greatest percentage of atoms in the reactant end up in the product

B

back titration a method used to determine the mass or concentration of a substance that is not able to be determined directly

base dissociation equilibrium constant the equilibrium expression of a weak base

β-pleated sheet or **beta-pleated sheet** two or more segments of a polypeptide chain lie alongside one another, to form a sheet-like structure held together by hydrogen bonds

biodegradable a substance that will decay naturally as a result of enzyme produced by living bacteria

biofuels fuels produced from plants, algae or animal waste

biosensor a structure that can detect a change in a biological component

bottom-up approach building a desired structure from the atomic and molecular scale, by adding atoms individually or by adding molecules together to make a larger, more complex molecule

branching where a polymer chain is not a single straight-chain, but has 'offshoots'

buffer region the part of a titration curve during which the pH changes little as titrant is added; occurs when one of the reagents is a weak acid or a weak base and is the result of a buffer solution being set up

buffer solution a solution that maintains a constant pH when small amounts of acid and base are added

C

carbohydrates food group consisting of molecules such as sugars and starches; a naturally occurring compound with the general formula $C_x(H_2O)_y$

carbon skeleton the arrangement of carbon atoms that other atoms join to in an organic molecule

catalyst a substance that increases the rate of a reaction without being consumed in the reaction

catalytic cracking the process of heating larger organic molecules and converting them into smaller, more useful molecules

catenate the ability of carbon atoms to bond with other carbon atoms to form chains and rings

cathode the electrode where oxidation occurs

cation exchange resin a polymer that acts as a stationary phase by attracting cations present in a solution

chemical change a change involving the creation of a new substance

chemical system the chemicals involved in a reaction

chirality two isomers that do not have a mirror image; when placed over one another, they are not the same

chromatography a technique for separting mixtures due to differing interactions with different media

closed system where the chemicals involved in a reaction are all contained within a fixed space

co-enzymes molecules that assist the operation of enzymes

collision theory is the theory that a reaction will occur when two particles collide with sufficient energy. The faster the collisions occur, the higher the rate of reaction.

complete combustion burning of an organic compound in sufficient oxygen to produce carbon dioxide and water

concentration the amount of substance per unit volume

condensation polymer when two monomer molecules join together to eliminate a small molecule (often water)

condensation reaction where two molecules combine to form a larger molecule and produce water as a by-product

conjugate acid the acid that is formed when a base accepts a proton from an acid

conjugate base the base that is formed when an acid donates a proton to a base

conjugate pairs acid–base pairs that differ from each other by one proton

constructive interference two waves mutually reinforcing each other, producing a combined wave with amplitude equal to the sum of the constituent waves

contact process the industrial production of sulfuric acid

copolymer a polymer made from more than one type of monomer

cross-linking linear chains linked together to form a more rigid two- or three-dimensional structure

cross-links covalent bonds that exist between polymer chains, holding them together firmly

crystalline having a regular, ordered arrangement of atoms

D

dehydration an elimination reaction where a molecule of water is lost from an alcohol to form an alkene

denaturing the permanent change than can occur to the structure of protein molecules when heated, or exposed to solutions of high acidity or alkalinity

density the mass per unit volume

destructive interference two waves opposing each other and negating the effect of each other

detergent a water-soluble agent which makes dirt and oils soluble yet unlike a soap does not form a scum in hard water

diffraction waves are spread when passing through a crystal

dipole–dipole interactions intermolecular forces that exist between molecules that have a permanent dipole

diprotic a substance that can donate two protobs to a base

disaccharide a sugar made from two monosaccharide units

dispersion forces the weakest intermolecular forces that exist between all molecules

disproportionation reaction typically a redox reaction, where a molecule is transformed into two or more dissimilar products

dissociation reaction a reaction in which an ionic substance separates in a solution 1

dynamic equilibrium a system in balance but where forwards and backwards reactions occur at the same rate

E

***E*° values** electrode potential is a measure of the electrical potential of an electrochemical cell; the standard electrode potential is represented by E° values

electric field a region of influence around a charged particle where a force is exerted on other charged objects

electrochemical cells transforms energy between electrical energy and chemical potential energy

electrolyte a substance that conducts an electric current

electrolysis an electric current is passed through a substance to create a chemical change

electrolytic cells a type of electrochemical cell that transforms electrical energy and chemical potential energy

electronegativity the tendency of an atom to attract electrons from outside a covalent bond

elimination reaction reaction where a molecule is lost from a larger molecule, producing an unsaturated product

endothermic reaction the products have more enthalpy than the reactants, meaning that energy will be absorbed from the surroundings

end point the physical sign that indicates that the equivalence point has been reached; achieving the correct end point depends on using an appropriate method that will undergo a physical change at the appropriate point

enthalpy heat energy which is either absorbed or released in the breaking and making of chemical bonds during a reaction

enzyme a biological catalyst that increases the rate of a reaction without being used up in the reaction

equilibrium a system in balance

equilibrium constant the value ratio between the concentrations of the reactants and products, represented as K_C

equilibrium expression the ratio of the concentration of products to reactants used to calculate the equilibrium constant

equivalence point the point when the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction

ester link the —COOC— group that links two alkyl chains in an ester molecule

esterification the condensation reaction where an ester is formed from an alcohol and a carboxylic acid

excess reagent the reactant which is still remaining after a reaction is complete

exothermic reaction the reactants have more enthalpy than the products and therefore energy will be released to the surroundings

external circuit the external circuit of an electrochemical cell consists of the connecting wires and the voltmeter or electrical appliance

F

fat food group consisting of chains of triglyceride molecules; essential for life

fatty acid a carboxylic acid with a long hydrocarbon chain attached to a carboxyl group

fingerprint region region of absorption of 1400 cm^{-1} or less, where it is difficult to assign absorption peaks to specific bonds; the only way of using the information from this region is to compare the overall absorption spectrum to a library standard, to identify the molecule

fraction one of the substances being separated from a mixture by chromatography

fractional distillation separation of a mixture of organic compounds according to their different boiling points

free radical substitution UV-light-initiated reaction, where a hydrogen atom is replaced with a halogen atom

fuel cell a galvanic cell in which a fuel, such as hydrogen or methanol, is oxidised and oxygen is reduced, releasing electrical energy

functional group a group of atoms in a molecule that causes the molecule to chemically react in a distinctive way

G

galvanic cells a type of electrochemical cell that transforms chemical potential energy to electrical energy in a spontaneous chemical reaction

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gel electrophoresis the process of separating large charged molecules by placing them in an electric field and observing their subsequent migration through a medium such as a gel

glycerol propane-1,2,3-triol

graphene covalently bonded carbon

H

Haber process the industrial production of ammonia

half-cells the part of a galvanic cell where oxidation or reduction occurs

half-equation when an equation has been split into its two components: the oxidation reaction and the reduction reaction

halogenation addition reaction involving a halogen molecule

heterogeneous system a system where there is a mixture of phases of reactants and products

homogeneous system a system where all the reactants and products are in the same phase

homologous series a series of organic molecules with the same functional group but different length carbon chains

hydrogen bonds strong intermolecular forces that exist between molecules that possess O—H, N—H or F—H bonds

hydrogenation an addition reaction where hydrogen is the molecule added

hydrolysis a reaction where a larger molecule is split into two smaller molecules by reacting with water and an acid or base catalyst

hydronium ion the ion that forms when a proton is donated to a water molecule (H_3O^+)

hydrophilic a molecule that bonds attractively with water

hydrophobic a molecule that does not bond attractively with water

I

incomplete combustion burning of an organic compound in limited oxygen to produce carbon monoxide or carbon and water

internal circuit the internal circuit of an electrochemical cell consists of the strips of metal, solutions and the salt bridge

ionisation energy the energy required to remove one electron from an atom or ion of an element in a gaseous state

ionisation reaction a chemical reaction when an uncharged molecule becoms an ion

intermediate species species formed during a reaction pathway as precursors to the desired product

intermolecular forces forces that act between molecules; these forces largely determine the physical properties of molecules

isoelectric point the pH value at which there is no net charge on a protein

isotactic a polymer where the side-chain functional groups are regularly arranged on the same side of the chain

K

ketose a sugar containing a ketone group

kinetically stable where the cell potential indicates that a reaction will occur but, in practice, there will be no perceptible reaction because of the high activation energy

L

Le Chatelier's principle if a change is imposed on a system at equilibrium, then the system will act in order to partially oppose the change

limiting reagent the reactant molecule that is completely used up during a reaction

M

mechanosynthesis positioning molecules so that the desired functional groups line up

messenger RNA (mRNA) a copy of the DNA code in the nucleus

mobile phase a liquid or gas that carries the sample through a chromatography column

molecular formula the number of atoms of each element present in a molecule

molecular ion the ion formed when the molecule is ionised without being fragmented in a mass spectrometer

molecular manufacturing the production of molecules, crystals and other chemical structures, that have been designed to have a specific shape or chemical composition

monomer an individual unit of a polymer

monoprotic a substance that can donate one proton to a base; an acid that dissociates producing one hydrogen ion per molecule

monosaccharide a sugar that cannot be decomposed into simpler sugars

N

nanometre (nm) one-billionth of a metre

nanosensor a sensor that is nanosized

nanotechnology science, engineering and technology that occur at the nanoscale, around 1–100 nanometres

nanotube a tube constructed on the nano scale; most commonly made from carbon

neutral neither acidic or basic; has a pH of 7

nucleophilic substitution reaction of haloalkanes where the halogen atom is replaced by an electron-rich species called a nucleophile

O

oil a lipid that is liquid at room temperature

open system where one or more reactants or products in a reaction can be either added or lost

oxidant or **oxidising agent** a chemical species that causes another species to be oxidised

oxidation the loss of electrons; a reaction where an oxidising agent is used to convert primary alcohols to aldehydes, and carboxylic acids and secondary alcohols to ketones

oxidation state the number of electrons that an atom would have gained or lost to get to its present state; it assumes that each species is completely ionic

P

parallax error an error in measurement due to the observer's position relative to the meaningful scales; if the reading is taken at an angle to the scale, then an error is introduced

passivating metal a metal that can become less reactive because of the addition of a less-reactive surface layer

percentage ionisation the percentage of acid that has ionised in water

percentage yield the percentage of the maximum possible amount of product from a reaction that has actually been produced

physical change a change where no new substance is created

planar a molecule, or portion of a molecule such as a ring, where all of the atoms lie in the same plane

plastic a synthetic polymer that is malleable, pliable and capable of being moulded by heat and pressure

polarity a bond is polar when there is a significant difference in electronegativity between the atoms of a covalent bond, and therefore an unequal distribution of electron density across the bond

polyamide a polymer held together by amide bonds – formed between the amino group of one monomer and a carboxyl group of the next monomer

polymer a large molecule made from many thousands of repeating units

polymerisation the process by which monomers link together to form a polymer

polypeptide a polyamide chain which constitutes a protein

polysaccharide a carbohydrate molecule made from many monosaccharide units

prefix a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the start of the name

primary alcohol an alcohol where the —COH group is joined to one other carbon atom

primary standard a solution of accurately known concentration that remains stable under common laboratory conditions for extended periods of time

primary structure the sequence of monomers in a copolymer chain

protein an organic compound made from long chains of amino acids; food group essential for life

proton a particle found in the nucleus of an atom possessing a positive charge equal and opposite to that of an electron

Q

quaternary structure the shape of two or more polymer chains aggregated together, held by intermolecular interactions

R

radical a species formed with an unpaired, high-energy electron in an excited state

reaction mechanism an understanding and description of how a reaction has taken place

reaction pathway a series of reactions leading to a specific outcome or product

reaction quotient the value of the equilibrium expression when calculated, Q

redox reaction a reaction that involves the oxidation of one species and the reduction of another species

reducing sugar another name for an aldose sugar

reductant or **reducing agent** a chemical species that causes another to be reduced

reduction the gain of electrons; a hydrogenation reaction to either alkenes or amines

reference cell electrode used for reference on half-cell potential reactions

retention time the length of time taken for a particular fraction to move through a column

reversible a reaction where the products can be converted back to the reactants

S

salt bridge a link containing electrolyte between the oxidation and reduction half-cells of a galvanic cell

saturated compound a chemical compound that resists addition reactions; less reactive than unsaturated compounds

saturated fatty acid a hydrocarbon molecule with no C═C bond

secondary alcohol an alcohol where the —COH group is joined to two other carbon atoms

secondary structure minor features of the shape of a polymer chain, caused by intermolecular interactions between side chains

self-ionisation constant (K_w) the equilibrium expression that shows water ionising into two ions

semi-structural formula a condensed version of the structural formula showing the sequence of atoms listed by carbon atom but not the bonds

side groups the different functional groups that can exist in a polymer chain, but which are not part of the main chain

standard temperature and pressure (STP) a measurement commonly used when performing calculations on gases, such as gas density; the standard temperature is 273 Kelvin (0° Celsius) and the standard pressure is 1 atm pressure.

stationary phase a solid to which the sample molecules adsorb as they move through the chromatography column

stem the part of the name of an organic molecule that denotes the length of the longest carbon chain

stereoisomers or **geometric isomers** two molecules with the same structural formula but different arrangement of atoms in space

stereoregular polymers polymers with small, regularly ordered units in a single chain

strong acids an acid that readily donates a proton to water; K_a is large

structural formula a displayed arrangement of the atoms in a molecule, showing all bond

structural isomers two molecules with the same molecular formula but a different arrangement of the atoms

substrate the molecule that is taking part in the reaction which the enzyme is catalysing

suffix a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the end of the name

surroundings everything except the chemicals involved in a reaction

syntactic a polymer where the side-chain functional groups alternate above and below the chain

synthesis to create a product artificially rather than find it occurring naturally

T

tensile strength the resistance of a substance to being pulled or stretched

tertiary alcohol an alcohol where the —COH group is joined to three other carbon atoms

tertiary structure the overall shape of a single polymer chain

thermoplastic polymers that can be melted and re-formed

thermosetting polymers that cannot be melted and re-formed

triprotic a substance that can donate three protons to a base

titrant the solution in a burette

titration a type of volumetric analysis that determines the end point

titration curve a graphical representation of a titration with the x-axis showing the volume of titrant added and the y-axis showing the pH of the solution

top-down approach starting with a larger substance and converting it into a smaller, more useful substance

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transesterification the process of converting one ester into another, for example, in the industrial production of biodiesel, converting a lipid into methyl esters of fatty acids, and by replacing the glycerol with methanol

transfer RNA (tRNA) collects a specific amino acid, then lines up with the matching part of the mRNA

triglyceride an ester formed from glycerol and three fatty acid molecules

U

unsaturated compound a chemical compound that contains carbon-carbon double bonds or triple bonds, such as those found in alkenes or alkynes, respectively

unsaturated fatty acid a hydrocarbon molecule containing at least one C═C bond

W

weak acids an acid in which only a small proportion of the molecules will donate their proton; K_a is small

Z

zwitterion the form of an amino acid where the amino group is protonated at the same time as the carboxyl group is deprotonated, so that there is no net charge

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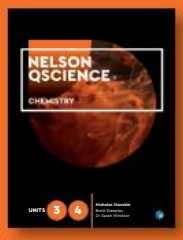

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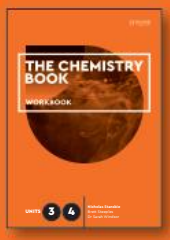

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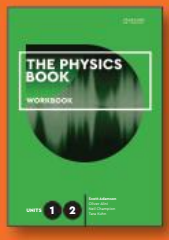

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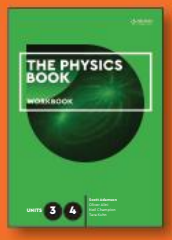

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